1,3-Dimethylcyanuric Acid Derivatives

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1,3-Dimethylcyanursäure Derivaten

DISSERTATION

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My Parents

Glossary of chemical abbreviations and Units

1. List of Abbreviations

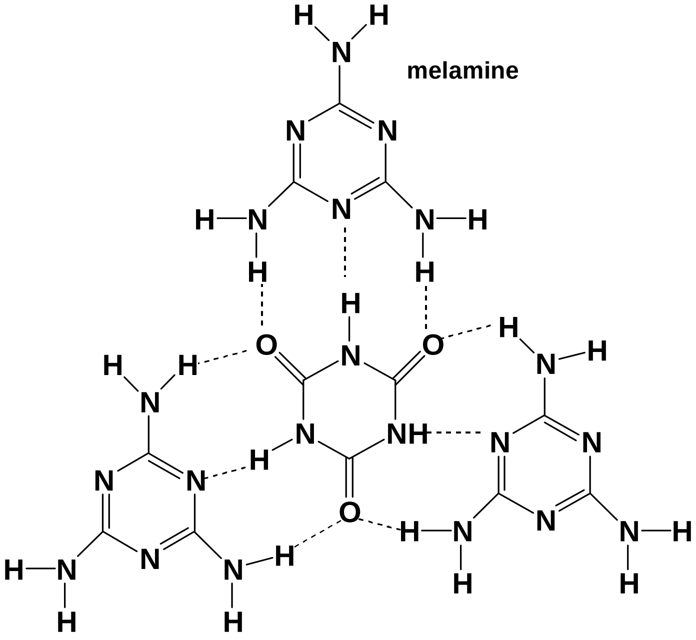
Ad	adamantyl
Anal.	analysis
aq.	aqueous
acac	acetylacetonate
br	broad
Cat.	catalytic
Calcd.	calculated
CH_2Cl_2	dichloromethane
DMSO	dimethylsulfoxide
d	doublet
E	trans
EI	electron impact (mass spectroscopy)
en	ethylenediamine (1,2-diaminoethane)
Et	ethyl
Et_2O	diethyl ether
EtOH	ethanol
FAB	fast atom bombardment (mass spectroscopy)
FT-IR	Fourier-transformation Infrared spectroscopy
Im	imidazole
i-Pr	*iso*-propyl
IR	Infrared spectroscopy
J	coupling constant
DRIFT	diffuse reflectance infrared fourier transform spectroscopy
m	mutiplet
M	a metal
Me	Methyl
MeCN	acetonitrile
MeOH	methanol

Mes	mesityl
m.p.	melting point
m/z	mass/charge ratio
MS	mass spectroscopy
NMR	Nuclear magnetic resonance
PPh_3	triphenylphosphine
Ph	phenyl
Py	pyridine
q	quartet (NMR)
RT	Room temperature
s	singlet (NMR)
spet	septet (NMR)
st	stretching (IR)
^{t}Bu	*tert*-butyl
THF	tetrahydrofuran
TMS	tetramethylsilane
δ	chemical shift
μ	bridging ligand
η^n	hapticity
ν	frequency (IR)
Z	cis

2. List of Units

Å	Angstrom (1Å = 10^{-10}m)
°	degree
eV	electron volt (1 eV = $1.602.10^{-19}$J)
g	grams
h	hour
Hz	hertz
L	liter
min	minute

mg	milligram
mL	milliliter
mmol	millimol
ppm	parts per million



Introduction & 1

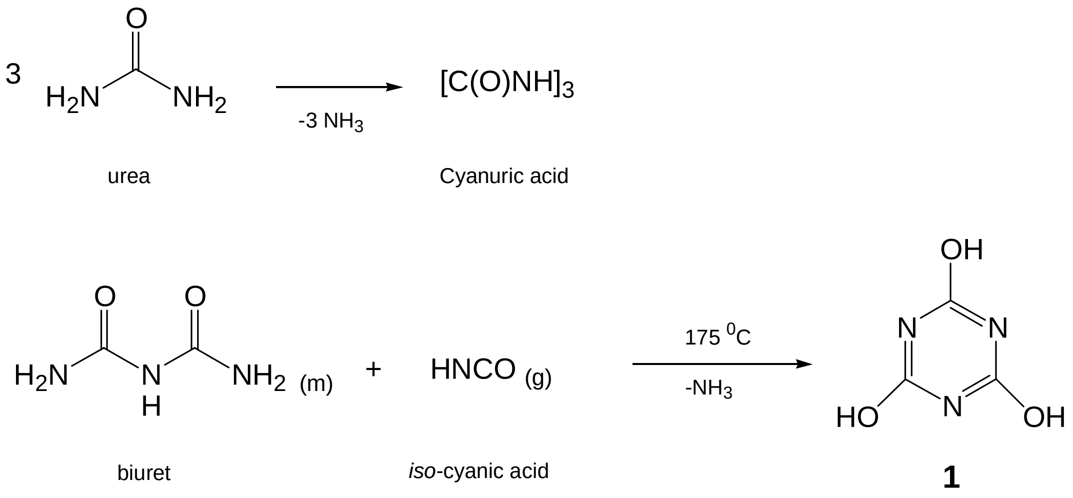
Backgrounds

1. Introduction

1.1 Cyanuric acid

1.1.1 Synthesis

Cyanuric acid (**1**, CYH_3 = 2,4,6-Trihydroxy-1,3,5-triazine) was first synthesized by Wöhler in 1829[1] from the thermal decomposition of urea with release of ammonia. The formation of CYH_3 starts at approx. 175 ºC, which involves both biuret and *iso*-cyanic acid as intermediates (scheme 1).[2]



Scheme 1. The formation of cyanuric acid by thermal decomposition of urea.

1.1.2 Applications

Cyanuric acid has a diverse role to play in chemistry, particular with regard to commercial or industrial use, for many years. It has featured in products ranging from flame retardants and plant growth feed to a catalyst for NO_x removal from exhaust gases and lavatory cleaning blocks.[3]

1.1.3 Properties and chemistry of cyanuric acid

CYH_3 exists in equilibrium with its tautomer **2** and has the attributes of high symmetry and planarity, coupled with three hydrogen bond donors and three acceptors. It is a middy acidic compound with pka values of 6.85, 10.91 and > 12,[4] allowing varying degrees of deprotonation, and the resulting anions can function as amide ligands for metals (figure 1).

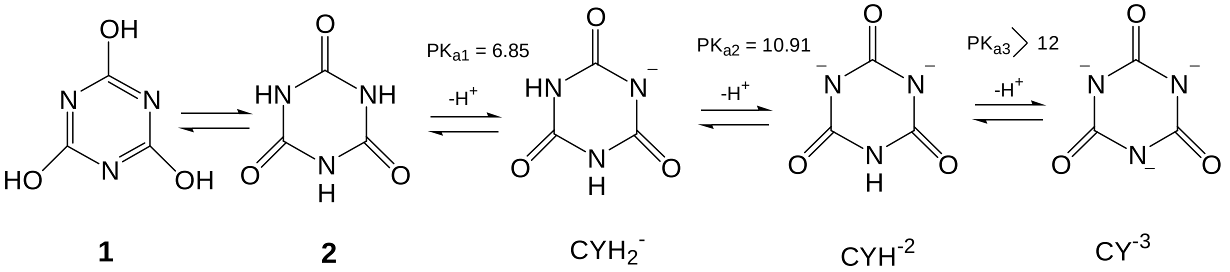


Figure 1. Cyanuric acid tautomer and its mono-, di- and tri- anions.

It was shown that the cyanurate coordination modes depend on the nature of the cyanurate anion (figure 2). According to its negative formal charge position the anion CYH_2^- ligand has found to be N- or O-coordinated.

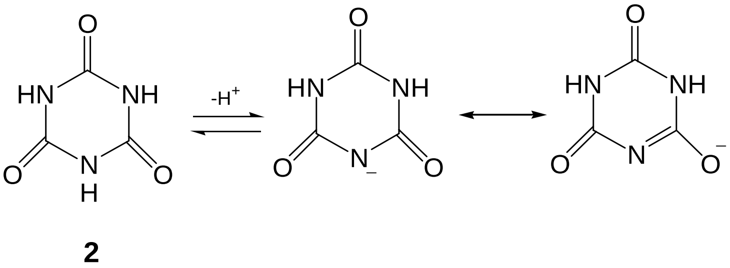
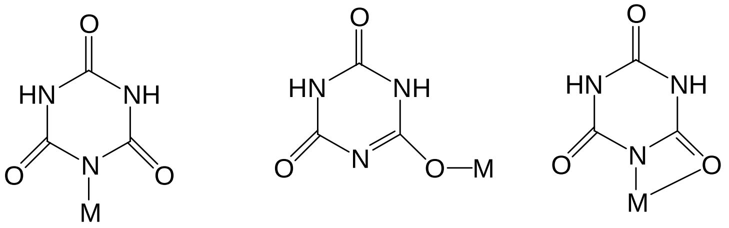


Figure 2. Tri-keto tautomer and its mono anion (CYH_2^-) resonance forms.

The ligand chemistry of cyanurato complexes of copper were first reported by Wöhler[5] and Wiedermann.[6] Further work on the copper complexes was carried out by Claus and Putensen who also prepared related compounds of nickel, zinc, cobalt, manganese and magnesium.[7] These were prepared from aqueous solutions of metal salts with sodium cyanurate or with cyanuric acid in ammoniacal solution. The first crystal structure of cyanurato complex of copper was reported in 1973.[8] Since that time, preparation and crystallographic characterization have been reported for cyanurates of Mn,[9,10] Co,[9-11] Ni,[9-12] Cu[10,13] and Ag.[14] These cyanurato complexes showed that the CYH_2^- ligand coordinate through a deprotonated N atom **3** (figure 3).

On the other hand, it was recently reported that the hard centers of the main group elements (M = K,[3,15] Rb,[3] Ca[16]) are O-coordinated **4**. Furthermore in the case of di- and tri-anionic ligands the metal centers M = Ba,[17], Sb,[18] Ti,[19] Nb,[20] Mo,[21] Zn[4] are N-O-coordinated **5**. The tri-keto tautomer was found to be the only form in all of these cyanurato complexes.



3 **4** **5**

Figure 3. The type of coordination modes of cyanurate ion.

Cyanuric acid has played a role in supramolecular systems outside of coordination chemistry. Whitesides et al. have reported extensive studies of complexes of cyanuric acid with melamine (figure 4).[22]

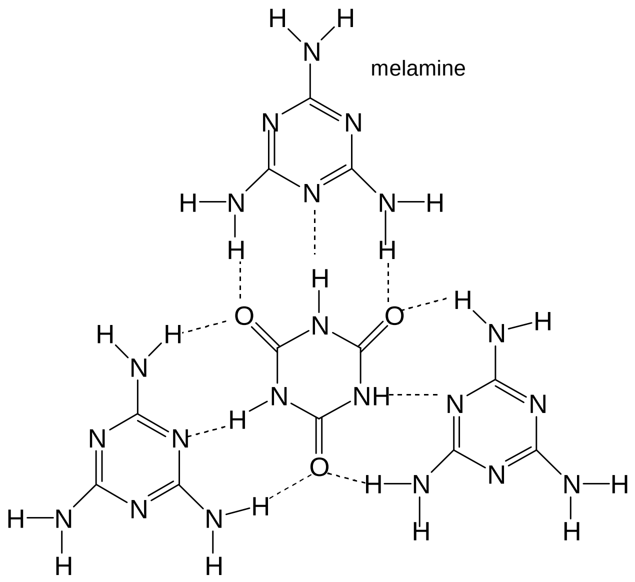


Figure 4. Melamine cyanurate is commonly used as a flame retardant.

1.2 Carbenes

1.2.1 Definition

Carbenes are neutral two–coordinate carbon compounds with two nonbonding electrons and no formal charge on the carbon :CXY.[23] The singlet-triplet splitting in carbene correlates with increasing electronegativity of the π-donor substituents X and Y. Although several combinations of heteroatoms (O, S, N) are conceivable, only singlet carbenes with two nitrogen atoms (amino groups) were mostly used in carbene chemistry. Because of the lower electronegativity of carbon, they are stronger electron-pair donors than amines and the amino groups are π-donating (mesomeric) and σ-withdrawing (inductive), e.g. 2,3-dihydro-1H-imidazol-2-ylidenes (figure 5).[24]

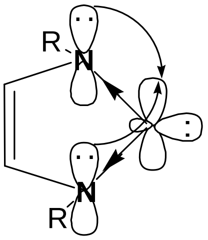
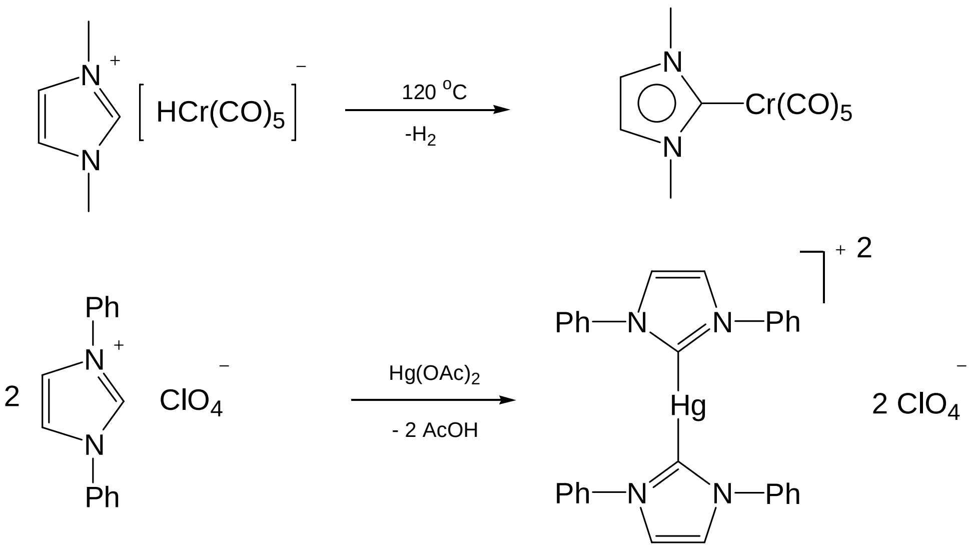


Figure 5 . Electronic effects in diaminocarbenes.

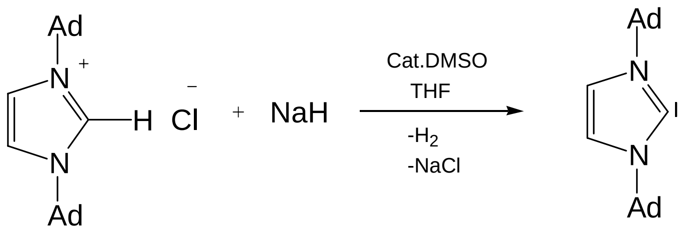
1.2.2 Diaminocarbenes

It is now more than 40 years since Öfele and Wanzlick independently published the first structures and preparation of complexes containing N-heterocyclic carbenes (NHCs).[25,26] Both reports used the deprotonation of an imidazolium salt by a basic metal precursor to form the imidazolin-2-ylidene complexes shown in scheme 2.



Scheme 2. Preparation of the first transition metal complexes of NHCs by Öfele and Wanzlick.

In 1991 Arduengo *et al.* succeeded in crystallizing the first free diaminocarbene **7**, which was prepared by deprotonation of the 1,3-bis(adamantly)imidazolium chloride **6**.[27] Despite being highly air and moisture sensitive, Arduengo's carbene is stable up to 240 ºC (scheme 3).

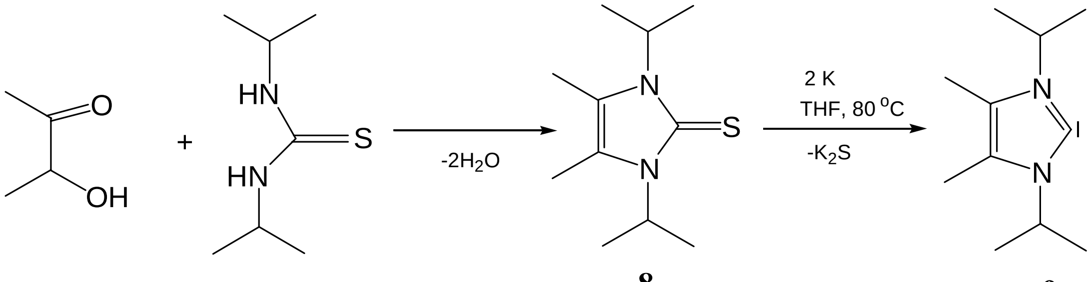


6 **7**

Scheme 3. Preparation of the first stable diaminocarbene.

Various methods have been developed to prepare NHCs from suitable precursors. Azolium salts can be deprotonated by NaH and KO^{t}Bu or dimsyl-anions (DMSO$^-$) in THF.[27,28] The generation of NHCs by reaction with NaH in a mixture of liquid ammonia and THF is a high-yield and the most general method.[29,30]

In 1993 Kuhn *et al.* developed a new effective route from cyclic thiourea derivatives like 1,3-diisopropyl-4,5-dimethylimidazol-2(3H)-thione **8**- prepared by condensation of substituted thioureas with α-hydroxyketones- which can be converted into the corresponding imidazolin-2-ylidene **9** (scheme 4)[31] by reducing with potassium in boiling THF yielded analytically pure NHC after filtration and removal of the solvent under vacuum. This method was adopted for the preparation and isolation of 1,3-bis-neo-pentylbenzimidazolin-2-ylidene through reaction with Na-K.[32]



8 **9**

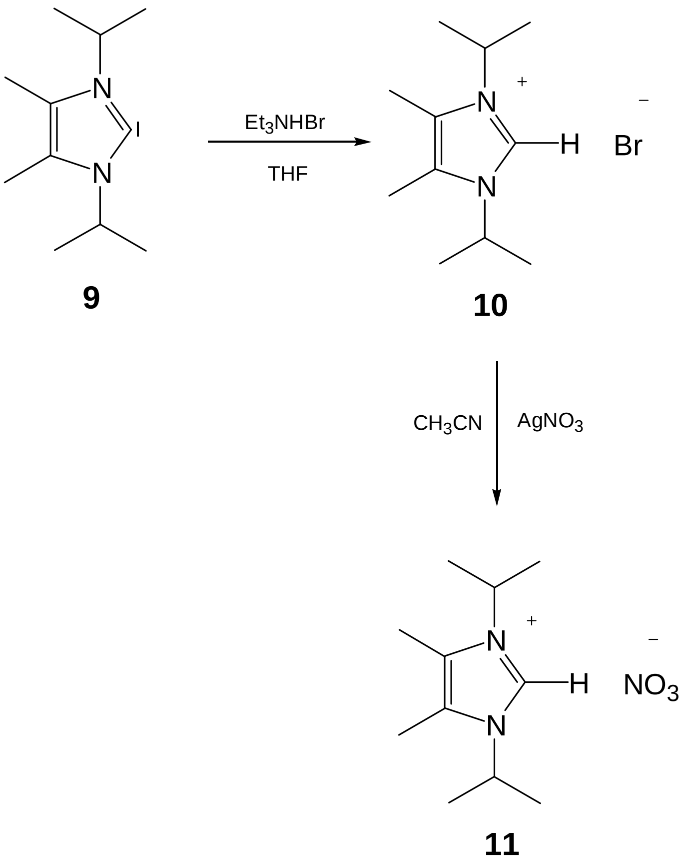
Scheme 4. Synthesis of imidazolin-2-ylidenes from thiourea derivatives.

The source of the remarkable stability of these carbenes is due to the large singlet-triplet gap in imidazol-2-ylidenes (~ 80 kcal/ mol), along with π-interactions in the imidazole ring, electronegativity effects from the nitrogen, steric effects, and kinetic factors have all been offered as explanations of the enhanced stability of these carbenes.[33]

1.2.3 Reactions with hydrogen compounds

As a result of the strongly basic character of heterocyclic carbenes,[34] their reactions with alkyl ammonium salts give interesting results. For example, the carbene **9** reacts readily with Et_3NHBr to give the imidazolium bromide salt **10** (scheme 5), which reacts with $AgNO_3$ in acetonitrile to give the salt **11**.[35]

Other imidazolium salts containing ion pairs linked by hydrogen bonds **12 (**figure 6**)** have been reviewed recently. Apparently their properties are influenced by interionic interactions which have been detected mainly in their 2H-derivatives as hydrogen bonds.[36]



Scheme 5. A couple of salts containing ion pairs linked by hydrogen bonds.

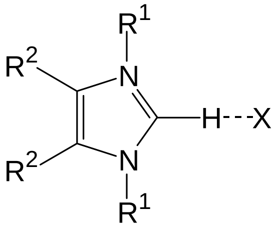


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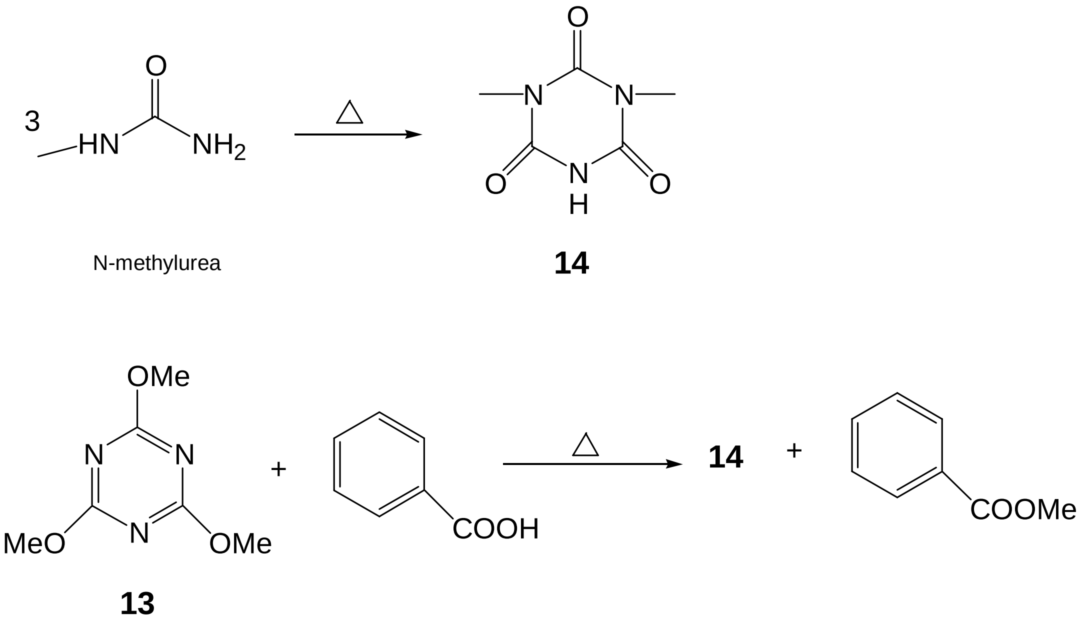
Figure 6. Imidazolium salt linked by hydrogen bond.

1.3 Goal of Research

We are currently interested to explore the chemistry of 1,3-dimethylcyanuric acid (**14**, DMCH = 1,3-Dimethyl-2,4,6-trioxo-1,3,5-triazine). DMCH was known since 1881[37] but its chemistry is not explored. It can be prepared either by thermal decomposition of N-methylurea[38] or under thermal conditions of 1:1 mole mixture of trimethoxy-1,3,5-triazine **13** with benzoic acid (scheme 6).[39]



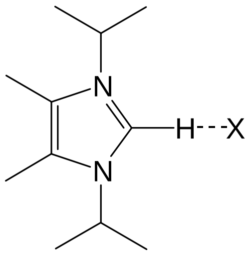
Scheme 6. The synthesis of 1,3-dimethylcyanuric acid (DMCH).

The presence of several potential donor sites such as one amine nitrogen atom and three carbonyl oxygen atoms makes 1,3-dimethylcyanuric acid a very interesting polyfuctional ligand in coordination and organometallic chemistry. By comparing with CYH_3, DMCH has two methyl groups which lower the tendency for making intra and intermolecular hydrogen bonding,[40] so this also prompted us to investigate its coordination behavior. In addition to the chemistry of DMCH **14**, and as a part of our research we are also interested in exploring the structural chemistry of imidazolium salts.[36,41] Hydrogen atoms bound to nitrogen and oxygen atoms form classical hydrogen bonds with lone electron pairs, or negative charge, on other oxygen and nitrogen atoms. In recent years, close interaction of the C-H…X (X = N, O) hydrogen bonds have attracted considerable interest and suggested in various organic compounds to understand their crystal structures.[40] The C-H…X interaction is typically weak. Nevertheless, much attention had been given to the potential significance of these bonds in biological molecules.[42] The possibility of 2H-imidazolium ions to form stable C-H…X bonds[35,41] have been reported recently, suggesting that C-H…X hydrogen bonds may act as an additional stabilizing factor in their crystal structures, and we focus on how the C^2-H of the imidazolium ring participate in this environment rich in hydrogen bonds. We hope this study will shed more light on the C-H…X interactions in imidazolium salts.

Thus the present work aims at the synthesis, chemistry and solid-state structure of complexes containing 1,3-dimethylcyanuric acid ligand and new NHCs **15** containing ion pairs linked by C-H…X hydrogen bonds.

The new derivatives can be classified into:

1.3.1 Salt derivatives of the types of 2,3-dihydroimidazole-2-ylidenes



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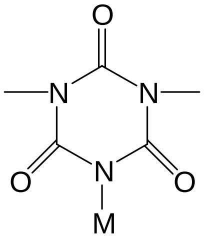
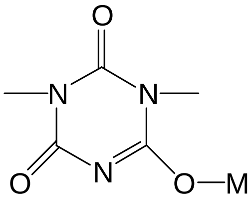
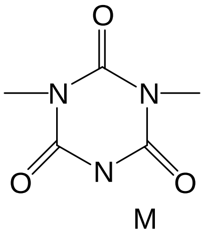
1.3.2 Neutral and anionic derivatives of coordinated and uncoordinated 1,3-dimethylcyanurate ligand to different metal centers

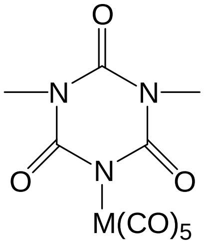






16 **17** **18**

1.3.3 Organometallic complexes of the 1,3-dimethylcyanurate ligand containing group-6 metal carbonyls compounds



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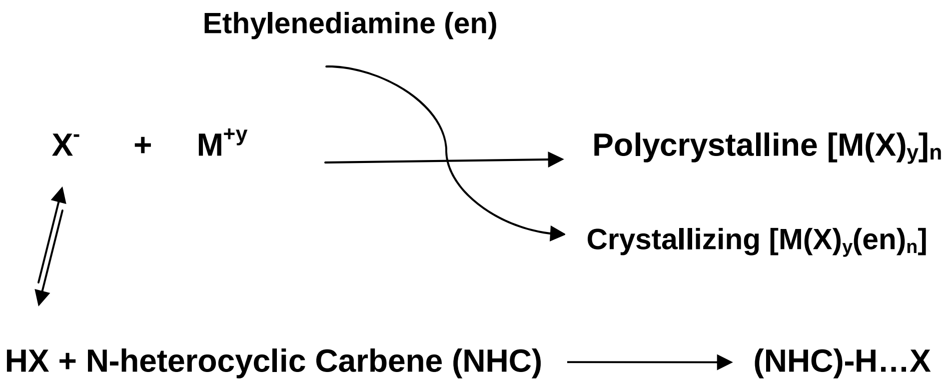


2

Synthesis & Spectroscopy

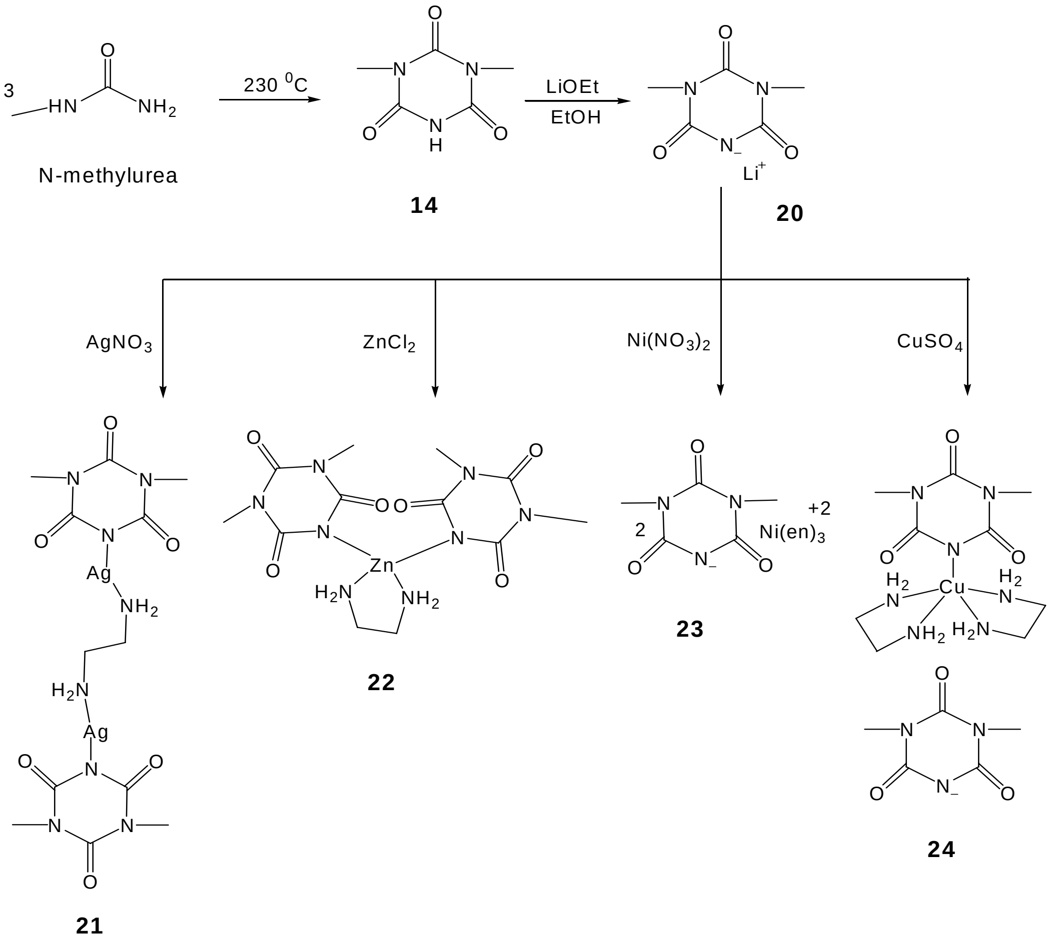
2. Results and Discussion

This chapter is divided into two main sections: (i) Synthesis and chemistry of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene, coordination and organometallic complexes of 1,3-dimethylcyanurate ligand (section 2.1) and (ii) Characterization (IR and ^{1}H-, $^{13}C\{^{1}H\}$ NMR Spectroscopy Studies) (section 2.2).

2.1 Synthesis and chemistry of 2,3-dihydroimidazole-2-ylidene, coordination and organometallic complexes of 1,3-dimethylcyanurate ligand

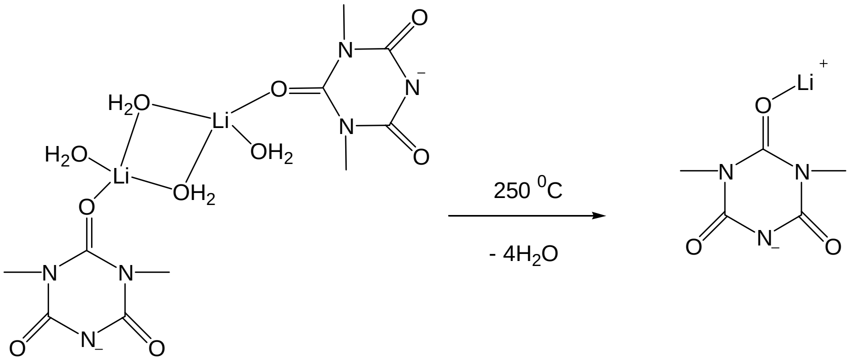
2.1.1 Coordination and organometallic complexes of the 1,3-dimethylcyanurate ligand (Class A and B)

2.1.1.1 Synthesis of 1,3-dimethylcyanurate complexes of Li, Ag, Zn, Ni and Cu (scheme 7) (Class A)



Scheme 7. Synthesis of coordination complexes of 1,3-dimethylcyanurate ligand.

1,3-dimethylcyanuric acid (**14**, DMCH = 1,3-Dimethyl-2,4,6-trioxo-1,3,5-triazine) was prepared by thermal decomposition of N-methylurea in moderate yield. Complexes containing DMCH are not known and therefore, a proton loss from the amine N atom to form amide is necessary for the complexation of DMC. Therefore, the DMC$^-$ anion was synthesized by the reaction of DMCH with LiOEt in ethanol at room temperature for 3h to give Li[DMC] in excellent yield which upon crystallization from not dry methanol gives the dihydrate LiDMC.2H_2O (**20**). Attempts for the deprotonation of **14** with *n*-BuLi have been failed due to its low solubility in THF and for the hydrogen bonds found in its molecular structure (figure 10, chapter 3). LiDMC.2H_2O (**20**) can be dehydrated completely by heating in the range 230-250 ºC under vacuum to give a non-hygroscopic anhydrous salt, and the absorption band at 3435 cm^{-1} due to water molecules disappears. The dehydration of this salt can be represented in scheme 8 **(**table 1). Attempts to crystallize the anhydrous salt were unsuccessful, so the water molecules seemed to be an important integral part of the crystal structure.



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Scheme 8. Dehydration of LiDMC.2H_2O.

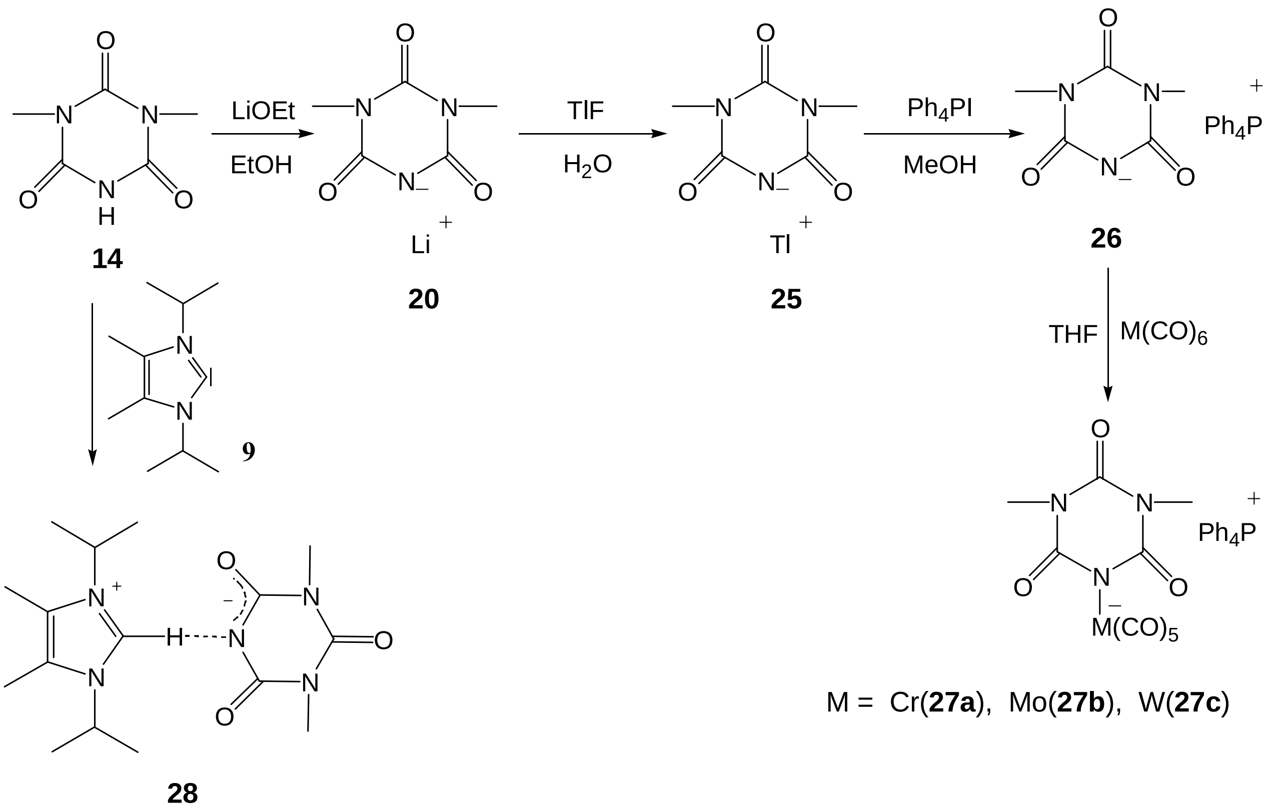
Table 1. Elemental analysis results after dehydration (%).

T range, ºC	Found (Calc.) C	 H	 N	Formula
-----	30.08 (30.16),	5.14 (5.06),	21.03 (21.11)	LiDMC.2H_2O
100-150 ºC	34.85 (33.16),	4.10 (4.45),	23.51 (23.21)	LiDMC.H_2O
230-250 ºC	36.84 (36.83),	3.81 (3.71),	25.94 (25.77)	LiDMC

The silver complex (**21**) was obtained by the direct reaction of LiDMC.2H_2O (**20**) with $AgNO_3$ in the presence of ethylenediamine (en) as co-ligand. Initially, we aimed to prepare AgDMC in the absence of en, but the reaction resulted in the rapid precipitation of a polycrystalline powder, presumably $[Ag(DMC)]_n$, which is barely soluble in known solvents. In the same way, 1,3-dimethylcyanurato complexes of zinc **22** and nickel **23** are produced when the lithium salt **20** is reacted in aqueous solution at 25 ºC with $ZnCl_2$ and $Ni(NO_3)_2$, respectively. The addition of en ligand to those suspension solutions resulted in a clear solution. The copper complex **24** was prepared in two steps. In the first step, the starting complex $[Cu(DMC)_2(H_2O)_3]$ was obtained as a polycrystalline solid by the reaction of **20** with the corresponding copper (II) salt in solution. In the second step, the addition of en to the aqueous suspension of the starting complex resulted in the substitution of all the aqua ligands coordinated to the Cu (II) ion and the formation of the complex **24**. All the compounds (**14**-**24**) are air-stable, and the silver complex is found to be light sensible. After long exposure to light, the crystals become opaque. The analytical data (C, H, and N) are consistent with the expected formulations of the compounds. The DMCH and its lithium salt are soluble in water and methanol, DMCH is slightly soluble in acetonitrile and acetone. The complexes **21** and **22** are soluble in a mixture of water and 2-propanol (4:1). Both **23** and **24** are highly soluble in water.

2.1.1.2 Synthesis of 1,3-dimethylcyanurate complexes of group-6 metal carbonyls compounds (Class B)

We have interested in developing the organometallic chemistry of the DMC ligand and incorporating its metal complexes into designed crystals. Under aqueous conditions the transition metal complexes that are formed by the DMC ligand are barely soluble in organic solvents. Therefore we sought to use Ph_4P^+ salt of DMC in order to enable and control metal complex formation in non-aqueous solvents (scheme 9).



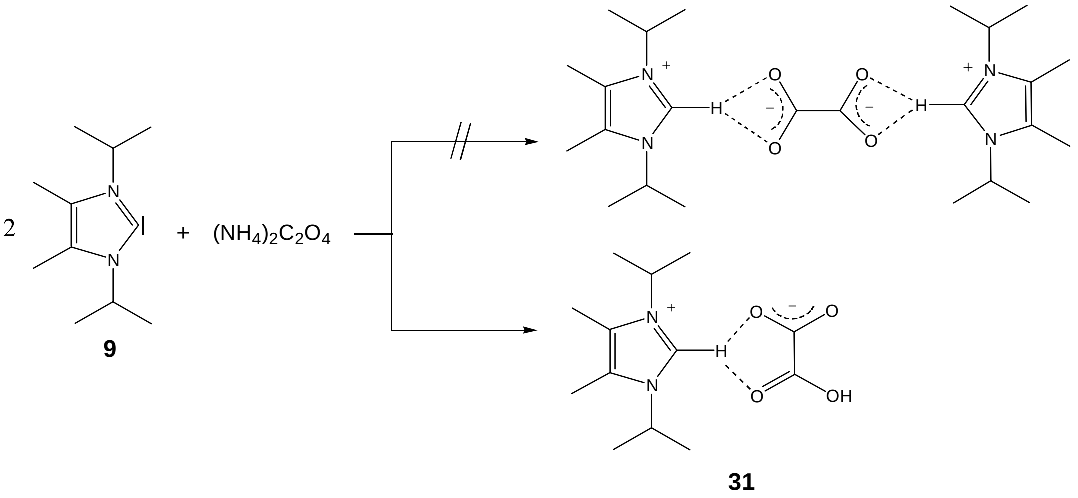
Scheme 9. Deprotonation of 1,3-dimethylcyanuric acid.

Therefore, we prepared the thallous salt Tl[DMC] (**25**), which is slightly soluble in water, from a basic aqueous solution of DMCH and thallous fluoride by a metathesis reaction with tetraphenylphosphonium iodide to give $[Ph_4P][DMC]$ salt **26.** Refluxing **26** with metal hexacarbonyls in THF gives $[Ph_4P][(DMC)M(CO)_5]$ (**27**, Cr (**a**), Mo (**b**), W (**c**)) as yellow crystals in high yields (over 70 %). The reactions are accompanied by a color change from colorless to intense yellow (**27, b** and **c**) or orange (**27a**). The analytical data are consistent with the expected formulations of the complexes. The complexes are stable in solid-state and can be stored at room temperature for long time but decomposed in chlorinated solvents especially in chloroform. Based on the rate of decomposition of $[Ph_4P][(DMC)M(CO)_5]$ (**27**) in solution, the stability increases from going to molybdenum to tungsten to chromium. This indication explains the difficulty of crystallizing the molybdenum complex **27b**. The spectroscopic data of all new metal carbonyl complexes in scheme **9** are given in the experimental section.

As a part of our research in exploring new structural chemistry of imidazolium salts $[H(4,5\text{-}Me)(^iPr)_2Im][X]$, **15**, the 1,3-dimethylcyanuric acid **14** has played a role in classical hydrogen bonded systems having C-H…X interactions outside of coordination chemistry. DMCH is reacted with N-heterocyclic carbene **9** to give **28** (scheme 9) forming a stable C-H…N hydrogen bond in its crystal structure. To illustrate the possibility of 2H-imidazolium ions to form stable C-H...X (X = N, O) bonds and how C-H…X interactions affect on the C^2-H of the imidazolium ring, new imidazolium salts containing ion pairs held together either by a monofunctional or bifurcated C-H…X hydrogen bonds have been synthesized for comparison. Synthesis, reaction and characterization of **28** and other imidazolium salts based on 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene **9** moiety, were compiled and discussed further in details in sections 2.1.2 and 2.2.

2.1.2 Nucleophilic reactions of 2,3-dihydroimidazole-2-ylidene (Class C)

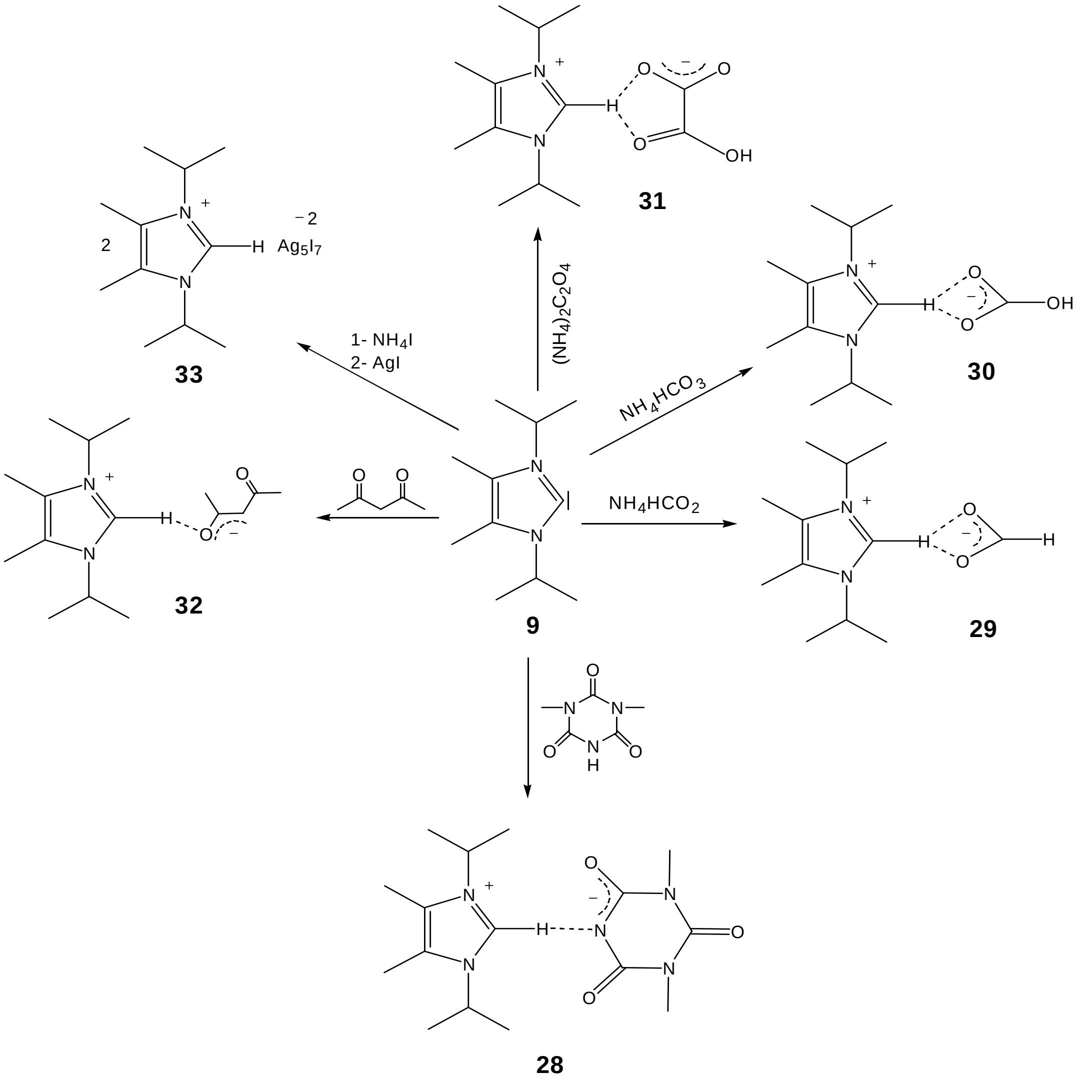
Synthesis and reactions of new imidazolium salts based on 2,3-dihydroimidazole-2-ylidene **9** moiety, are outlined in scheme 11. The reaction of **9** with 1,3-dimethylcyanuric acid **14** in 1:1 molar ratio in tetrahydrofuran at 0 ºC gives the salt **28** in very good yield. Owing to their strongly basic character of heterocyclic carbenes, their reactions with ammonium salts give interesting results.[34] Therefore **29**, **30** and **31** were prepared by the reaction of **9** in 1:1 molar ratio at room temperature with NH_4HCO_2, NH_4HCO_3 and $(NH_4)_2C_2O_4$, respectively to give the salts **29-31** and in high yield (over 80 %). The formation of **31** is independent of reaction conditions and stoichiometry. The same product is obtained whether two equivalents of **9** are added to $(NH_4)_2C_2O_4$ at room temperature or while refluxing in tetrahydrofuran (scheme 10); this result is supported by its IR, ^1H NMR and single-crystal X-ray diffraction (figure 24, chapter 3).



Scheme 10. Synthesis of 31.

The reaction of **9** with acetylacetone in 1:2 molar ratio in THF at -30 ºC gives the *E/Z* isomer **32** in good yield. The silver complex **33** was prepared in two steps. In the first step, the imidazolium iodide [$C_{11}H_{21}N_2I$] was prepared according to published procedures.[43] In the second step, the refluxing of a suspension solution of AgI in 1:1 molar ratio in acetonitrile producing finally the polymeric **33** as colorless block crystals after cooling the solution at -30 ºC for one day in low yield. No NMR solution on **33** could be carried out, due to the poor solubility in most of common organic solvents.

The newly synthesized compounds **28-32** are soluble in polar organic solvents, while they are insoluble in non-polar organic solvents. However, these compounds are air sensitive except the stable imidazolium bicarbonate **30**. The analytical data (C, H, and N) are consistent with the expected formulations of the compounds. The spectroscopic data of these compounds are given in the experimental section.



Scheme 11. Nucleophilic reactions of 2,3-dihydroimidazole-2-ylidene.

2.2 Characterization (IR and ^{1}H-, ^{13}C {1H } NMR Spectroscopy Studies)

2.2.1 Infrared Spectroscopy

2.2.1.1 Class A compounds (Coordination complexes of the 1,3-dimethylcyanurate ligand)

The most characteristic IR absorption bands of the compounds **14**, **20-24** are listed in table 2. The absorption bands in the frequency range 3115-3336 cm^{-1} correspond to the ν(NH) vibrations of the ethylenediamine ligands in **21-24**, while the higher two absorption bands at 3362 and 3435 cm^{-1} are assigned to the ν(O-H) vibration of the hydrogen-bonded water molecules[44] in agreement with the structural information of **20**. The strong and broad absorption bands at 3067 and 3200 cm^{-1} are attributed to the ν(NH) vibrations of the amine group of the DMCH **14**. This intensity of the N-H absorption in **14** is somewhat shifted downfield by 7-10 cm^{-1} than in CYH_3 (**8**)[45], as a result of replacing two of the three imino hydrogens of the cyanuric acid **8** by two methyl groups.

The relatively weak bands in the 2835-3002 cm^{-1} range are characteristic of the ν(CH) stretching vibrations of the methyl and ethylene groups. The DMC ligand exists in its triketo form, three types of strong absorption bands were observed for **14**, **20, 21, 22** and **24** in the frequency range 1621-1764 cm^{-1} as characteristic vibrations of the carbonyl groups. Because some of the carbonyl groups of the DMC ligand participate in bonding either by hydrogen bonding or in coordinating with metal center as in **20**. The carbonyls will no longer be equivalent and will, therefore, give rise to separate bands. In contrast to complexes **14**, **20, 21, 22** and **24**, the uncoordinated DMC ligands in **23**, in which two carbonyl groups participate in bonding by monofunctional O...HN hydrogen bonding being as structurally identical, while in the remaining carbonyl O atom bifurcated hydrogen bonds are observed (figure 15, chapter 3). Therefore, only two types of strong absorption bands of the carbonyl groups were observed at 1701 and 1632 cm^{-1}. The higher absorption bands in the 1706-1729 cm^{-1} range indicate carbonyl groups that are not involved in bonding. As a result of the negative charge from the nitrogen atom in **20**-**24** the corresponding carbonyl vibrations are displaced toward lower frequencies, shifting by ca 58 cm^{-1}. Whereas the bands at lower frequencies involved in coordination or associated with hydrogen bonding of the DMC ligand through the carbonyl groups, shifting in the range 68-99 cm^{-1}.

Table 2. Selected IR spectral data$^{a)}$ for Class A compounds (band position in cm^{-1}).

				IR			
Compd.	ν (O-H)	ν (N-H)$_{en}$	ν (N-H)$_{DMCH}$	ν (C-H)	ν (C=O)	ν (C-H)	ν (C-N)
14			3200 s, br 3067 s	2896 w 2835 m	1764 vs 1750 vs 1689 vs	1404 s	1267 s
20	3435 vs, br 3362 s			3002 w 2964 m	1729 vs 1651 vs 1635 sh	1437 s	1275 s
21		3280 vs 3176 s		2935 m 2893 w	1728 vs 1716 s 1696 s	1436 s	1262 s
22		3336 vs 3275 s		2950 m 2882 w	1727 vs 1701 sh 1632 vs	1482 s	1275 s
23		3333 vs 3278 s		2936 m 2894 w	1701 vs 1632 vs	1460 s	1278 s
24		3272 vs 3115 s		2941 m 2887 w	1706 vs 1668 sh 1621 vs	1449 s	1274 s

$^{a)}$ br: broad; vs: very strong; s: strong; m: medium; sh: shoulder; w: weak.

The strong and broad absorption band at 1457 cm^{-1} in the spectrum of **14** is attributed to the N-H deformation vibrations. The absence of this band in the spectrum of **20** and rise to a strong sharp and intense band at 1558 cm^{-1}, which corresponds to the vibrations of the C=N[46] group that may form as a result of the enolization process, clearly suggests the deprotonation of the amine group. These conclusions are supported by the results of X-ray diffraction studies. This band persists in the 1,3-dimethylcyanurate complexes, the position of 1558 cm^{-1} band is not quite so constant in the range 1558-1595 cm^{-1}. Because of the variable contributions afforded by the C=N bonds formed in DMC ligand to complex formation.

The strong band at 1597 cm^{-1} of the free ethylenediamine ligand is assigned to N-H vibrations. In the spectra of **21-24** this strong absorption band is shifted to higher frequencies in the range 1609-1652 cm^{-1} due to coordination, this is also supportive of the metal-amine complex.[47] The bands with strong intensity between 1482 and 1388 cm^{-1} correspond to the ν(C-H) deformation vibrations and the strong band in the range 1263-1278 cm^{-1} is attributed to the ν(C-N) stretching vibrations.[46,48] The weak or medium intensity bands in the region 415-451 cm^{-1} can be assigned to the ν(M-N) stretching vibrations suggesting that the amine nitrogen atom is coordinating to the metal ion.[22,49] In the spectra of **20**, the strong band at 512 cm^{-1} can be assigned to the Li-OH$_2$ stretching mode, and the medium intensity band at 369 cm^{-1} can also be assigned to the Li-O stretching mode. This assignment appears reasonable, because in the case of strong metal-OH$_2$ interactions such vibrations are often found in this spectral region.[44]

2.2.1.2 Class B compounds (Organometallic complexes of the 1,3-dimethylcyanurate ligand)

The most characteristic IR absorption bands of the compounds **27a, 27b** and **27c** are listed in table 3. The medium and weak bands in the range 2847-3063 cm^{-1} are characteristic of both aromatic and aliphatic ν(C-H) vibrations. The stretching vibrations of the carbonyl groups in **26** appear as two strong absorption bands at 1704 and 1691 cm^{-1}.

Table 3. Selected IR spectral data$^{a)}$ for Class B compounds (band position in cm^{-1}).

	IR			
Compd.	ν (C-H)	ν co$_{(DMC)}$	ν (M-CO)	ν (C-N)
27a	3063 w 3018 w 2959 m	1740 sh 1708 s 1675 sh	2053 w 1971 s 1904 vs 1863 sh 1827 vs	1252 s
27b	3046 w 2939 w 2847 m	1745 sh 1700 s 1640 s	2062 w 1963 s 1902 vs 1864 sh 1834 vs	1254 s
27c	3061 m 3014 w 2945 m	1708 s 1679 sh 1642 sh	2061 w 1942 s 1890 vs 1830 sh 1808 vs	1257 s

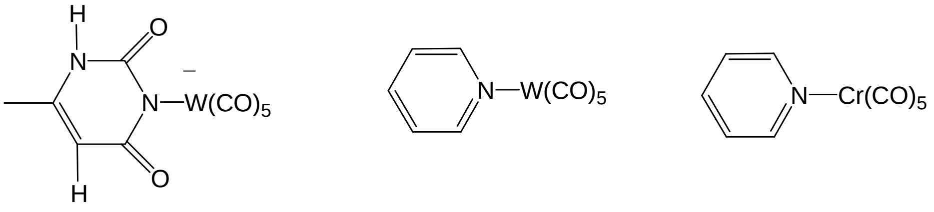
$^{a)}$ br: broad; vs: very strong; s: strong; m: medium; sh: shoulder; w: weak.

In contrast to **26,** the carbonyl vibrations in the spectra of **25** were observed as three bands at 1724, 1690 and 1659 cm^{-1}, indicating that the interaction of the carbonyl groups differ from that of **26**. The complexes **27a, 27b** and **27c** consist of five bands of appropriate intensity pattern for a M(CO)$_5$ fragment with the symmetry-less structure of the complex anions (C$_1$). Since the CO stretching vibrations are such good probes of the electronic character of the substituted ligand in metal carbonyl derivatives, it is of interest to compare these parameters observed herein with similar derivatives. Table 4 contains the carbonyl vibrational frequencies for closely and related carbonyl derivatives (figure 7). It is clear from a close scrutiny of the ν(M-CO) spectra of complexes **27c**, [W(CO)$_5$(6-methyluracilate)]$^{-}$[50] **34** and W(CO)$_5$(pyridine)[51] **35** that the ligand donor properties of the heterocyclic ligands increase only slightly in the series pyridine < 6-methyluracilate < 1,3-dimethylcynurate in their pentacarbonyl tungsten complexes. This difference seems to be more pronounced on comparison of the corresponding pentacarbonyl chromium complexes. This conclusion is also confirmed by comparison of the ^{13}C NMR chemical shift values for their carbon atoms of CO$_{trans}$ (table 9, section 2.2.2.2). The bands with strong intensity between 1252 and 1257 cm^{-1} corresponds to the ν(C-N) stretching vibrations.

Table 4. Stretching frequencies of the carbonyl ligands in other related complexes.

	IR			
Compd.	ν (M-CO) [cm^{-1}]			
[W(CO)$_5$(6-methyluracilate)]$^{-}$ (**34**)[a)]	2059	1912	1840 [b)]	
W(CO)$_5$(pyridine) (**35**)	2072	1934	1921[c)]	
Cr(CO)$_5$(pyridine) (**36**)	2080	1990	1940	1920

[a)] As tetraethylammonium salt.[b)] Spectra determined in CH$_3$CN. [c)] Spectra determined in hexane.



34 **35** **36**

Figure 7. Pentacarbonyl metal complexes.

2.2.1.3 Class C compounds (NHCs)

The most characteristic IR absorption bands of the compounds **28-33** are listed in table 5. Figure 8a shows an example of the observed IR spectra for [H(4,5-Me)(^{i}Pr)$_2$Im][HCO$_2$] **29** in the C-H stretching mode region. Bands in the 2797-2985 cm^{-1} range are attributed to the ν(C-H) stretching vibrations of the methyl and isopropyl groups, while one band at 3122 cm^{-1} is due to the ν(C-H) stretching vibration in the imidazolium ring C^2-H. Since there is one hydrogen atom attached to the imidazolium ring (position 2), one normal mode for the ring C-H stretching is expected. These assignments of **29** are based on comparison of the observed IR spectra for 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene **9** (figure 8b).

Table 5. Selected IR spectral data[a] for Class C compounds (band position in cm^{-1}).

	IR		
Compd.	ν N(C^2-H)N	ν (C-H)$_{alkyl}$	ν (C=O)
28	3114 m	2978 s 2934 s 2883 m 2792 m	1704 vs 1674 s 1631 s
29	3122 m	2985 s 2953 s 2865 m 2797 m	1632 vs
30	3124 m	2966 s 2936 s 2860 m 2783 w	1662 s 1624 s
31	3115 m	2980 s 2937 s 2894 s 2786 w	1679 s 1659 s
32	3110 m	2985 s 2925 s 2789 m 2752 w	1631 s 1585 s
33	3108 m	3008 s 2975 s 2939 m 2836 w	

[a] br: broad; vs: very strong; s: strong; m: medium; sh: shoulder; w: weak.

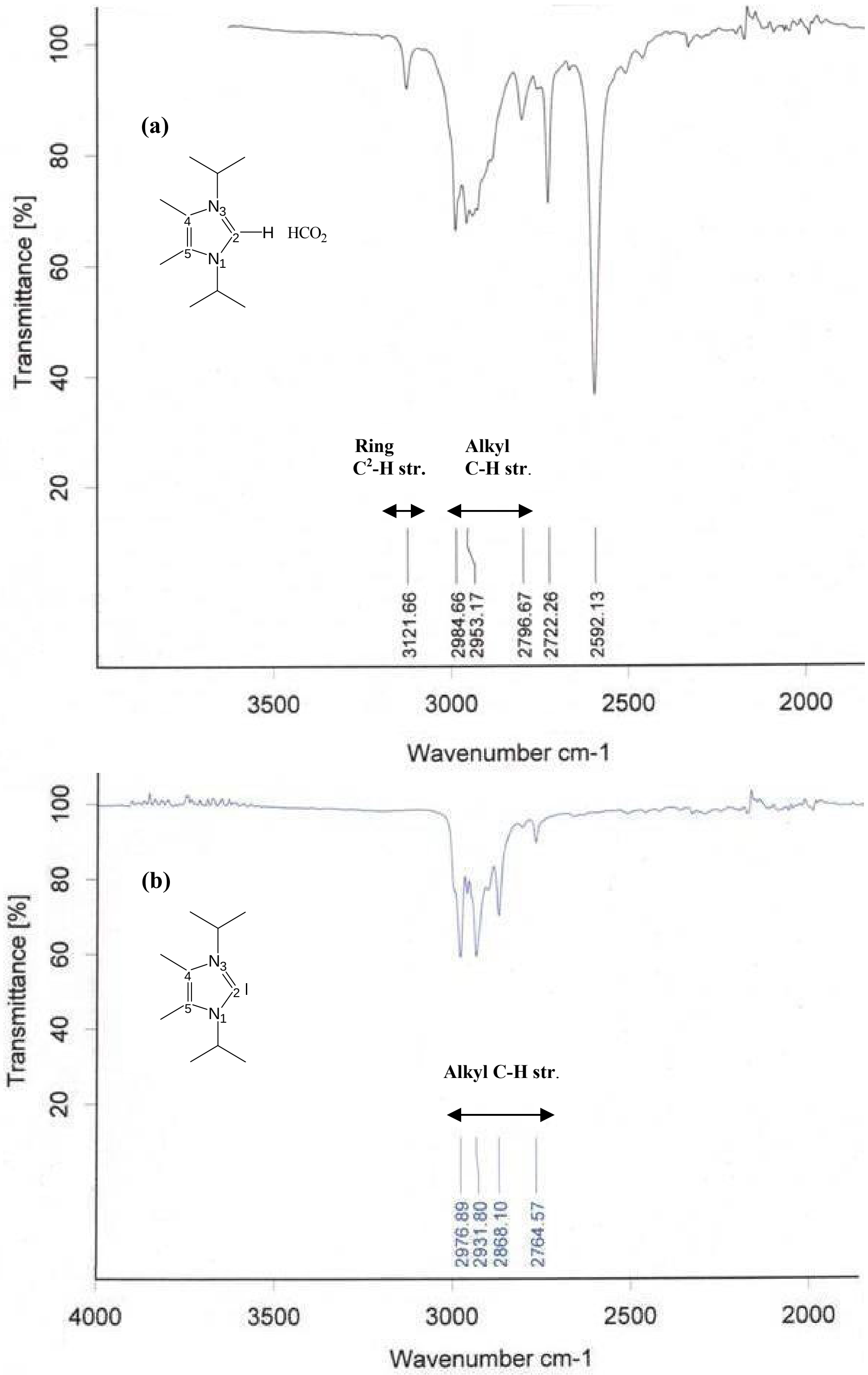


Figure 8. Observed IR spectra of the C-H stretching mode region for (a) 29, (b) 9.

The alkyl groups C-H stretching vibrations at 2977, 2932, 2868 and 2765 cm^{-1} in figure **8b** are shifted downfield to 2985, 2953, 2865 and 2797 cm^{-1}for the corresponding HCO_2^- salt due to the high positive charge in the imidazolium ring, as revealed in figure **8a**. The two strong absorption bands at 2722 and 2592 cm^{-1} are attributed to the ν(C-H) stretching vibrations of the H-CO_2^- anion. When the HCO_2^- was replaced by the HCO_3^- anion **30**, two hydrogen bonds are observed in X-ray structure analysis for the imidazolium cation (figure 23). It is instructive to note that this bifurcate C^2-H…O hydrogen bond causes change in the C^2-H stretching frequency shifted downfield to 3124 cm^{-1}. A possible explanation proposed here may be that the C^2-H hydrogen is pushed toward the carbon by the oxygen atoms due to modification of C-H…O interactions upon increasing the electron density comes from the OH group in HO-CO_2^- anion versus H-CO_2^- anion. We have noticed that, in a number of cases, the formation of C-H…O hydrogen bonds causes shortening of the bridging C-H bond,[53] which leads to a blue-shift (higher) frequency. The strong broad band at 2629 cm^{-1} in **30** is assigned to the ν(O-H) vibration of the acid group in HO-CO_2^- anion. The ν(O-H) vibration in **31** is not observed as evident from the X-ray crystallography (figure 24).

The hydrogen bond formed between the 1,3-dimethylcyanurate and imidazolium groups through C-H…N hydrogen-bonding interactions in **28** causes the C^2-H stretching frequency shifted to 3114 cm^{-1}. On the other hand, the relatively short C-H…O hydrogen bond in the acetylacetone derivative **32** leads to the lengthening of C^2-H bond and thus shifting the frequency upfield to 3110 cm^{-1}. The appearance of this red-shift (lower) frequency in β-diketone enolate is associated with a charge flow through the system of the conjugated double bonds.[54] The weak C-H…I hydrogen bond in **33** is not established, and the C^2-H stretching frequency appears at 3108 cm^{-1}, where the $Ag_5I_7^{-2}$ anion has no effect on the C^2-H bond length.

The two strong absorption bands in the frequency range 1585-1679 cm^{-1} are characteristic of the stretching vibrations of the carbonyl groups in **30**, **31** and **32**, while one strong absorption band appears at 1632 cm^{-1} in **29**. The 1,3-dimethylcyanurate ligand in **28** exists in its triketo form and three types of strong absorption bands were observed at 1704, 1674 and 1631 cm^{-1}.

2.2.2 ^{1}H and ^{13}C{^{1}H}-NMR Spectroscopy Studies

2.2.2.1 Class A compounds (Coordination complexes of the 1,3-dimethylcyanurate ligand)

The ^{1}H NMR spectra for compounds **14**, **20** and **21** are consistent with their proposed formulation. ^{1}H NMR data are summarized in table 6. In DMSO, DMCH displays a signal at 11.60 ppm as a sharp band which was attributed to the NH proton. This band is absent in the spectra of **20**, confirming deprotonation of DMCH **14** to its anion as anticipated from the ν(NH) infrared data (table 2, section 2.2.1). The protons of the water molecules in the spectra of **20** appear as a broad band at 3.50 ppm. In the NMR spectra of **21**, signals at 2.84 and 3.42 ppm correspond to the CH_2-NH_2 and NH_2 groups, respectively, and shifted upfield compared to those of free en; this is quite similar to findings reported for platinum complexes with ethylenediamine derivatives.[55] The signal at 3.20 ppm was assigned to the methyl groups of the DMC ligand and was slightly shifted to downfield compared to the lithium salt **20**.

Table 6. ^{1}H-NMR data of 14, 20 and 21.

	^{1}H NMR [ppm]				
Compd. [a]	NH_{DMCH}	CH_3	H_2O	CH_2-NH_2	NH_2
14	11.60 (s)	3.09 (s)			
20		3.08 (s)	3.50 (br, s)		
21		3.20 (s)		2.84 (s)	3.42 (s)

[a] Spectra determined in DMSO-d_6.

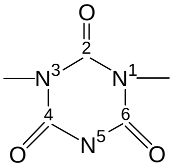
In general, the ^{13}C NMR spectra of compounds **14**, **20** and **21** show three signals one for the methyl groups and two for the carbonyl groups. New signal was observed for the bridging organic ethylenediamine ligand at 43.80 ppm in the silver complex is assigned to CH_2-NH_2 group, and shifted upfield compared to those of free ethylenediamine. The ^{13}C NMR data of these compounds are listed in table 7. The deprotonation of DMCH slightly shifted the methyl groups to upfield by 0.12 ppm, while upon coordination of the nitrogen atom to Ag^I, the signal is shifted downfield by 0.70 ppm compared to those of the lithium salt **20**.

The ^{13}C NMR spectra of the three compounds display two signals for the carbonyl groups in an approximate 2:1 intensity ratio. The more intense resonance for the two carbonyl groups near the N atom which is the deprotonation site is observed upfield (δ = 148.9 ppm) from the smaller signal assigned to the carbonyl group near both the N-methyl groups in DMCH **14**. The order of these signals of the carbonyl groups was observed to be opposite in **20**. The enolization process is highly shifted the carbonyl groups downfield by 3.2-7.5 ppm, this shift may attributed to the delocalization of the negative charge in the heterocyclic ring and the exocyclic carbonyl oxygen atoms. When compared with the coordination of the N atom in **20** to Ag^I only slightly shifted the carbonyl groups upfield by 1.4-1.5 ppm. This small shift may indicate that the coordination of the DMC anion to silver (I) takes place forming a neutral silver complex **21**. The solid state ^{13}C NMR spectrum (MAS) for **22** confirms the result of the crystal structure analysis, the chemical shift values being δ = 30.90, 30.95 (NMe), 42.29, 43.74 (CH_2), 148.60, 153.29 and 155.85 (CO).

Table 7. ^{13}C NMR data of 14, 20 and 21.

	^{13}C NMR [ppm]			
Compd. [a)]	CH_3	*CH_2*-NH_2	$C^{(2)}$	$C^{(4,6)}$
14	28.02		150.4	148.9
20	27.9		153.6	156.4
21	28.6	43.8	152.2	154.9

a) Spectra determined in DMSO-d_6.



2.2.2.2 Class B compounds (Organometallic complexes of the 1,3-dimethylcyanurate ligand)

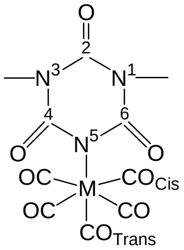
The ^1H NMR spectra for compounds **25-27** are consistent with their proposed formulation. In DMSO the signal in the range 3.04-3.20 ppm was assigned to the methyl groups of DMC ligand. The phenyl ring protons display two multiplets in the range 7.54-8.02 ppm.

The ^{13}C NMR spectra (DMSO) of the carbonyl groups in the heterocyclic ligand for class B compounds are listed in table 8. The salts **25** and **26** are also included in table 8 for comparison. Precipitating of TlI from **25** by a metathesis reaction with tetraphenylphosphonium iodide to give **26** shifted the carbonyl group near both the N-methyl groups (position C^2) to downfield by 0.60 ppm, while no change was observed in the ^{13}C NMR chemical shifts for the carbonyl groups near the deprotonation site in $C^{4,6}$ positions. Upon coordination of the heterocyclic ring to the metal center via the deprotonated N atom to form [Ph_4P][(DMC)M$(CO)_5$], **27**, the ^{13}C NMR spectra ($CDCl_3$) for both the carbonyl groups in C^2 and $C^{4,6}$ positions are shifted upfield by 2.0 and 1.4 ppm (**27a**), 2.8 and 2.4 ppm (**27b**) and 3.2 and 2.6 ppm (**27c**).

Table 8. Selected ^{13}C NMR data of DMC ligand in 25-27.

	^{13}C NMR [ppm]		
Compd.	CH_3	$C^{(2)}$	$C^{(4,6)}$
25 [a)]	27.9	153.1	156.3
26	27.8 28.4	153.7 154.8	156.3 [a)] 157.8 [b)]
27a [b)]	29.4	152.8	156.4
27b [b)]	28.4	152.0	155.4
27c [b)]	28.6	151.6	155.2

[a)]Spectra determined in DMSO-d_6. [b)]Spectra determined in $CDCl_3$.



^{13}C NMR spectroscopic data for the carbonyl ligands M$(CO)_5$ were compiled for complexes **27, 34, 35** and **36**, and are listed in table 9. Complexes exhibit two signals for the carbonyl carbons in an approximate 4:1 intensity ratio (figure 9). The intense upfield peak is assigned to the four carbonyl ligands cis to the nitrogen atom of 1,3-dimethylcyanurate (DMC) ligand while the smaller downfield peak is attributed to the carbonyl ligand trans to the DMC ligand. The appearance of only one signal for the four equatorial CO groups indicates that the molecules are fluxional with respect to rotation about the metal-nitrogen bond axis in solution.[56]

As anticipated from the ν(CO) infrared data (table 3, 4) the ^{13}C NMR chemical shifts for the carbonyl ligands in trans position in the pentacarbonyl tungsten complexes **34**[50] and **35**[51] are upfield of the corresponding value in complex **27c**, further indication of a more electron-donor properties of DMC ligand. This difference seems to be more pronounced on comparison of the corresponding pentacarbonyl chromium complexes [^{13}C NMR $(CO)_{trans}$: $\delta = 225.4$ **(27a)** and 220.7 (**36**)[52]].

Table 9. ^{13}C NMR data for the carbonyl ligands in complexes 27, 34, 35 and 36.

	^{13}C NMR [ppm]	
Compd.	CO_{cis}	CO_{trans}
27a	216.9	225.4 [a)]
27b	205.7	217.2 [a)]
27c	199.5	206.2 [a)]
$[W(CO)_5$(6-methyluracilate)$]^-$ (**34**)[b)]	202.0	204.8 [a)]
$W(CO)_5$(pyridine) (**35**)	199.2	202.7 [c)]
$Cr(CO)_5$(pyridine) (**36**)	214.3	220.7 [a)]

[a)] Spectra determined in $CDCl_3$. [b)] As tetraethylammonium salt. [c)] Spectra determined in C_6D_6.

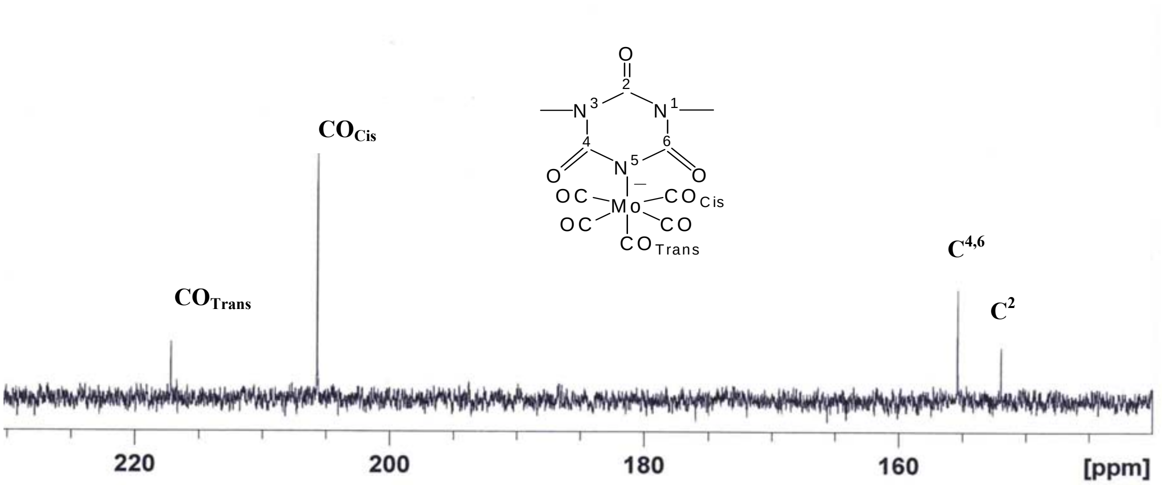


Figure 9. ^{13}C NMR spectrum of $[Ph_4P][(DMC)Mo(CO)_5]$ (27b) in $CDCl_3$ at 100 MHz.

2.2.2.3 Class C compounds (NHCs)

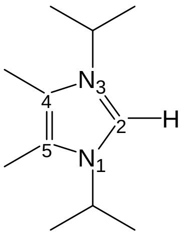
The ^{1}H NMR spectra (DMSO) for NHC compounds **28-31** are consistent with their proposed formulation. For [H(4,5-Me)(^{i}Pr)$_2$Im][X], **15**, system the changes in the counter anion produce much more subtle changes in the chemical shift (table 10). The carbene precursor, [H(4,5-Me)(^{i}Pr)$_2$Im][X], **15**, shows four independent resonances with the two resonances for the isopropyl groups appearing in the range 1.39-1.62 ppm as doublets and as septet centered in the range 4.47-4.70 ppm were assigned to the methyl and methine protons respectively. The imidazolium proton appears downfield in the range 9.23-9.78 ppm as singlet, while the remaining imidazolium-backbone methyl protons resonance upfield in the range 2.19-2.42 ppm.

The downfield resonance in **29** assigned to the formate anion (HCO_2) appears as singlet at 8.62 ppm, this downfield resonance is not observed in HCO_3 **30** and HC_2O_4 **31** anions as evident from the X-ray crystallography and infrared data. The ^{1}H NMR of **32** shows only signals for the carbene moiety. It was not possible to obtain NMR spectra for the acetylacetonate anion. Indicating that this result may arise from the rotation around bonds within the molecule, or it is probably due to their rapid *E/Z* isomerization.

Table 10. Selected ^{1}H-NMR data for NHCs compounds (Class C).

	^{1}H NMR [ppm]			
Compd. [a]	1,3-CH**Me**$_2$	4,5-Me	**CH**Me$_2$	2-H$_{Im}$
28	1.49 (d)	2.29 (s)	4.56 (sept)	9.23 (s)
29	1.50 (d)	2.30 (s)	4.58 (sept)	9.54 (s)
30	1.39 (d)	2.19 (s)	4.47 (sept)	9.38 (s)
31	1.62 (d)	2.42 (s)	4.70 (sept)	9.78 (s)

[a] Spectra determined in DMSO-d_6.

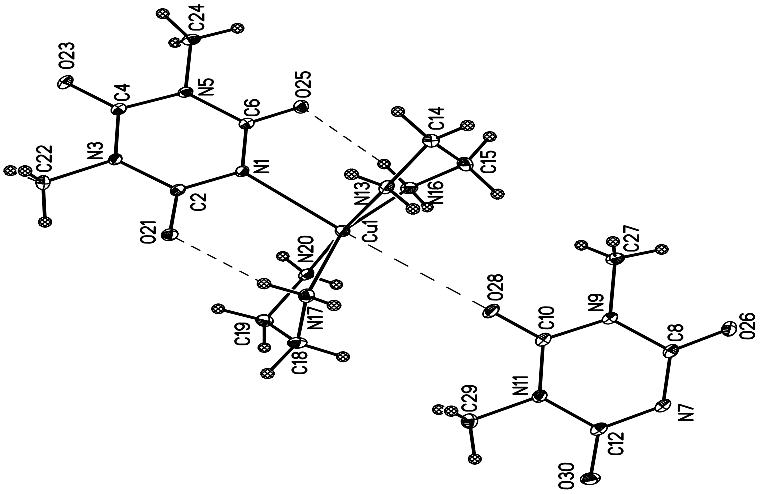


In general, the ^{13}C NMR spectra (DMSO) of the carbene precursor, [H(4,5-Me)(^{i}Pr)$_2$Im][X], **15**, displays five signals (table 11) with subtle changes in chemical shift due to different counteranions [X] = DMC$^-$, HCO_2^-, HCO_3^-, $HC_2O_4^-$, acac$^-$ and $Ag_5I_7^{-2}$. As mentioned above for the rapid dynamic process of the acetylacetonate ion, solid state ^{13}C NMR (MAS) on **32** carried out, and the chemical shift for the anion being δ = 26.0, 30.9 (Me$_{acac}$), 101.7 (CH$_{acac}$) and 190.3 ppm (CO). The signals at 164.96, 158.18 and 168.70 ppm were assigned to the carbonyl group in HCO_2, HCO_3 and HC_2O_4 respectively, while the carbonyl groups in C^2 and C^{4,6} positions for DMC ligand in **28** were observed at 153.73 and 156.35 ppm. The solid state ^{13}C NMR spectrum (MAS) for [H(4,5-Me)(^{i}Pr)$_2$Im]$_2$[Ag_5I_7] **33** carried out due to its poor solubility in most organic common solvents. The chemical shifts for the cation are δ = 12.06 (4,5-Me), 26.93 (1,3-CH**Me$_2$**), 53.08 (1,3-**CH**Me$_2$), 128.13 (C$^{2}_{Im}$) and 134.76 (C$^{4,5}_{Im}$).

Table 11. Selected ^{13}C-NMR data for NHCs compounds (Class C).

	^{1}H NMR [ppm]				
Compd. [a]	4,5-Me	1,3-CH**Me**$_2$	**CH**Me$_2$	C^2	C^{4,5}
28	7.81	22.14	49.61	125.90	130.64
29	7.82	22.16	49.59	125.77	131.24
30	7.83	22.13	49.61	125.75	130.26
31	7.85	22.12	49.65	125.63	131.78

[a] Spectra determined in DMSO-d_6.



Solid-State 3

Structure & Bonding

3. Solid-State Structures and bonding

3.1 Description of the crystal structures

3.1.1 1,3-dimethylcyanuric acid (14)

The crystals are stabilized by forming two hydrogen bonds, creating a planar structure through molecular self-assembly (Figure 10). Bond lengths and angles are given in table 12. The crystal crystallizes in the monoclinic space group $P2_1/n$.

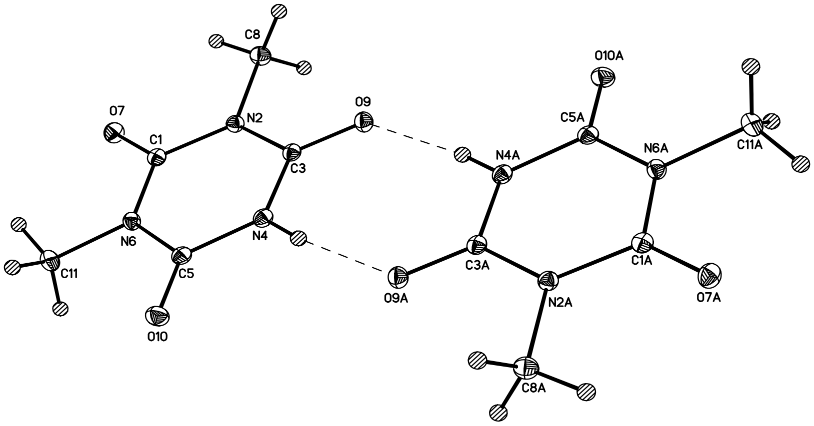


Figure 10. Molecular self-assembly through hydrogen bonds, showing the atom numbering scheme.

The C_3-O_9 bond associated with hydrogen bond forming ring linkage has a length of 1.223(2) Å is comparable with similar bond in cyanuric acid.[45] The average intermolecular difference in length between the hydrogen bonds in cyanuric acid (N-H…O = 2.788(3) Å)[57] is large in comparison with 1,3-dimethylcyanuric acid **(14)** (N_4-H_4…O_{9A} = 2.014(1) Å; N_4-H_4-O_{9A} 173.2, C_3-O_9-H_{4A} 127.7 º). Further bond lengths and angles are listed in table 12.

The triazine ring is planar, the two methyl groups and the three carbonyl groups are not displaced from the mean plane of their attached triazine ring.

Table 12. Bond lengths (Å) and angles (º) for 14.

C(1)-O(7)	1.208(2)	O(7)-C(1)-N(6)	122.59(16)
C(1)-N(6)	1.387(2)	O(7)-C(1)-N(2)	121.82(16)
C(1)-N(2)	1.398(2)	N(6)-C(1)-N(2)	115.57(14)
N(2)-C(3)	1.373(2)	C(3)-N(2)-C(1)	123.55(14)
N(2)-C(8)	1.480(2)	C(3)-N(2)-C(8)	117.80(14)
C(3)-O(9)	1.223(2)	C(1)-N(2)-C(8)	118.65(15)
C(3)-N(4)	1.368(2)	O(9)-C(3)-N(4)	122.00(16)
N(4)-C(5)	1.377(2)	O(9)-C(3)-N(2)	122.36(15)
C(5)-O(10)	1.209(2)	N(4)-C(3)-N(2)	115.62(14)
C(5)-N(6)	1.378(2)	C(3)-N(4)-C(5)	126.09(15)
N(6)-C(11)	1.471(2)	O(10)-C(5)-N(4)	122.21(16)
		O(10)-C(5)-N(6)	123.26(16)
		N(4)-C(5)-N(6)	114.53(15)
		C(5)-N(6)-C(1)	124.53(14)
		C(5)-N(6)-C(11)	116.84(15)
		C(1)-N(6)-C(11)	118.56(14)

3.1.2 1,3-Dimethyl-O-lithiumcyanurate dihydrate [LiDMC.2H_2O] (20)

The selected bond lengths and angles are listed in table 13. The crystal crystallizes in the triclinic space group $P\bar{1}$ in a dimer form **(**LiDMC.2H_2O)$_2$ with inversion center (figure 12a). The 1,3-dimethylcyanurate molecule acts as a monodentate ligand through one of its carbonyl oxygen atoms with high bond angle speaks for an electrostatically dominated reciprocal effect (Li-O_9 = 1.937(4) Å; C_3-O_9-Li 132.5(2) º). The 1,3-dimethylcyanurate ligand is planar with Li_2O_2 core. Two water molecules bridge a pair of inversion related **(**LiDMC.H_2O) complexes in **20** through its electron pairs (Li-O_1 = 2.161(6), Li-O_{1A} = 1.938(5) Å; Li-O_1-Li_A 87.8(2), O_1-Li-O_{1A} 92.2(5) º), the intermetallic distance (Li…Li_A 2.847(11) Å) lies at the borders of *van der Waals* range. Whereas the terminal water ligands coordinate the lithium ion through one of its electron pairs at Li-O_2 distance of 1.925(4) Å, in relation of an expected tetrahedron narrowed angles (O_2-Li-O_1 93.6(2), O_2-Li-O_{1A} 103.4(2), O_2-Li-Li_A 101.8(3) º).

The bonds are most significantly different in the region near N atom which is the deprotonation site. As a result of deprotonation, the internal ring angle at N_4 closes from 126.09º in DMCH (**14**) to 120.85º (N_6) in its anion. A similar effect has been noted in a variety of pyrimidine crystal structures.[58] The opening of each of the internal ring angles at the adjacent carbon atoms C_5 and C_1 by 4-5 º over-compensates for the closing of the angle at N_6 by 5º. This suggests that all three angular changes are a consequence of the deprotonation. It is interesting to compare the structural parameters of DMCH (**14**) with its anion present; the N_6-C_5, N_6-C_1, C_3-N_4

and C_3-N_2 bond lengths are somewhat shorter in the lithium complex whereas N_4-C_5, N_2-C_1, C_1-O_7 and C_3-O_9 bonds are slightly longer (figure 11). These variations can be explained in the terms of the resonance structures of the 1,3-dimethylcyanurate anion in comparison with the DMCH acid (**14**).

The hydrated lithium complex has two types of intermolecular hydrogen bonds ($N_{6C}\ldots H_{2B}O$ 2.049 Å; O_2-H_{2B}-N_{6B} 174.8°) and ($O_{7AA}\ldots H_{1A}O$ 1.846 Å; O_1-H_{1A}-O_{1AA} 170.7°) linking the 1,3-dimethylcyanurate moieties forming a polymeric structure (figure 12b).

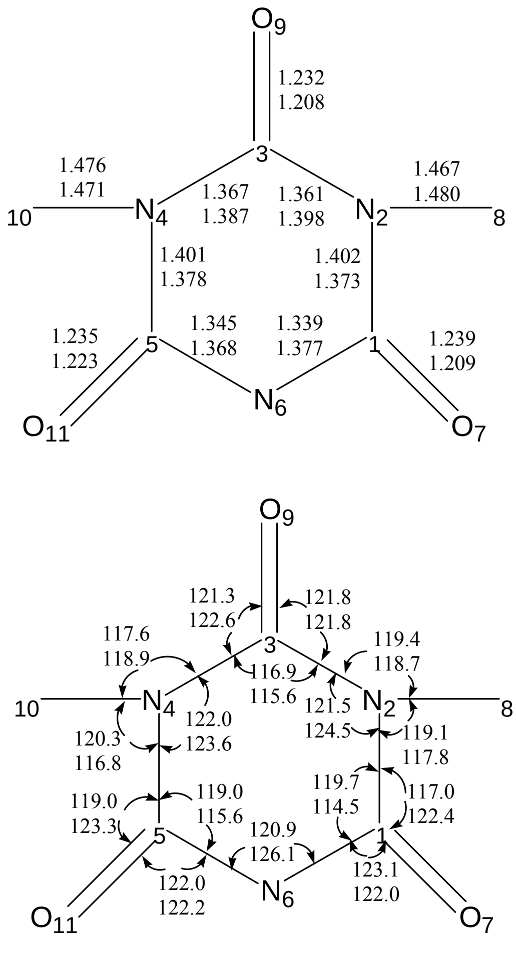


Figure 11. Bond length (Å) and bond angles (°) for the DMC$^-$ anion (upper number) and the DMCH molecule (lower number).

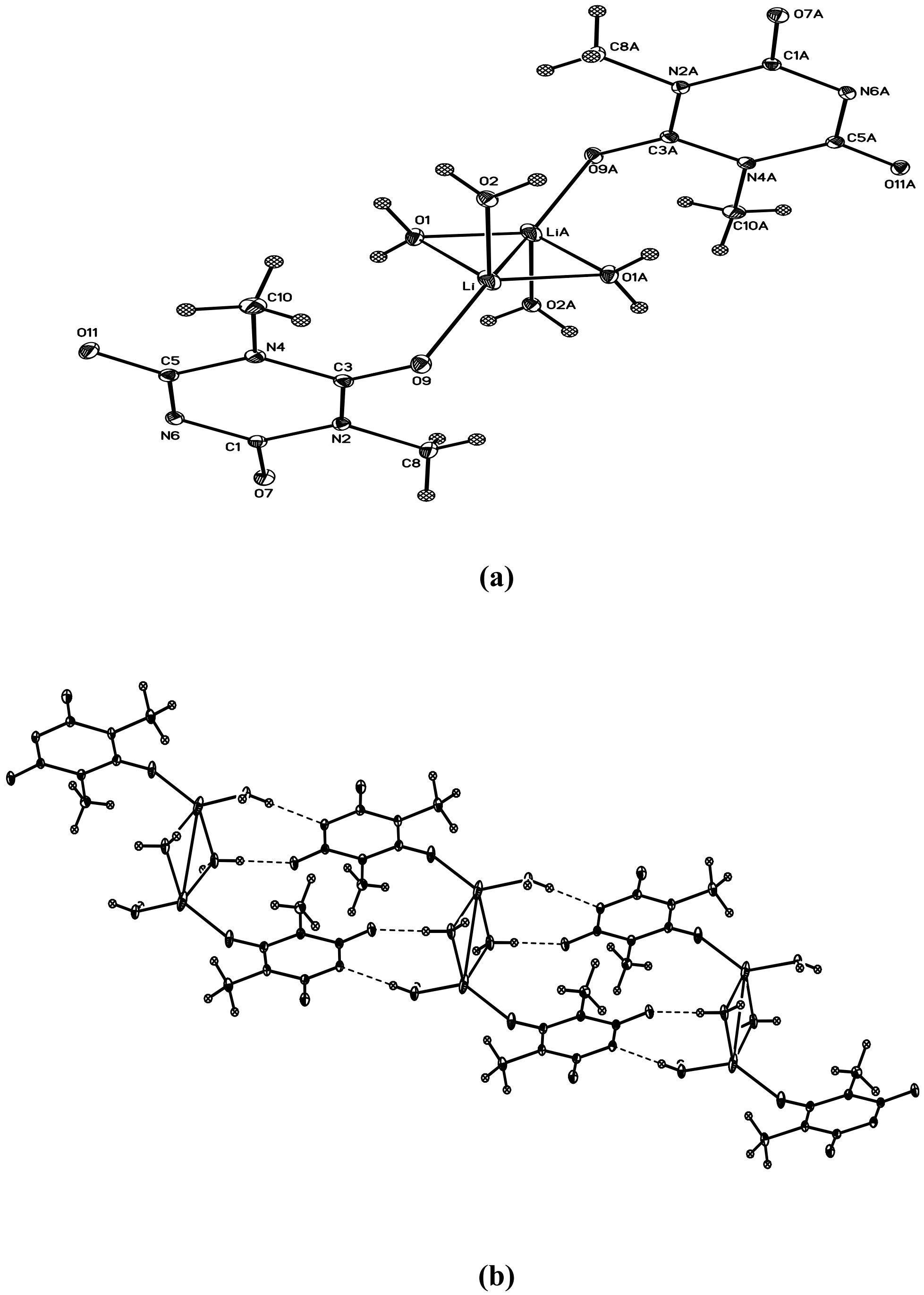


Figure 12. (a) A view of $(LiDMC.2H_2O)_2$, showing the dimeric unit with the atom labeling scheme. (b) Part of helical chain shows N…H-O and O…H-O hydrogen bonds are shown as dashed lines.

Table 13. Bond lengths (Å) and angles (°) for 20$^{a)}$.

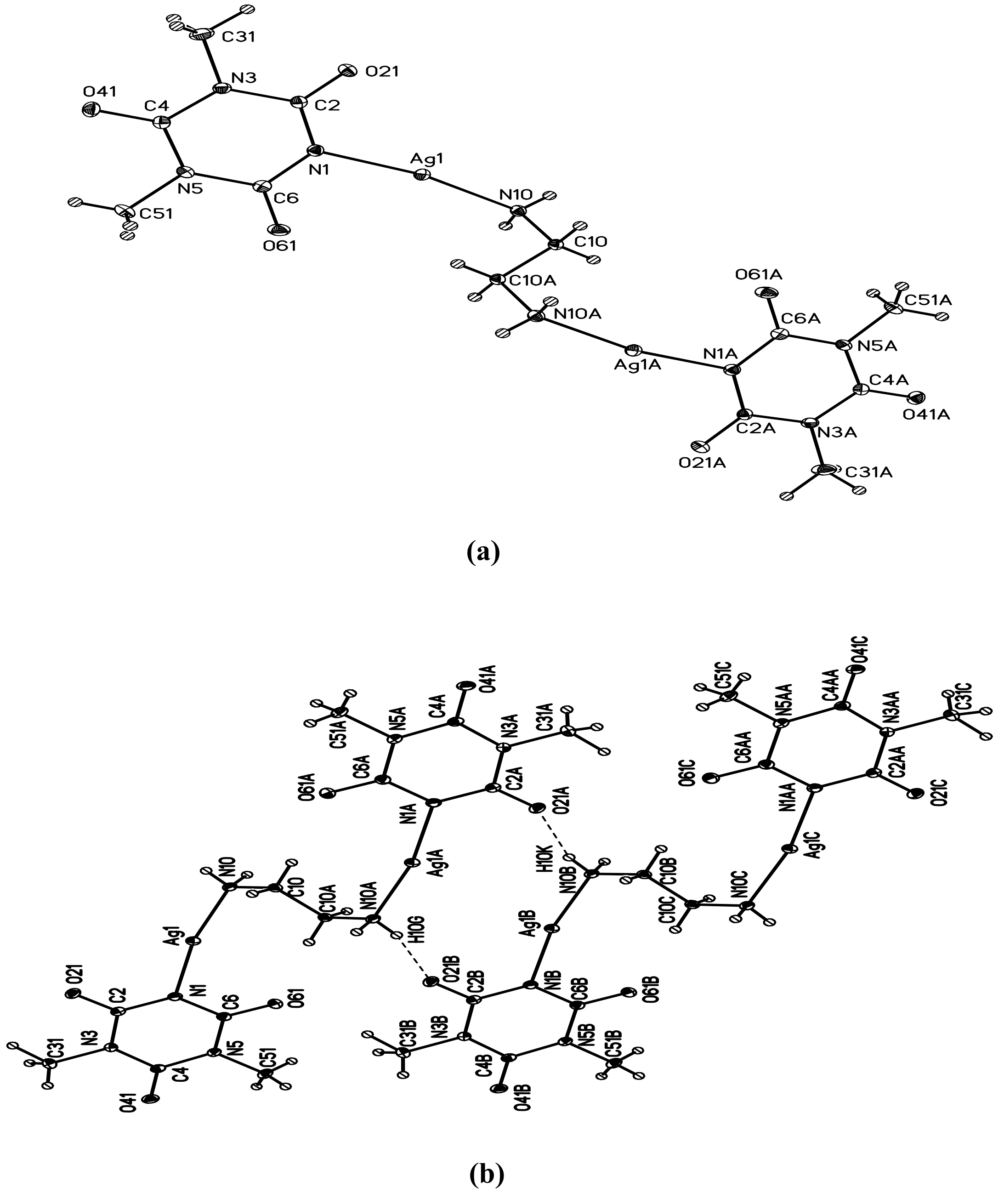
C(1)-O(7)	1.239(2)	O(7)-C(1)-N(6)	123.31(17)
C(1)-N(6)	1.339(3)	O(7)-C(1)-N(2)	116.95(17)
C(1)-N(2)	1.402(2)	N(6)-C(1)-N(2)	119.74(16)
N(2)-C(3)	1.361(2)	C(3)-N(2)-C(1)	121.51(16)
N(2)-C(8)	1.467(3)	C(3)-N(2)-C(8)	119.41(17)
C(3)-O(9)	1.232(2)	C(1)-N(2)-C(8)	119.07(17)
C(3)-N(4)	1.367(3)	O(9)-C(3)-N(2)	121.84(18)
N(4)-C(5)	1.401(2)	O(9)-C(3)-N(4)	121.31(18)
N(4)-C(10)	1.476(3)	N(2)-C(3)-N(4)	116.85(16)
C(5)-O(11)	1.235(2)	C(3)-N(4)-C(5)	122.04(16)
C(5)-N(6)	1.345(2)	C(3)-N(4)-C(10)	117.62(17)
O(9)-Li$^{\#1}$	1.937(4)	C(5)-N(4)-C(10)	120.34(17)
Li-O(2)	1.925(4)	O(11)-C(5)-N(6)	121.96(17)
Li-O(9)$^{\#1}$	1.937(4)	O(11)-C(5)-N(4)	119.04(17)
Li-O(1)$^{\#2}$	1.938(5)	N(6)-C(5)-N(4)	119.00(16)
Li-O(1)	2.161(6)	C(1)-N(6)-C(5)	120.85(16)
Li-Li$^{\#2}$	2.85(1)	C(3)-O(9)-Li$^{\#1}$	132.5(2)
O(1)-Li$^{\#2}$	1.938(5)	O(2)-Li-O(9)$^{\#1}$	134.8(3)
		O(2)-Li-O(1)$^{\#2}$	103.4(2)
		O(9)$^{\#1}$-Li-O(1)$^{\#2}$	119.1(2)
		O(2)-Li-O(1)	93.6(2)
		O(9)$^{\#1}$-Li-O(1)	99.1(2)
		O(1)$^{\#2}$-Li-O(1)	92.2(2)
		O(2)-Li-Li$^{\#2}$	101.8(3)
		O(9)$^{\#1}$-Li-Li$^{\#2}$	116.8(3)
		O(1)$^{\#2}$-Li-Li$^{\#2}$	49.3(2)
		O(1)-Li-Li$^{\#2}$	42.9(2)
		Li$^{\#2}$-O(1)-Li	87.8(2)

a) Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ x, y, z, $^{\#2}$ -x, -y, -z

3.1.3 Bis(1,3-dimethyl-N-silvercyanurate)(ethylenediamine) [(AgDMC)$_2$(en)](21)

The bond lengths and angles are listed in table 14. The crystal crystallizes in the monoclinic space group *P*2$_1$/n. The 1,3-dimethylcyanurate ligand (DMC) is *N*-coordinated through the negatively charged N atom to a metal center forming AgDMC fragment. The AgDMC is further bridged by ethylenediamine ligand using both amine N atoms forming a neutral complex (figure 13a). This Ag^{I} center has a distorted linear AgN$_2$ (N$_1$-Ag$_1$-N$_{10}$ 169.11(9) °) coordination geometry. The Ag-N$_{en}$ bond distance (2.125(2) Å) is similar to that observed in [Ag$_2$(sac)$_2$(en)(H$_2$O)]$^{[59]}$, but is noticeably longer than the Ag-N$_{DMC}$ bond distance (2.098(2) Å) in **21**. The C-N bonds are almost equal resulting in a symmetric π-electron distribution in the sense of an effective delocalization within the heterocyclic ring. Also the C-O distances have been little affected as a result of ligand coordination (table 14).

Complex **21,** exhibits a weak intermolecular hydrogen bond ($NH_{10K}...O_{21A}$ = 2.12(1) Å; N-H_{10k}-O_{21A} 156(1) °). The complex is in pairs through weak intermolecular hydrogen bonds formed by the amine hydrogen atoms of ethylenediamine coordinating with the O atom of DMC ligand (figure 13b). The Ag…Ag separations (4.205 Å) in Ag_{1A}-Ag_{1B} are longer than the *van der Waals* radius sum of silver (3.44 Å)[60] indicates no direct Ag…Ag interactions.



(a)

(b)

Figure 13. (a) A view of symmetric unit of $(AgDMC)_2(en)$, showing the atom numbering scheme. (b) Pair of complexes linked by NH…O hydrogen bonds are shown as dashed lines.

Table 14. Bond lengths (Å) and angles (°) for 21[a].

Ag(1)-N(1)	2.098(2)	N(1)-Ag(1)-N(10)	169.11(9)
Ag(1)-N(10)	2.125(2)	C(4)-N(3)-C(2)	123.4(2)
O(21)-C(2)	1.231(3)	C(4)-N(3)-C(31)	117.9(2)
O(41)-C(4)	1.212(3)	C(2)-N(3)-C(31)	118.6(2)
O(61)-C(6)	1.231(3)	C(4)-N(5)-C(6)	123.2(2)
N(3)-C(4)	1.381(3)	C(4)-N(5)-C(51)	118.0(2)
N(3)-C(2)	1.387(3)	C(6)-N(5)-C(51)	118.8(2)
N(3)-C(31)	1.465(4)	C(2)-N(1)-C(6)	122.2(2)
N(5)-C(4)	1.382(3)	C(2)-N(1)-Ag(1)	122.3(2)
N(5)-C(6)	1.390(3)	C(6)-N(1)-Ag(1)	115.6(2)
N(5)-C(51)	1.468(3)	O(21)-C(2)-N(1)	122.1(2)
N(1)-C(2)	1.353(3)	O(21)-C(2)-N(3)	119.8(2)
N(1)-C(6)	1.362(3)	O(21)-C(2)-N(3)	119.8(2)
N(10)-C(10)	1.479(3)	N(1)-C(2)-N(3)	118.0(2)
C(10)-C(10)$^{\#1}$	1.51(1)	O(41)-C(4)-N(3)	122.4(2)
		O(41)-C(4)-N(5)	122.5(2)
		N(3)-C(4)-N(5)	115.1(2)
		O(61)-C(6)-N(1)	122.0(2)
		O(61)-C(6)-N(5)	120.1(2)
		N(1)-C(6)-N(5)	117.9(2)
		C(10)-N(10)-Ag(1)	114.7(1)
		N(10)-C(10)-C(10)$^{\#1}$	110.6(3)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1,-y+1,-z

3.1.4 Bis(1,3-dimethylcyanurate)(ethylenediamine)Zinc(II) [Zn(DMC)$_2$(en)] (22)

Figure 14 shows the molecular structure of **22** with atom labeling. The bond lengths and angles are listed in table 15. The complex **22** crystallizes in the orthorhombic space group *P*bca. The zinc(II) ion is tetrahedrally coordinated by en (ethylenediamine) ligand and two DMC anions, forming a distorted tetrahedral ZnN$_4$ core. The en ligand behaves as a bidentate N,N' donor chelating ligand, forming a five-membered chelate ring, while each DMC ligand is coordinated through the negatively charged N atom. The bite angle of en ligand N$_{13}$-Zn$_1$-N$_{16}$ is 86.16(8)° and significantly contributes to the distortion of the coordination geometry around the Zn(II) ion.

The Zn-N$_{DMC}$ bond distances are almost identical (Zn$_1$-N$_1$ 1.9715(17), Zn$_1$-N$_7$ 1.9978(17) Å) and are shorter than the Zn-N$_{en}$ bond distances (Zn$_1$-N$_{13}$ 2.077(2), Zn$_1$-N$_{16}$ 2.043(2) Å). The bond angles at the metal center show considerable fluctuations in relation to the theoretical tetrahedron internal angle of 109°. The highest value (N$_1$-Zn$_1$-N$_7$ 125.11(7) °) is for the angle between the nitrogen atoms of the DMC ligands, we may refer this to the space requirement of the ligands. Bond lengths and angles of the DMC ligands are similar to those found in **21**. The dihedral angle between the two DMC mean planes ($N_1N_3N_5$ // $N_7N_9N_{11}$ 91(1) º) is perpendicular to each other.

Complex **22,** exhibits hydrogen bonds (O_{04}-H_{16A} = 2.24(1), O_{012}-H_{13A} 2.29(1) Å). These intramolecular hydrogen bonds are formed by the amine hydrogen atoms of en coordinating with the neighboring O atoms of DMC ligand.

Table 15. Bond lengths (Å) and angles (º) for 22.

Zn(1)-N(1)	1.971(2)	N(1)-Zn(1)-N(7)	125.13(7)
Zn(1)-N(7)	1.997(2)	N(1)-Zn(1)-N(16)	118.09(8)
Zn(1)-N(16)	2.043(2)	N(7)-Zn(1)-N(16)	102.85(7)
Zn(1)-N(13)	2.077(2)	N(1)-Zn(1)-N(13)	110.08(8)
N(1)-C(2)	1.359(3)	N(7)-Zn(1)-N(13)	107.40(8)
N(1)-C(6)	1.365(3)	N(16)-Zn(1)-N(13)	86.16(8)
C(2)-O(02)	1.223(3)	C(2)-N(1)-C(6)	122.56(18)
C(2)-N(3)	1.395(4)	C(2)-N(1)-Zn(1)	120.75(14)
N(3)-C(4)	1.382(3)	C(6)-N(1)-Zn(1)	116.65(14)
N(5)-C(4)	1.380(3)	N(1)-C(2)-N(3)	117.71(18)
N(5)-C(6)	1.392(3)	C(4)-N(3)-C(2)	122.03(18)
C(6)-O(06)	1.219(3)	C(4)-N(5)-C(6)	122.30(18)
N(7)-C(8)	1.358(3)	N(1)-C(6)-N(5)	117.51(19)
N(7)-C(12)	1.358(3)	C(8)-N(7)-C(12)	122.34(17)
C(8)-C(08)	1.222(3)	C(8)-N(7)-Zn(1)	113.22(13)
C(8)-N(9)	1.398(3)	C(12)-N(7)-Zn(1)	123.19(14)
N(9)-C(10)	1.375(3)	N(7)-C(8)-N(9)	118.15(18)
C(10)-O(010)	1.218(3)	C(10)-N(9)-C(8)	123.01(18)
C(10)-N(11)	1.380(3)	N(9)-C(10)-N(11)	115.38(18)
N(11)-C(12)	1.400(3)	C(10)-N(11)-C(12)	123.63(18)
C(12)-O(012)	1.221(3)	N(7)-C(12)-N(11)	117.36(19)
N(13)-C(14)	1.484(3)	C(14)-N(13)-Zn(1)	105.39(15)
C(14)-C(15)	1.514(3)	N(13)-C(14)-C(15)	109.42(19)
C(15)-N(16)	1.478(3)	N(16)-C(15)-C(14)	108.7(2)
C(4)-O(04)	1.219(3)	C(15)-N(16)-Zn(1)	105.27(15)
		N(5)-C(4)-N(3)	115.62(18)

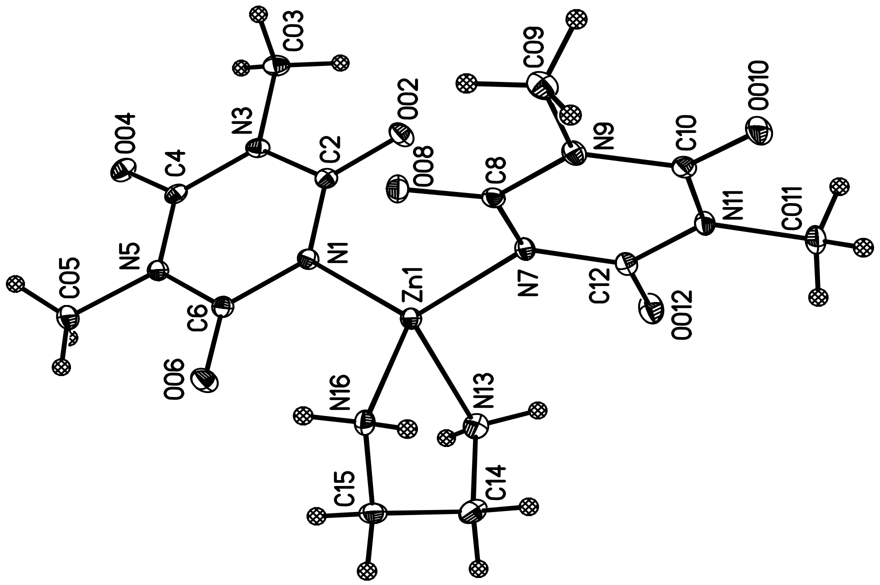


Figure 14. Molecular structure of 22.

3.1.5 Tris(ethylenediamine)Nickel(II) Bis(1,3-dimethylcyanurate) $[Ni(en)_3][DMC]_2$ (23)

The bond lengths and angles are listed in table 16. The dark-purple **23** crystallizes in the monoclinic space group *C*2/c. The crystal structure reveals that the coordination sphere of the metal center is occupied with ethylenediamine ligands exclusively, while the cyanurate ions remain as uncoordinated ions (figure 15). The bond lengths of the cyanurate ions are slightly deviated from those values found in DMCH **14**, while for the C-O bond lengths a slight expansion is observed as a consequence of the negative charge located mainly at the oxygen atoms (C_5-O_1 1.236(2), C_7-O_2 1.233(2), C_6-O_3 1.226(2) Å).

In complex **23**, the cyanurate anions are linked to the cation by both a monofunctional ($O_1…H_{3C}N$ 2.20(1), $O_2…H_{3D}N$ 2.51(1) Å) and bifurcated hydrogen bonds ($O_3…H_{1C}N$ 2.32(1), $O_3…H_{2CA}N$ 2.41(1) Å). The bond lengths and angles of the tris(ethylenediamine)Nickel(II) cation are similar to those reported for $[Ni(en)_3][NO_3]_2$.[61]

Table 16. Bond lengths (Å) and angles (°) for 23$^{a)}$.

Ni(1)-N(1)	2.1282(17)	N(2)-Ni(1)-N(2)$^{\#1}$	91.41(10)
Ni(1)-N(2)	2.1139(16)	N(2)-Ni(1)-N(3)	174.51(7)
Ni(1)-N(3)	2.1199(17)	N(2)$^{\#1}$-Ni(1)-N(3)	93.63(7)
O(1)-C(5)	1.236(2)	N(2)-Ni(1)-N(3)$^{\#1}$	93.63(7)
O(2)-C(7)	1.233(2)	N(2)$^{\#1}$-Ni(1)-N(3)$^{\#1}$	174.51(7)
O(3)-C(6)	1.226(2)	N(3)-Ni(1)-N(3)$^{\#1}$	81.41(9)
N(1)-C(1)	1.473(3)	N(2)-Ni(1)-N(1)$^{\#}$1	92.65(7)
N(2)-C(2)	1.473(2)	N(2)$^{\#1}$-Ni(1)-N(1)$^{\#1}$	81.76(6)
N(3)-C(3)	1.466(3)	N(3)-Ni(1)-N(1)$^{\#1}$	90.21(7)
N(4)-C(6)	1.374(2)	N(3)$^{\#1}$-Ni(1)-N(1)$^{\#1}$	95.84(7)
N(4)-C(5)	1.410(2)	N(2)-Ni(1)-N(1)	81.76(6)
N(5)-C(6)	1.370(2)	N(2)$^{\#1}$-Ni(1)-N(1)	92.65(7)
N(5)-C(7)	1.412(2)	N(3)-Ni(1)-N(1)	95.84(7)
N(6)-C(5)	1.340(2)	N(3)$^{\#1}$-Ni(1)-N(1)	90.21(7)
N(6)-C(7)	1.342(2)	N(1)$^{\#1}$-Ni(1)-N(1)	172.03(9)
C(1)-C(2)	1.515(3)	C(1)-N(1)-Ni(1)	108.52(12)
C(3)-C(3)$^{\#1}$	1.517(4)	C(2)-N(2)-Ni(1)	108.61(11)
		C(3)-N(3)-Ni(1)	109.08(12)
		C(6)-N(4)-C(5)	122.43(15)
		C(6)-N(5)-C(7)	122.92(15)
		C(5)-N(6)-C(7)	121.04(16)
		N(1)-C(1)-C(2)	109.54(15)
		N(2)-C(2)-C(1)	108.23(16)
		N(3)-C(3)-C(3)$^{\#1}$	108.91(13)
		N(6)-C(5)-N(4)	119.38(16)
		N(5)-C(6)-N(4)	115.27(15)
		N(6)-C(7)-N(5)	118.74(16)

$^{a)}$ Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1, y,-z+3/2

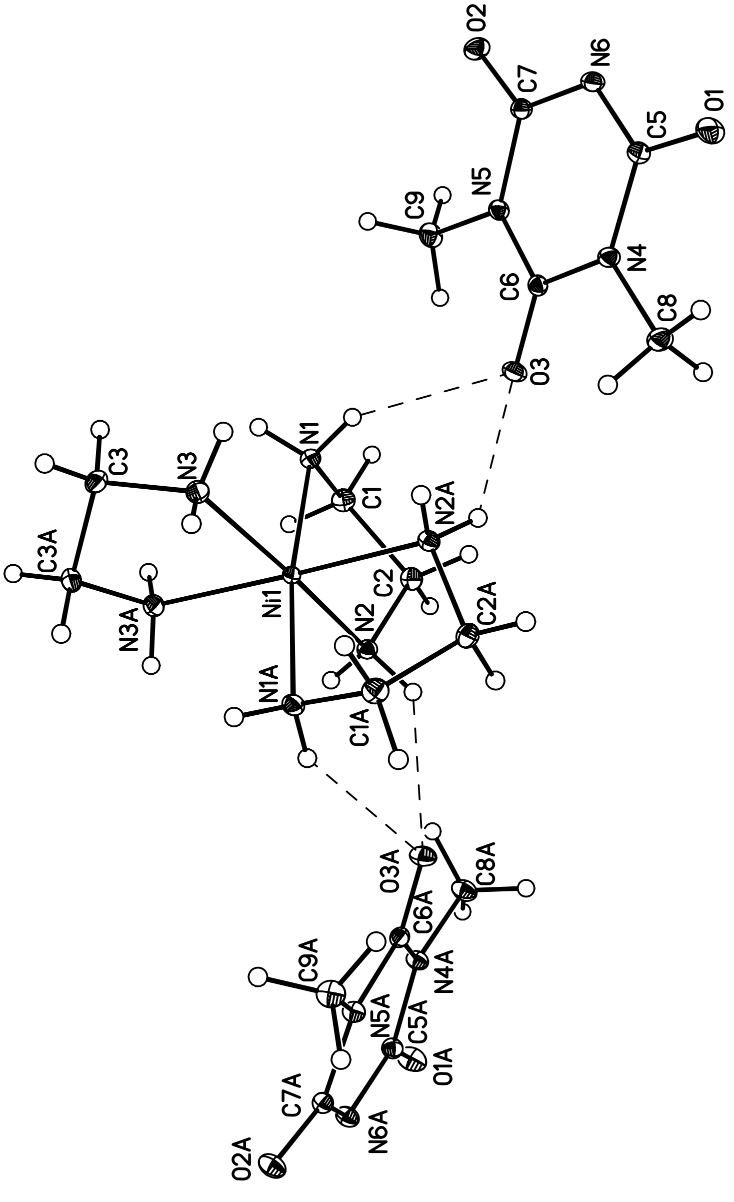


Figure 15. Bifurcated N-H…O_3 hydrogen bonds in 23 are shown as dashed lines.

3.1.6 (1,3-Dimethylcyanurate)bis(ethylenediamine)Copper(II) (1,3-dimethylcyanurato) [Cu(DMC)(en)$_2$][DMC] (24)

3.1.6.1 Description of crystal structure of [Cu(DMC)(en)$_2$][DMC] (24)

Figure 16 shows the crystal structure of **24** with atom labeling. The dark blue **24** crystallizes in the triclinic space group *$P\bar{1}$*. The copper(II) ion is coordinated by two en (ethylenediamine) ligands and one DMC anion, forming a highly distorted trigonal bipyramidal (TBP) CuN_5 core. The en ligands behave as a bidentate N,N' donor ligands, forming two five-membered chelate rings, while one DMC ligand is coordinated through the negatively charged N_1 atom and the other DMC ligand remains as uncoordinated.

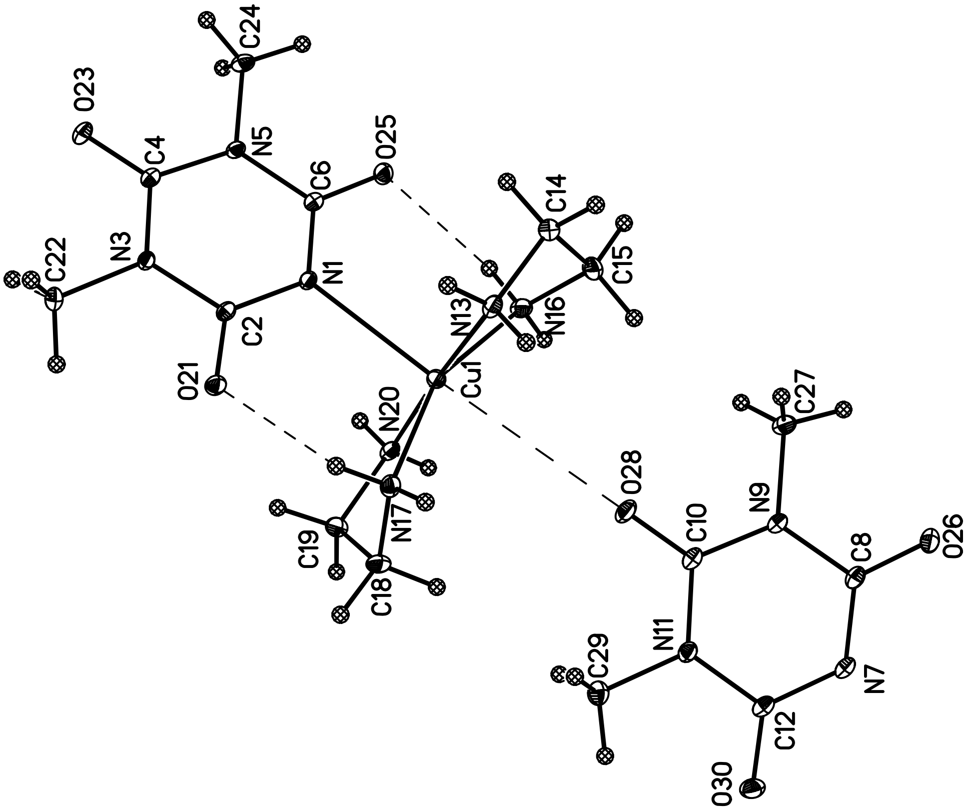


Figure 16. View of the [Cu(DMC)(en)$_2$][DMC] units, showing the atom labeling.

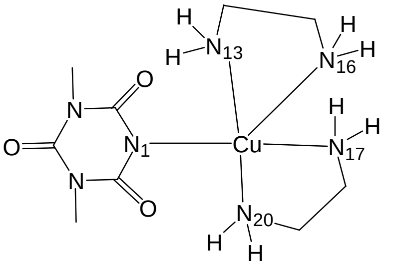
The bite angles of en ligands are 85.01(7)° (N_{13}-Cu_1-N_{16}) and 84.77(6)° (N_{20}-Cu_1-N_{17}) and significantly contribute to the distortion of the coordination geometry around the Cu(II) ion. Three nitrogen atoms define the trigonal plane; one of each ethylenediamine molecule (N_{16}, N_{17}) and the third, N_1 from the DMC$^-$ anion. The bond angles in the trigonal plane (99.17(6), 157.83(6), 103.0(6) °) are considerably distorted from the ideal trigonal angle of 120° (table 17). The sum of these equatorial angles is 360°. The N_{13}-Cu_1-N_{20} group, which defines the axis in the TBP description, is approximately linear with an angle of 176.78(6)°. In the equatorial plane the two Cu_1-N_{16} (2.026(2) Å) and Cu_1-N_{17} (2.024(2) Å) bond distances are not significantly different and shorter than Cu_1-N_1 (2.382(1) Å) bond in the coordinated cyanurate ion. The Cu_1-N_{16} and Cu_1-N_{17} bond lengths are in the normal range as Cu-amine in-plane distances of TBP, whereas Cu_1-N_1 bond length is longer. This Cu_1-N_1 bond length value is probably the longest among the five-coordinate copper(II) complexes characterized by X-ray analysis. These large deformations in bond angles and distances allow the CuN_5 geometry of **24** to be regarded also as a highly distorted square pyramid (SP), in which the four nitrogen atoms from en ligands could frame a square equatorial plane and the remaining terminal nitrogen atom N_1 of DMC could occupy the apex of the square pyramid. The bond lengths and angles of the coordinated and uncoordinated DMC ligands are almost equal (table 17). The crystal structure of **24** exhibits O-H-N hydrogen bonds ($N_{17}H_{17a}\ldots O_{21}$ = 2.12(1), $N_{16}H_{16b}\ldots O_{25}$ = 2.16(1) Å) formed by the amine hydrogen atoms of en ligands coordinating with the O atoms of the coordinated DMC ligand. From the crystal packing of **24**, the uncoordinated cyanurate ion is involved in O-H-N and N-H-N hydrogen bonds through its N_7 and O_{26} atoms with the amine groups of en ligand in another [Cu(DMC)(en)$_2$] unit. Such a type of hydrogen bonding prevents the uncoordinated DMC$^-$ ion from approaching the copper(II) ion, thereby inhibiting the formation of the neutral six-coordinate cyanurate-bridged complex. The shortest interionic distance between the heavy atoms ($Cu_1\ldots O_{28}$ 3.41(1) Å) lies outside the *van der Waals range*.

Table 17. Bond lengths (Å) and angles (°) for 24.

Cu(1)-N(13)	2.011(2)	N(13)-Cu(1)-N(20)	176.78(6)
Cu(1)-N(20)	2.012(2)	N(13)-Cu(1)-N(17)	94.07(7)
Cu(1)-N(17)	2.024(2)	N(20)-Cu(1)-N(17)	84.77(6)
Cu(1)-N(16)	2.026(2)	N(13)-Cu(1)-N(16)	85.01(7)
Cu(1)-N(1)	2.382(1)	N(20)-Cu(1)-N(16)	94.93(7)
N(1)-C(2)	1.349(2)	N(17)-Cu(1)-N(16)	157.83(7)
N(1)-C(6)	1.354(2)	N(13)-Cu(1)-N(1)	91.91(6)
C(2)-O(21)	1.233(2)	N(20)-Cu(1)-N(1)	91.27(6)
C(2)-N(3)	1.407(2)	N(17)-Cu(1)-N(1)	103.00(6)
N(3)-C(4)	1.372(2)	N(16)-Cu(1)-N(1)	99.17(6)
C(4)-O(23)	1.227(2)	C(2)-N(1)-C(6)	120.70(14)
C(4)-N(5)	1.374(2)	N(1)-C(2)-N(3)	119.34(14)
N(5)-C(6)	1.410(2)	C(4)-N(3)-C(2)	122.57(14)
C(6)-O(25)	1.229(2)	N(3)-C(4)-N(5)	115.33(14)
N(7)-C(12)	1.344(2)	C(4)-N(5)-C(6)	123.06(13)
N(7)-C(8)	1.351(2)	N(1)-C(6)-N(5)	118.57(14)
C(8)-O(26)	1.234(2)	C(12)-N(7)-C(8)	121.15(14)
C(8)-N(9)	1.408(2)	N(7)-C(8)-N(9)	118.60(15)
N(9)-C(10)	1.375(2)	C(10)-N(9)-C(8)	123.03(14)
C(10)-O(28)	1.216(2)	N(9)-C(10)-N(11)	115.09(14)
C(10)-N(11)	1.381(2)	C(10)-N(11)-C(12)	122.54(14)
N(11)-C(12)	1.408(2)	N(7)-C(12)-N(11)	119.14(15)
C(12)-O(30)	1.236(2)	C(14)-N(13)-Cu(1)	108.90(12)
N(13)-C(14)	1.481(2)	N(13)-C(14)-C(15)	107.70(15)
C(14)-C(15)	1.506(3)	N(16)-C(15)-C(14)	108.12(15)
C(15)-N(16)	1.482(3)	C(15)-N(16)-Cu(1)	107.02(12)
N(17)-C(18)	1.477(3)	C(18)-N(17)-Cu(1)	107.41(12)
C(18)-C(19)	1.510(3)	N(17)-C(18)-C(19)	108.36(14)
C(19)-N(20)	1.481(2)	N(20)-C(19)-C(18)	107.76(15)
		C(19)-N(20)-Cu(1)	109.54(11)

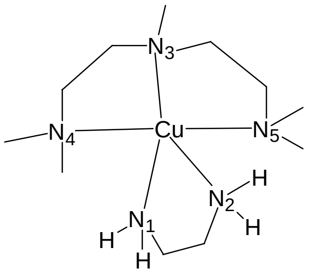
3.1.6.2 Correlation between TBP and SP geometries in 24

For the intermediate geometries between regular TBP and SP for five-coordinate complexes, several methods which attempt to estimate the degree of distortion from the regular geometries have been developed. Here, two of them will be applied to complex **24**, as well as to the other complexes ([Cu(en)(pmdt)][$(ClO_4)_2$] (**A**)[62], [Cu(SS-chxn)(pmdt)] (**B**)[62], [Cu(phen)$_2$(CYH)] (**C**)[63], where pmdt = N,N,N',N",N"-pentamethyldiethylenetriamine, SS-chxn = (1S,2S)-1,2-diaminocyclohexane) with the CuN_5 geometry for comparison. A convenient method devised by Addison *et al*. utilizes the angle between the donor atoms that could form the tetragonal basal plane in a SP-based structure.[64] A parameter τ, defined as $\tau = \left|(\beta-\alpha)/60\right| \times 100$ where the β and α are the two observed basal angles ($\beta > \alpha$), represents the percentage trigonal distortion from regular SP geometry: $\tau = 0\%$ for an ideal SP, whereas $\tau = 100\%$ for an ideal TBP. In complexes **A** and **B** the Cu-N_5 is the longest of the trigonal in-plane bonds, whereas the Cu-N_1 bond is the longest in complexes **24** and **C**. The values of τ are calculated for the four complexes. Thus, τ = 89% for the CuN_5 core of **A**, where β(N_1-Cu-N_3) = 179.4º and α(N_2-Cu-N_4) = 126.1º, τ = 57% (β = 178.2º and α = 143.8º) for **B**, τ = 57% [β(N_2-Cu-N_4) = 169.5º and α(N_3-Cu-N_5)= 135.5º)] for **C** and τ = 32% [β(N_{13}-Cu-N_{20}) = 176.79º and α(N_{16}-Cu-N_{17})= 157.83º)] for **24**. The τ value for **A** indicates that its geometry is very close to regular TBP, whereas the τ values of **B**, **C** and **24** indicating that their geometries can be best described as a highly square-pyramidally distorted TBP. For complex **24** the TBP character is greatly more reduced compared with **A**. As can be seen from figure 17, other complexes also adopt similar square-pyramidal-based structures; their τ values were found in the range 26-36%.[62]



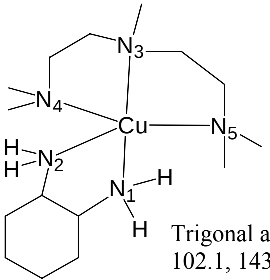
24

Trigonal angles
99.17, 157.83, 103.0º
Cu-N_1 = 2.382(1)Å



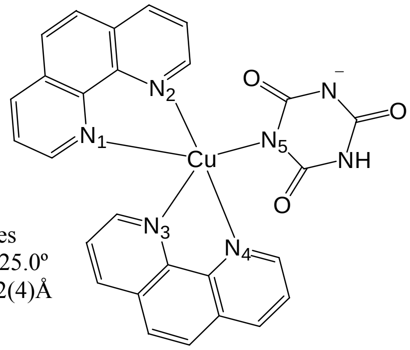
Trigonal angles
112.1, 126.1, 121.8º
Cu-N_5 = 2.205(6)Å

A [Cu(en)(pmdt)]$(ClO_4)_2$



Trigonal angles
102.1, 143.8, 113.4º
Cu-N_5 = 2.298(6)Å

B [Cu(SS-chxn(pmdt)]$(ClO_4)_2$



Trigonal angles
99.4, 135.5, 125.0º
Cu-N_1 = 2.152(4)Å

C [Cu(phen)$_2$(CYH)]

The method of Hathaway,[65] which can be used to calculate the degree of distortion based on the bond length changes, is also applicable to complex **24**. A parameter T^5, defined as the ratio of the mean distance of the four in-plane coordinate bonds (L_{4av}) to the distance of the single long out-of-plane bond (L_5), represents the tetragonality of SP geometries. The value of T^5 becomes unity for an ideal SP geometry and also for an ideal TBP. Thus, the value of T^5 is calculated to be 0.942, 0.899 and 0.940 for complexes **A**, **B** and **C** respectively, while for complex **24**, T^5 = 0.847, where L_{4av} = 2.018 and L_5[Cu-N$_1$] = 2.382 Å. Thus, the deviation in bond distances from the regular geometries is quite large for **24**, as well as in the angular distortion.

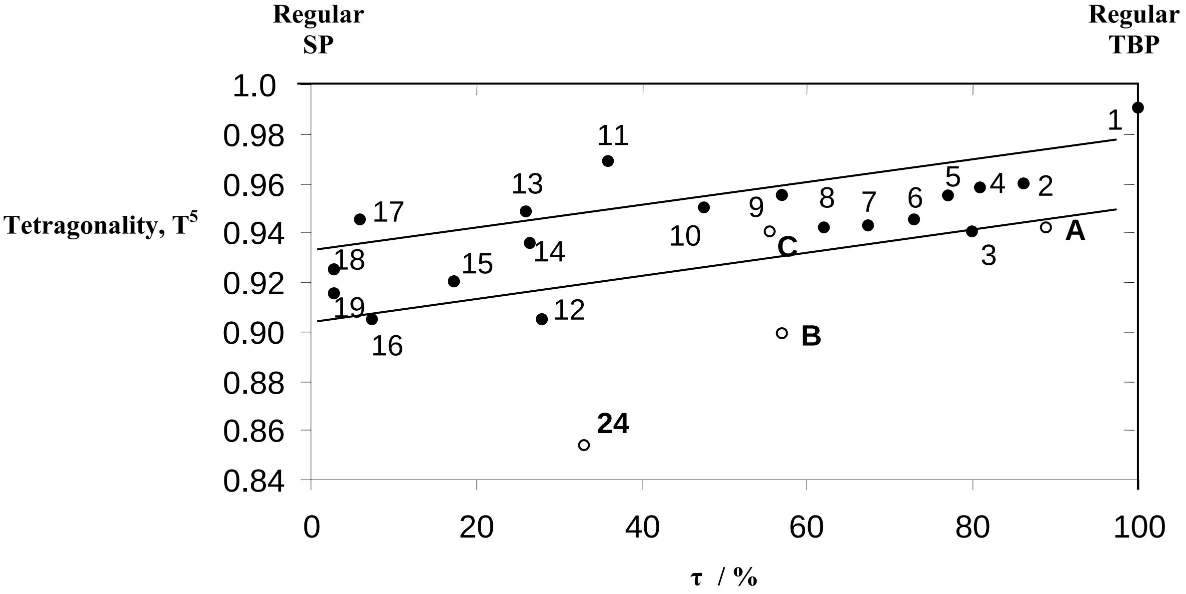


Figure 17. Plots of T^5 versus τ for a series of five-coordinate copper(II) complexes containing the CuN_5 geometry. Open circles represent the plots for $[Cu(en)(pmdt)][(ClO_4)_2]$ (A), [Cu(SS-chxn)(pmdt)] (B), $[Cu(phen)_2(CYH)]$ (C) and $[Cu(DMC)(en)_2][DMC]$ (24). Closed circles are taken from the complexes already reported; 1:$[Cu((NH_3)(tren)_2][(ClO_4)_2]$, 2:[Cu(Ade)(tren)][Cl], 3:[Cu(NCS)(tren)](NCS), 4:$[Cu(achmH)(tren)][(ClO_4)_2]$, 5:$[Cu(NH_3)(bpy)_2][(BF_4)_2]$, 6:$[Cu(NCS)(bpy)_2](NCS)$, 7:$[Cu(2MImH)(tren)][(ClO_4)_2]$, 8:$[Cu(NCS)(bpy)_2][(BF_4)]$, 9:$[Cu(bipyam)(dien)][(NO_3)_2]$, 10:$[Cu(trenpy)][(ClO_4)_2]$, 11:$[Cu(NCS)(trien)][(C1O_4)_2]$, 12:$[Cu_2(N_3)_2(pmdt)_2][(BPh_4)_2]$, 13:$[Cu(NCBH_3)_2(pmdt)]$, 14:$[Cu(bipyam)(dien)](ClO_4)_2$, 15:$[Cu(trenimpy)][(ClO_4)_2]$, 16:$[Cu(NH_3)(en)_2][(BF_4)_2]$, 17: $[Cu(bipyam)(dien)][Cl_2]$, 18: $[Cu(NH_3)_5][(PF_6)_2]$, 19: $[Cu(dien)]_2[Fe(CN)_6]$.

When discussing the distortion from regular TBP and SP geometries on the basis of the changes in bond angles and distances, the correlation between the two parameters, τ and T^5, will be very significant.[66] Murakami and co-workers[62] have studied this correlation for a series of complexes with CuN_5 chromophores. They pointed out that there is a significant increase in T^5 values with increasing τ values as described in the review.[66] Therefore, in figure 17 are plotted T^5 values against τ for some complexes with CuN_5 chromophores. As can be seen in the figure, complexes **A** and **C** are on this linear tendency observed for most of the CuN_5 complexes. On the other hand, complex **B** significantly deviates from this tendency, while large deviation for complex **24** was observed. This clearly results from the long Cu-N_1 bond extended more than expected as a complex with a τ value of 32%. Thus, the large distortion in complex **24** is attributable to an extraordinary bond extension of Cu-N_1, in addition to the large deformations in trigonal angles compared with those found in **A**, **B** and **C**.

3.1.7 Tetraphenylphosphonium (1,3-dimethylcyanurate) [PPh_4][DMC] (26)

Figure 18 shows the molecular structure of **26** with atom labeling. The selected bond lengths and angles are listed in table 18. The crystal crystallizes in the monoclinic space group $P2_1/c$. In the cyanurate ion, the two C-N bonds at the deprotonated nitrogen atom are equal and significantly (1.34 Å) shorter than the corresponding average bonds in 1,3-dimethylcyanuric acid **14** (1.37 Å). Conversely, the flanking carbonyl bonds C_{55}-O_{60} and C_{51}-O_{56} are significantly longer (~1.24 vs. 1.21 Å). These results and the symmetry about N_{50} in the O_{56}-C_{51}-N_{50}-C_{55}-O_{60} grouping indicate that the formal negative charge on the cyanurate is mostly distributed equally between the O_{56} and O_{60} oxygen atoms. As anticipated from the ν(CO) infrared data (table 3, chapter 2) that only two types of strong absorption bands were observed, this is a further indication in which the two carbonyl groups being as structurally identical.

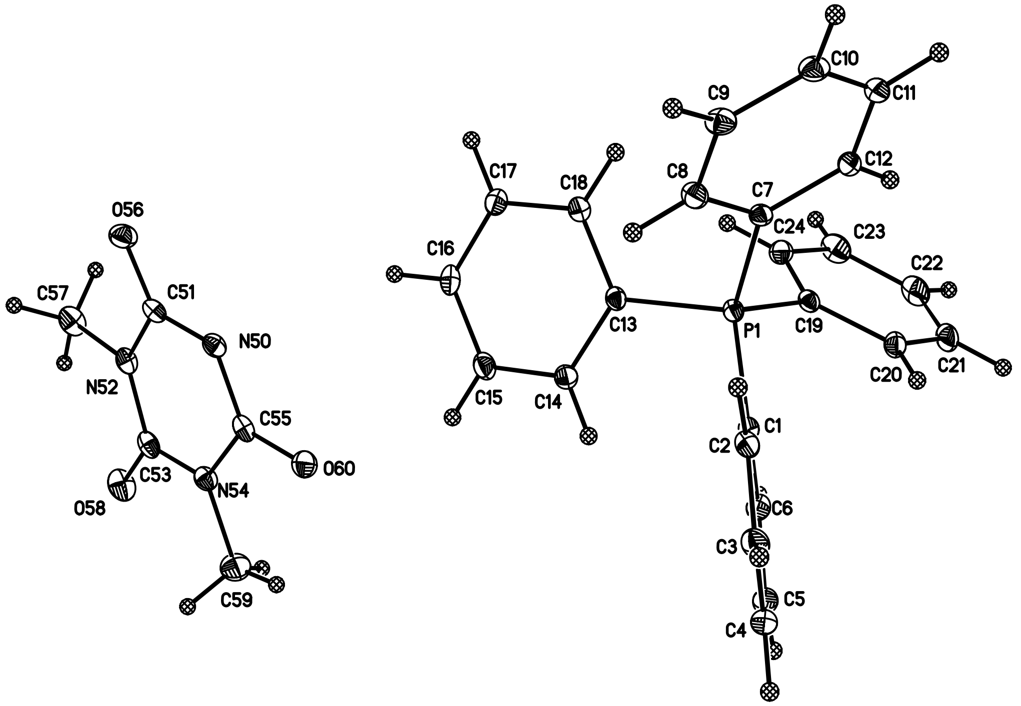


Figure 18. Molecular structure of 26.

Table 18. Selected bond lengths (Å) and angles (º) for 26.

C(51)-O(56)	1.231(3)	C(51)-N(50)-C(55)	120.5(2)
C(51)-N(52)	1.419(3)	O(56)-C(51)-N(50)	124.0(2)
N(50)-C(51)	1.338(3)	O(56)-C(51)-N(52)	117.2(2)
N(50)-C(55)	1.338(4)	N(50)-C(51)-N(52)	118.9(2)
N(52)-C(53)	1.370(4)	C(53)-N(52)-C(51)	122.9(2)
N(52)-C(57)	1.464(4)	C(53)-N(52)-C(57)	118.3(2)
C(53)-O(58)	1.225(3)	C(51)-N(52)-C(57)	118.8(2)
C(53)-N(54)	1.371(4)	O(58)-C(53)-N(52)	122.6(3)
N(54)-C(55)	1.410(3)	O(58)-C(53)-N(54)	122.6(3)
N(54)-C(59)	1.466(4)	N(52)-C(53)-N(54)	114.9(2)
C(55)-O(60)	1.240(3)	C(53)-N(54)-C(55)	122.4(2)
		C(53)-N(54)-C(59)	118.2(2)
		C(55)-N(54)-C(59)	119.2(2)
		O(60)-C(55)-N(50)	123.6(2)
		O(60)-C(55)-N(54)	116.7(2)
		N(50)-C(55)-N(54)	119.7(2)

3.1.8 Tetraphenylphosphonium (1,3-dimethylcyanurate)(pentacarbonyl)Metalate $[PPh_4][M(DMC)(CO)_5]$ (M = Cr (27a) and W (27c))

The structures of complexes **27a** and **27c** suitable for X-ray analysis were obtained by the slow diffusion of hexane into a concentrated dichloromethane solution of the complexes maintained at -32 ºC and the crystals crystallize in the monoclinic space group $P2_1/n$. A molecular structure drawing of the anion, $M(CO)_5(DMC)^-$, is depicted in figure 19 along with the atomic numbering scheme. Selected bond lengths and angles are listed in table 19. The crystal lattice of complexes **27a** and **27c** contain tetraphenylphosphonium cation (for charge balance), as well as a two dichloromethane molecules of solvation. The distorted octahedral environment about the metal center consists of a 1,3-dimethylcyanurate anion bound to the metal center through the N_{31} atom of the cyanurate ring at a distance of 2.170 (2) Å for **27a** and 2.273 (2) Å for **27c**. These bond lengths are similar to those found in the structures of **34**[50], **35**[51] and **36**[52] which are summarized in table 20.

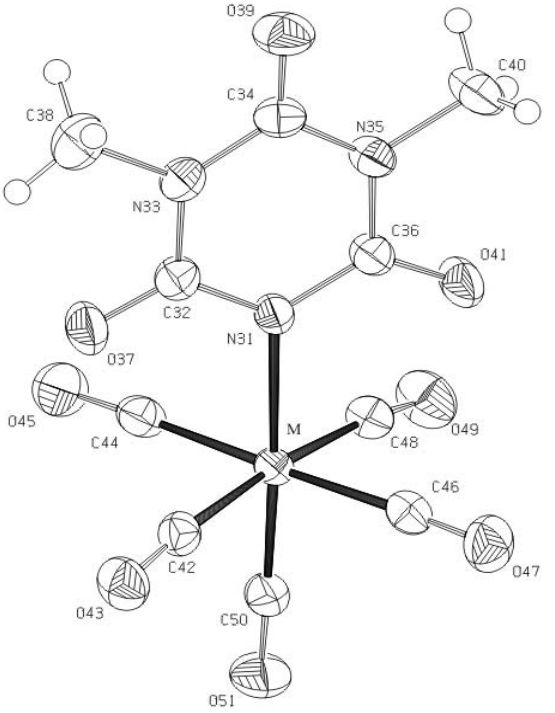


Figure 19. Molecular structure of the anion of complexes 27a and 27c, $M(CO)_5(DMC)^-$.

Table 19. Selected bond lengths (Å) and angles (º) for 27a (27c in square brackets).

M-N(31)	2.170(2) [2.273(3)]	N(31)-M-C(50)	177.57(11) [177.32(14)]
M-C(42)	1.904(3) [2.042(4)]	C(42)-M-C(48)	172.54(13) [172.68(16)]
M-C(44)	1.898(3) [2.046(4)]	C(44)-M-C(46)	178.12(13) [178.33(16)]
M-C(46)	1.918(3) [2.037(4)]	C(32)-N(31)-C(36)	120.6(3) [120.9(3)]
M-C(48)	1.911(3) [2.039(4)]	N(33)-C(32)-N(31)	118.2(3) [118.7(3)]
M-C(50)	1.829(3) [1.960(4)]	C(34)-N(33)-C(32)	124.0(3) [123.7(3)]
C(42)-O(43)	1.144(4) [1.143(5)]	N(35)-C(34)-N(33)	114.3(3) [115.1(4)]
C(44)-O(45)	1.143(4) [1.133(5)]	C(36)-N(35)-C(34)	124.1(3) [123.8(4)]
C(46)-O(47)	1.134(4) [1.136(5)]	N(31)-C(36)-N(35)	118.8(3) [1178.7(4)]
C(48)-O(49)	1.141(4) [1.144(5)]	C(50)-M-C(42)	86.59(13) [86.14(17)]
C(50)-O(51)	1.161(4) [1.161(5)]	C(50)-M-C(48)	86.02(13) [86.63(17)]
N(31)-C(32)	1.362(4) [1.364(5)]	C(50)-M-C(44)	90.56(14) [90.90(17)]
C(32)-N(33)	1.406(4) [1.395(5)]	C(50)-M-C(46)	91.24(13) [90.76(17)]
N(33)-C(34)	1.376(4) [1.367(5)]	N(31)-M-C(42)	92.31(11) [95.11(15)]
C(34)-N(35)	1.367(4) [1.377(6)]	N(31)-M-C(48)	95.12(11) [92.16(15)]
N(35)-C(36)	1.398(4) [1.404(5)]	N(31)-M-C(44)	87.28(11) [91.52(14)]
C(36)-N(31)	1.361(4) [1.373(5)]	N(31)-M-C(46)	90.93(11) [86.83(14)]
C(32)-O(37)	1.226(4) [1.222(5)]		
C(34)-O(39)	1.218(4) [1.227(5)]		
C(36)-O(41)	1.228(4) [1.218(5)]		

The metal-carbonyl bond distances in complexes **27a** and **27c** exhibit similar trends, with both exhibiting a *trans* effect. That is, in each the average M-C_{cis} bonds are longer than the M-C_{trans} bond, i.e., 1.91(3) vs 1.83(3) Å for **27a** and 2.04(4) vs 1.96(4) Å for **27c**. The plane of pseduoaromatic cyanurate ring almost bisects the cis C-M-C bond, and two of the cis carbonyls are bended away as seen from the C_{50}-M-C bond angles being smaller than 90º (C_{50}-Cr-C_{42} 86.59(13), C_{50}-Cr-C_{48} 86.02(13), and C_{50}-W-C_{42} 86.14(17), C_{50}-W-C_{48} 86.63(17) º). Accordingly, their N_{31}-M-C bond angles to the cis carbonyls are greater than 90º (N_{31}-Cr-C_{42} 92.31(11), N_{31}-Cr-C_{48} 95.12(11), and N_{31}-W-C_{42} 95.11 (15), N_{31}-W-C_{48} 92.16 (15) º).

Table 20. The M-N, M-C and $(C\text{-}O)_{trans}$ bond lengths for complexes 27a and 27c as well as other similar complexes.

	Bond length [Å]				
Compd.	M-N	$M\text{-}C_{Cis}$[a)]	$M\text{-}C_{trans}$	$(C\text{-}O)_{trans}$	Ref.
27a	2.170(2)	1.91(3)	1.83(3)	1.161(4)	this work
27c	2.273(3)	2.04(4)	1.96(4)	1.161(5)	this work
34	2.276(4)	2.04(6)	1.952(5)	1.170(6)	50
35	2.26(1)	2.04(2)	2.00(1)	1.130(1)	51
36	2.148(4)	1.904(4)	1.846(6)	1.152(6)	52

a) The average M-C distance for the four *cis*-CO ligands.

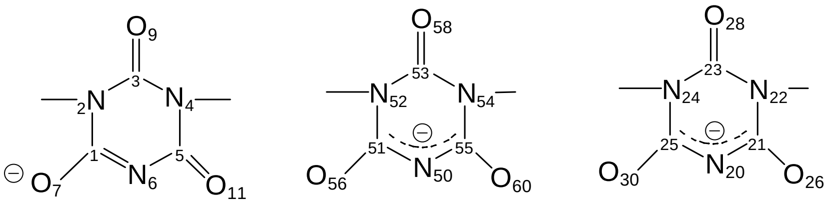
3.1.9 1,3-Diisopropyl-4,5-dimethylimidazolium-1,3-dimethylcyanurate (28)

The selected bond lengths and angles are listed in table 21. The colorless **28** crystallizes in the orthorhombic space group *P*bca. The bond lengths of the cyanurate ion are slightly deviated from those found in DMCH **14**, while for the C-O bond lengths a slight expansion is observed as a consequence of the negative charge (C_{25}-O_{30} 1.235(2), C_{21}-O_{26} 1.232(2), C_{23}-O_{28} 1.222(2) Å). The two C-N bonds at the deprotonated nitrogen atom are almost equal, this result is the same as found in **26**. This indicates that the formal negative charge on the cyanurate is mostly distributed equally around the N_{20} atom as drawn in figure 20.

The cyanurate anion is linked to the imidazolium cation by a monofunctional hydrogen bond through the negatively charged N_{20} atom forming a C-H…N type hydrogen bond (C_2-H_2 0.940(1) Å, C_2-H_2…N_{20} 2.241(1) Å, C_2-H_2-N_{20} 162.7(1)°) (figure 21). The dihedral angle between the two ring planes is 83.6°. The bond length and angles of the imidazolium cation are similar to those reported in literature.[67]

Table 21. Selected bond lengths (Å) and angles (°) for 28.

N(20)-C(21)	1.345(2)	C(21)-N(20)-C(25)	120.86(14)
N(20)-C(25)	1.349(2)	O(26)-C(21)-N(20)	123.09(17)
C(21)-O(26)	1.232(2)	O(26)-C(21)-N(22)	117.86(17)
C(21)-N(22)	1.409(2)	N(20)-C(21)-N(22)	119.03(16)
N(22)-C(23)	1.373(2)	C(23)-N(22)-C(21)	122.73(14)
N(22)-C(27)	1.462(2)	C(23)-N(22)-C(27)	117.44(15)
C(23)-O(28)	1.222(3)	C(21)-N(22)-C(27)	119.81(15)
C(23)-N(24)	1.371(2)	O(28)-C(23)-N(24)	122.29(16)
N(24)-C(25)	1.408(2)	O(28)-C(23)-N(22)	122.50(15)
N(24)-C(29)	1.465(2)	N(24)-C(23)-N(22)	115.21(14)
C(25)-O(30)	1.235(2)	C(23)-N(24)-C(25)	122.88(14)
		C(23)-N(24)-C(29)	116.74(14)
		C(25)-N(24)-C(29)	120.18(15)
		O(30)-C(25)-N(20)	122.74(16)
		O(30)-C(25)-N(24)	118.37(16)
		N(20)-C(25)-N(24)	118.88(15)



N_6-C_5 > N_6-C_1 N_{50}-C_{51} = N_{50}-C_{55} N_{20}-C_{25} = N_{20}-C_{21}

20 **26** **28**

Figure 20. Shows where the negative charge is mainly localized in 20, 26 and 28.

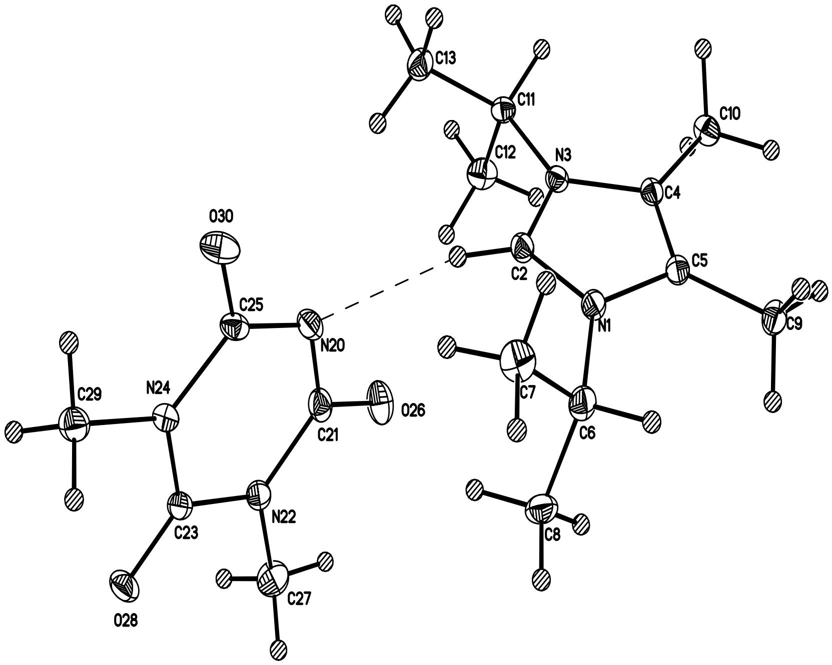


Figure 21. View of the ion pair of 28 linked by C-H…N hydrogen bond in the crystal.

3.1.10 1,3-Diisopropyl-4,5-dimethylimidazolium formate (29)

The ion pair of **29** is shown in figure 22 and selected bond lengths and angles are listed in table 22. The crystal crystallizes in the tetragonal space group $P4_12_12$. The crystal analysis shows a symmetric linkage of the ions through a bifurcated hydrogen bond (C_3-H_3…O_9 2.33(2) Å; C_3-H_3-O_9 151.5(1), O_9-H_3-O_{9A} 57(1) °). The dihedral angle between the ions ($N_1C_3H_3$ / $O_9C_8O_{9A}$ 89(1) °) is almost perpendicular to each other. The hydrogen atom of the formate ion is not involved into hydrogen bond. The bond length and angles of the imidazolium cation are similar to those reported in literature.[67]

Table 22. Selected bond lengths (Å) and angles (º) for 29$^{a)}$.

O(9)-C(8)	1.234(2)
N(1)-C(3)	1.329(2)
N(1)-C(2)	1.390(2)
C(2)-C(2)$^{\#1}$	1.363(4)
C(3)-N(1)-C(2)	109.14(17)
C(2)$^{\#1}$-C(2)-N(1)	106.60(10)
N(1)-C(3)-N(1)$^{\#1}$	108.5(3)
O(9)#1-C(8)-O(9)	129.2(3)

$^{a)}$ Symmetry transformations used to generate equivalent atoms: $^{\#1}$ y, x,-z

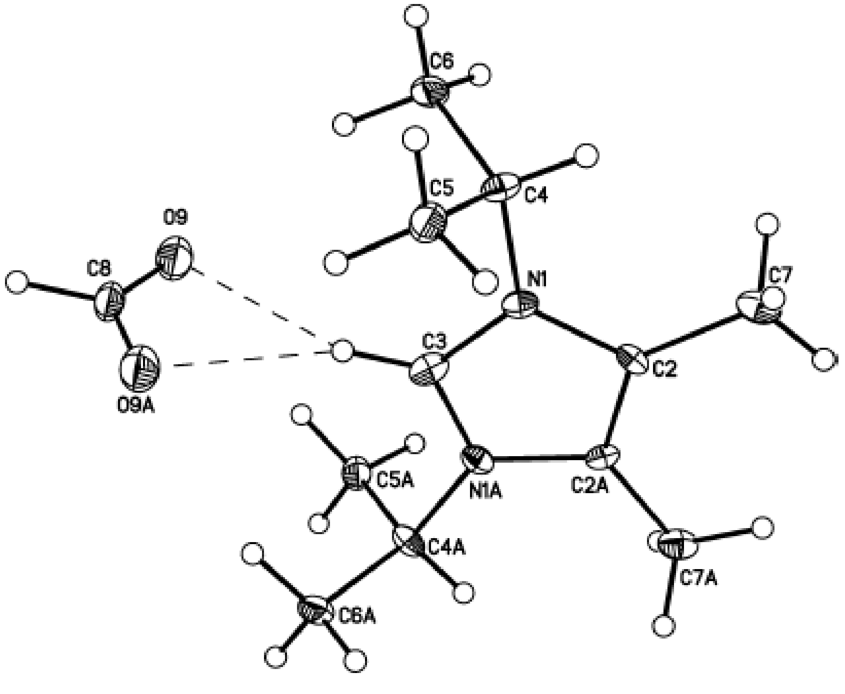


Figure 22. Bifurcated C-H…O hydrogen bonds in 29 are shown as dashed lines.

3.1.11 1,3-Diisopropyl-4,5-dimethylimidazolium bicarbonate (30)

The crystal structure analysis of **30** is shown in figure 23 and crystallizes in the orthorhombic space group *P*bca. The crystal structure analysis reveals the presence of symmetrical dimeric bicarbonate anions linked to each other with linear hydrogen bonds (O_{13}-H_2 1.20(5), H_2-O_{14A} 1.48(5) Å; O_{13}-H_2-O_{14A} 170(2) °), and to imidazolium cations also through hydrogen bonds (C_1-H_1 0.94(2), C_1H_1…O_{14} 2.62(2), C_1H_1…O_{15} 2.27(5) Å; C_1-H_1-O_{14} 174(1), C_1-H_1-O_{15} 133(1), O_{14}-H_1-O_{15} 53(1) °).

The binding of the imidazolium cation occurred here, as an additional part for the bonding of the "free" oxygen atom O_{15} arranged via almost weak linear reciprocal effect of the hydrogen atom H_1 with the oxygen atom O_{14} participated in the dimerization of the anion. In the CO_3 frame, the C-O bond is noticeably shortened for the oxygen atom O_{15} not involved into the dimerization of the anion (C_{12}-O_{13} 1.309(2), C_{12}-O_{14} 1.284(2), C_{12}-O_{15} 1.238 (2) Å). These findings as well as the clear expansion that we observe in O-C-O angle (O_{13}-C_{12}-O_{14} 117.9(2), O_{13}-C_{12}-O_{15} 120.4(2), O_{14}-C_{12}-O_{15} 121.6(2) °) associated to O-H-O fragments is related to only weak reciprocal effect of the oxygen atoms in the opposite dimer hydrogencarbonate with the imidazolium ion.

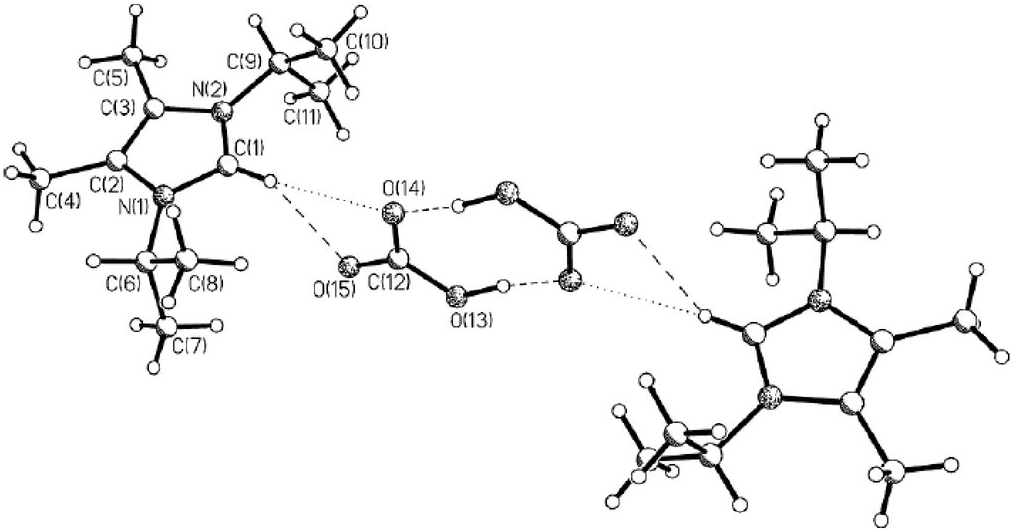


Figure 23. Bifurcated C-H…O hydrogen bonds in 30 are shown as dashed lines.

3.1.12 1,3-Diisopropyl-4,5-dimethylimidazolium hydrogenoxalate (31)

The selected bond lengths and angles are listed in table 23. The colorless **31** crystallizes in the monoclinic space group *C*2/c. The crystal structure analysis of **31** shows a bifunctional taking place binding the anion over two oxygen atoms of different carboxylate groups to the hydrogen atom in position 2 of the imidazolium rings (figure 24). Here the geometry lies in the center of C-C bond of the anion, so the ring of this C-C bond of the atom C_1 has two-fold crystallographic axis of rotation, this symmetry arrangement resulting in hydrogen bond (C_1-H_1 0.93(1), $C_1H_1 \ldots O_2$ 2.56(1) Å, C_1-H_1-O_2 146(1), O_2-H_1-O_{2A} 67(1) °). The hydrogenoxalate ions form polymer Strands linked over their hydrogen bonds; the hydrogen atom of the anion could not be found in the Fourier map. The hydrogenoxalate ions line up with intermolecular $O_1 \cdots O_{1B}$ contacts of about 2.61(1) Å, which clearly indicate H-bonding distances. The interplanar angle of CO_2 fragment is tilted 48.5(4)° from C_7-C_{7A} (1.531(6) Å).

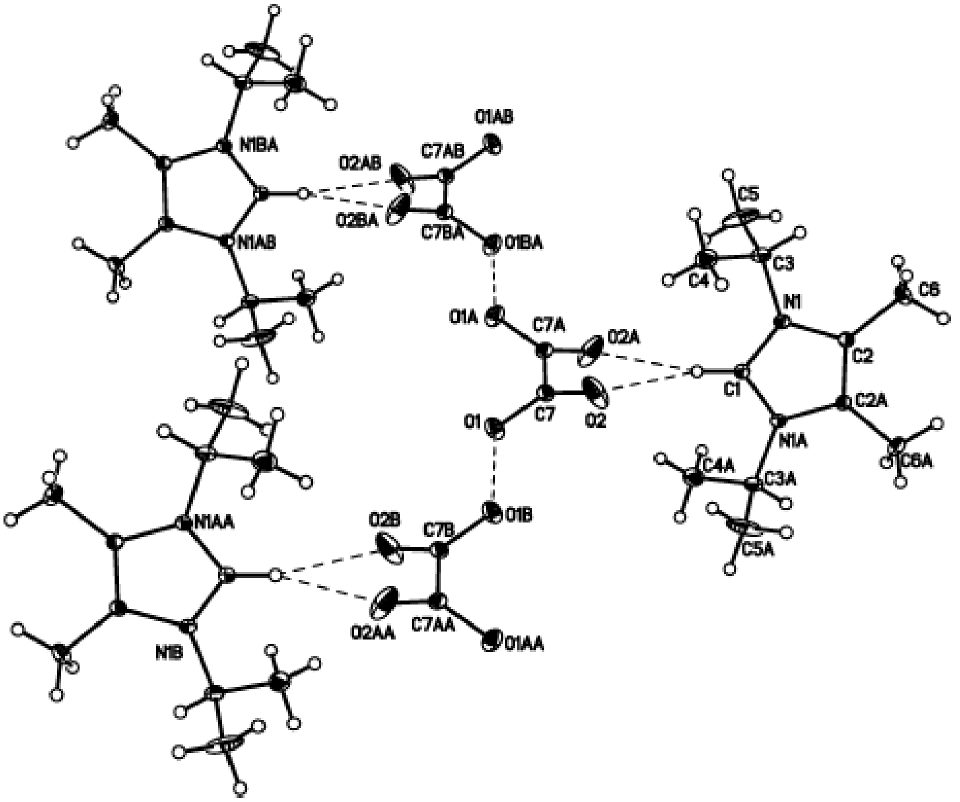


Figure 24. Bifurcated C-H…O hydrogen bonds in 31 are shown as dashed lines.

Table 23. Selected bond lengths (Å) and angles (°) for 31[a].

N(1) – C(1)	1.323(4)
N(1) – C(2)	1.388(4)
O(1) – C(7)	1.269(4)
O(2) – C(7)	1.211(4)
C(2) – C(2)$^{\#1}$	1.351(6)
C(7) – C(7)$^{\#1}$	1.531(6)
C(1) – N(1) – C(2)	108.7(3)
N(1)$^{\#1}$ – C(1) – N(1)	109.0(4)
C(2)$^{\#1}$ – C(2) – N(1)	106.8(2)
O(2) – C(7) – O(1)	118.6(2)
O(1) - C(7) – C(7)$^{\#1}$	116.2(2)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ 1-x, y, 0.5-z

3.1.13 1,3-Diisopropyl-4,5-dimethylimidazolium acetylacetonate (32)

The selected bond lengths and angles are listed in table 24. The colorless **32** crystallizes in the monoclinic space group $P2_1/c$. Its crystal structure analysis (Figure 25) reveals the presence of ion pairs linked by C-H…O hydrogen bond (C_5-H_{5A} 0.963, C_5-$H_{5A}\cdots O_{20}$ 2.132 Å; C_5-H_{5A}-O_{20} 172.6 °). The acetylacetonate ion in **32** adopts the structure of its *E*/*Z* isomer, the C_{21}-C_{22} bond (1.40 Å) at the deprotonated carbon atom is significantly shorter than C_{22}-C_{23} (1.42 Å). Conversely, the flanking carbonyl C_{21}-O_{20} bond (1.263(2) Å) is longer than C_{23}-O_{25} bond (1.245(2) Å) as a consequence of the negative charge. This indicates that the formal negative charge is mainly delocalized at O_{20}- C_{21}- C_{22} group.

Apparently, only minor differences in energy exist for the acetylacetone tautomers as concluded from neutron scattering experiments.[68] The configuration of β-diketone derivatives may be interpreted in terms of conflicting effects. The close approach of negative charges at the oxygen atoms favours the *E*/*Z* configuration in compounds containing un-coordinated or η^1-coordinated acetylacetonates. The different conformation of the acetylacetonate fragment in acetylacetone and **32** may be influenced by the tendency to avoid bifurcated hydrogen bridges.

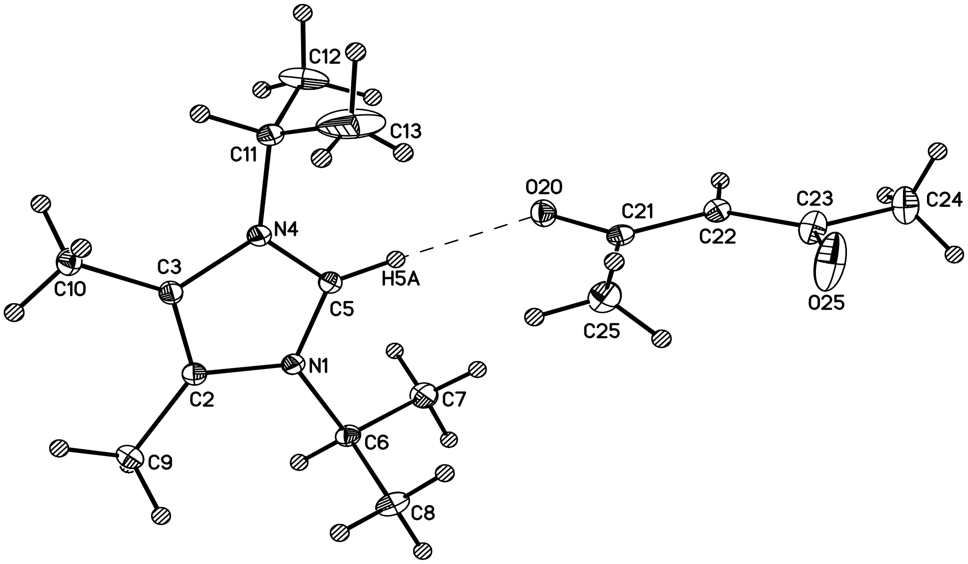


Figure 25. View of the ion pair of 32.

Table 24. Selected bond lengths (Å) and angles (º) for 32.

N(1)-C(5)	1.330(2)	C(5)-N(1)-C(2)	109.3(1)
N(1)-C(2)	1.393(2)	C(5)-N(4)-C(3)	109.1(1)
N(4)-C(5)	1.334(2)	C(3)-C(2)-N(1)	106.6(1)
N(4)-C(3)	1.392(2)	C(2)-C(3)-N(4)	106.7(1)
O(20)-C(21)	1.263(2)	N(1)-C(5)-N(4)	108.3(1)
O(25)-C(23)	1.245(2)	O(20)-C(21)-C(22)	122.9(1)
C(2)-C(3)	1.361(2)	O(20)-C(21)-C(25)	116.6(2)
C(21)-C(22)	1.402(2)	C(22)-C(21)-C(25)	120.5(2)
C(21)-C(25)	1.515(2)	C(21)-C(22)-C(23)	127.2(2)
C(22)-C(23)	1.415(2)	O(25)-C(23)-C(22)	126.4(2)
C(23)-C(24)	1.521(3)	O(25)-C(23)-C(24)	116.6(2)
		C(22)-C(23)-C(24)	117.1(2)

3.1.14 Bis(1,3-Diisopropyl-4,5-dimethylimidazolium) heptaiodopentaargentate(I) (33)

According to the structural analysis, the crystal structure of **33** shows a one-dimensional arrangement constructed from imidazolium fragments and $(Ag_5I_7)_n^{-2}$ chains, which are held together by electrostatic forces. The imidazolium cations are discrete, but the inorganic moiety $(Ag_5I_7)_n^{-2}$ is polymeric and exists in the crystal as an extended chain along the c axis (figure 26). In other words, this structure is an infinite polymeric anion accompanied by discrete cations. It should be mentioned that the chain is almost linear.

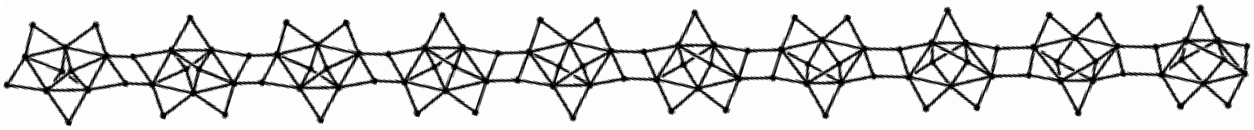


Figure 26. View of the 1D zigzag chain structure of $(Ag_5I_7)_n^{-2}$ **along the c axis.**

As shown in figure 27, the $(Ag_5I_7)_n^{-2}$ chain can be discussed in terms of $Ag_3I_4^{-1}$ ion in which each silver atom has an I_4 donor set and tetrahedral geometry when the Ag…Ag interactions are not taken into account. The Ag_5I_7 building block can be described as the result of five edge-sharing AgI_4 tetrahedra and argentophilic interactions. The infinite chain is built up by *trans*-edge-sharing Ag_5I_7 building blocks, where the shared edges are $I_{(1)}$-$I_{(1C)}$ and $I_{(1A)}$-$I_{(1B)}$. The anion of **33**, however, consists of two AgI_4 tetrahedra ($Ag_{(3)}$, $Ag_{(3A)}$) sharing a common $I_{(3)}$ face ($I_{(2)}$, $I_{(3)}$, $I_{(4)}$). Additional silver ($Ag_{(1)}$, $Ag_{(2)}$, $Ag_{(2A)}$) and iodine ($I_{(1)}$, $I_{(1A)}$, $I_{(4)}$, $I_{(4A)}$) atoms are connected via edge and corner shared tetrahedra to form, over all, a central Ag_5I_7 core.

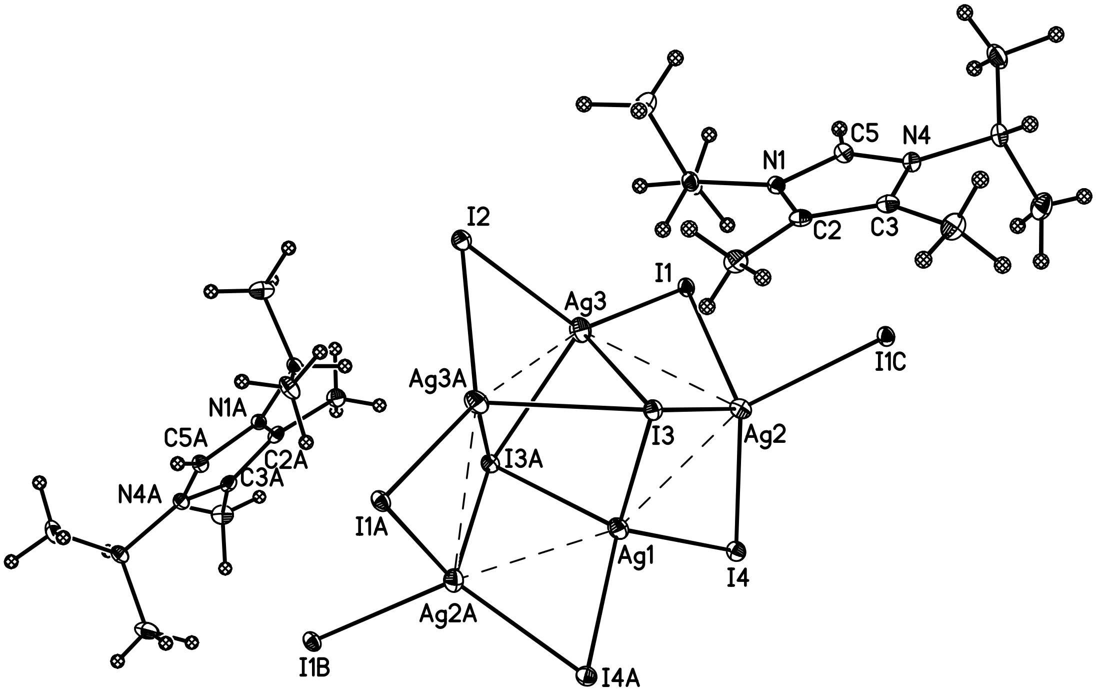


Figure 27. The molecular structure of [H(4,5-Me)(^{i}Pr)$_2$Im]$_2$[Ag$_5$I$_7$] (33).

Ag…Ag interactions have been found in many silver complexes, and the term argentophilicity has been adopted to describe this metal-metal interaction. The attraction between d^{10}-d^{10} closed shell metal atoms promotes the aggregation of silver(I) centers, as supported by spectroscopic and structural evidence.[69] In this work the central distance of the silver atoms Ag$_{(3)}$…Ag$_{(3A)}$ in **33** is 2.8852(9) Å. The further Ag…Ag distances range from 3.0361(5) Å (Ag$_{(1)}$-Ag$_{(2)}$) to 3.1139(7) Å (Ag$_{(2)}$-Ag$_{(3)}$), which are longer than that of metallic silver (2.88 Å) but shorter than the *van der Waals* radius sum of silver (3.44 Å).[60] The Ag…Ag separations (3.532 Å) in Ag$_{(1)}$-Ag$_{(3)}$ suggests that weak Ag…Ag interactions may exist, this is quite similar to findings reported for [(Et$_3$N)$_3$Ag$_6$(μ-2Br)(μ-4Br)$_3$]$_n$.[70] Compounds possessing argentophilicity can be potentially used in silver-containing antibacterial agents.[71]

This polymeric anion contains several very interesting features, the most extraordinary of which is the local environment of the $Ag_{(3)}$ atom. This atom is surrounded by $I_{(1)}$, $I_{(2)}$, $I_{(3)}$ and $I_{(3A)}$, although in order to form stable polyanions the distance $Ag_{(3)}$-$I_{(3)}$ (3.0772(6) Å) is relatively long in comparison with the normal Ag-I distance. The $Ag_{(3)}I_4$ tetrahedron is therefore highly distorted with Ag-I lengths ranging from 2.7561(5) to 3.0772(6) Å. The distorted pseudo-tetrahedron of $Ag_{(3)}I_4$ can also be extracted from the data of $I(_1)$-$Ag(_3)$-$I(_2)$ (130.03(2) º), $I(_2)$-$Ag(_3)$-$I(_{3A})$ (100.29(2) º) and $I(_2)$-$Ag(_3)$-$I(_3)$ (98.34(2) º), and furthermore, because $Ag_{(3)}$ is pseudo-tetrahedral, leads to the tetrahedron of corner-shared $Ag_{(2)}$ to be distorted with three short and one long Ag-I distances (2.7822(6), 2.8883(5), 2.9102(5), 3.0233(6) Å).

It is known that the formation of anionic complexes of the type $[Ag_lX_k]^{(k-l)-}$ is strongly dependent on the countercation and the nature of the halide.[72] In the case of iodide, a similar arrangement consisting of the central $[Ag_5I_7]^{-2}$ unit which also include face-shared AgI_4 tetrahedron and short Ag…Ag interactions has been found in salts containing the polymeric Ag_5I_7 anion.[73]A different structural type consisting also a face-shared AgI_4 tetrahedra has been reported for the $[Ag_3I_6]^{-3}$ anion.[74] To the best of our knowledge, polymer **33** is a new example of a 1D Ag/I coordination polymer containing imidazolium cation. The influence of the cation linked to the anion by a weak hydrogen bond (C_5-H_5 0.982, C_5-H_5…$I_{(4B)}$ 4.009 Å) is not established, and the geometry of the C-H…I fragment in **33** doesn't differ markedly from that observed in the corresponding imidazolium iodide salt.[75]

Table 24. Selected bond lengths (Å) and angles (°) for 33$^{a)}$.

Ag(1)-I(4)	2.7833(5)	I(4)-Ag(1)-I(4)$^{\#1}$	106.52(3)
Ag(1)-I(4)$^{\#1}$	2.7834(5)	I(4)-Ag(1)-I(3)	113.606(10)
Ag(1)-I(3)	2.8890(5)	I(4)$^{\#1}$-Ag(1)-I(3)	110.170(10)
Ag(1)-I(3)$^{\#1}$	2.8890(5)	I(4)-Ag(1)-I(3)$^{\#1}$	110.168(10)
Ag(1)-Ag(2)	3.0360(5)	I(4)$^{\#1}$-Ag(1)-I(3)$^{\#1}$	113.606(10)
Ag(1)-Ag(2$^{)\#1}$	3.0361(5)	I(3)-Ag(1)-I(3)$^{\#1}$	102.94(2)
Ag(2)-I(4)	2.7822(6)	I(4)-Ag(2)-I(1)$^{\#2}$	122.21(2)
Ag(2)-I(1)$^{\#2}$	2.8883(5)	I(4)-Ag(2)-I(1)	116.48(2)
Ag(2)-I(1)	2.9102(5)	I(1)$^{\#2}$-Ag(2)-I(1)	97.333(15)
Ag(2)-I(3)	3.0233(6)	I(4)-Ag(2)-I(3)	109.63(2)
Ag(2)-Ag(3)	3.1139(7)	I(1)$^{\#2}$-Ag(2)-I(3)	99.31(2)
Ag(3)-I(1)	2.7561(5)	I(1)-Ag(2)-I(3)	110.11(2)
Ag(3)-I(2)	2.8309(6)	I(1)-Ag(3)-I(2)	130.03(2)
Ag(3)-Ag(3)$^{\#1}$	2.8851(8)	I(1)-Ag(3)-I(3)$^{\#1}$	113.24(2)
Ag(3)-I(3)$^{\#1}$	2.9945(6)	I(2)-Ag(3)-I(3)$^{\#1}$	100.29(2)
Ag(3)-I(3)	3.0772(6)	I(1)-Ag(3)-I(3)	112.88(2)
I(1)-Ag(2)$^{\#2}$	2.8883(5)	I(2)-Ag(3)-I(3)	98.34(2)
I(2)-Ag(3)$^{\#1}$	2.8308(6)	Ag(3)$^{\#1}$-Ag(3)-I(3)	60.19(2)
I(3)-Ag(3)$^{\#1}$	2.9945(6)	I(3)$^{\#1}$-Ag(3)-I(3)	96.21(2)

$^{a)}$ Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ 1-x, y, 0.5-z, $^{\#2}$ 1-x, 1-y, -z

3.2 Preparation of crystal

The selected compounds for X-ray analysis were synthesized as discussed in section 4.4. Crystals of **14** and **20** were obtained by slow evaporation of boiling methanol-water solution and methanol respectively at room temperature. Yellow crystals of **27a** and **27c** were obtained by slow diffusion of hexane into concentrated dichloromethane solution maintained at -32 ºC. the purple **23** and dark blue **24** crystals can be obtained by slow evaporation of their aqueous reaction mixture at room temperature within 3-4 days. Colorless crystals suitable for X-ray structural measurements of **21** and **22** were obtained by standing of their reaction mixture at room temperature for 3 days. Compounds **28**, **29** and **32** can be obtained by slow vapor diffusion of diethylether into acetone solution. The acetonitrile solution of **33** is stored at -32 ºC, producing suitable block colorless crystals for X-ray experiments. Crystals of **26**, **31** and **30** were obtained by slow vapor diffusion of diethylether into chloroform and acteonitrile solution or in the case of **30** in DMSO-acetone solution.

The crystals of **26** and **28** were mounted on a glass fiber with epoxy cement at room temperature, whereas crystals of **14**, **20**, **21**, **22**, **23**, **24**, **27a**, **27c**, **29**, **30**, **31**, **32** and **33** were mounted on a glass fiber with epoxy cement at room temperature, and cooled in a cold stream of liquid nitrogen. Preliminary examination and data collection were performed with a Stoe IPDS 2 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXS-97[76], SHELXL-97[76] and SHELXTL V5.1 (NT). The details of data collection, refinement and crystallographic data are summarized in tables 25-29.

Table 25. Crystallographic data and structure refinement parameters for 14, 20, 21.

	14	**20**	**21**
Empirical formula	$C_5H_7N_3O_3$	$C_5H_{10}LiN_3O_5$	$C_6H_{10}AgN_4O_3$
Formula mass	157.14	199.10	294.05
Temperature	173(2) K	173(2) K	173(2) K
Crystal system, space group	monoclinic $P2_1/n$	triclinic $P\bar{1}$	monoclinic $P2_1/n$
a(Å)	10.288(2)	6.4240(17)	7.9182(12)
b(Å)	4.8220(6)	8.391(2)	4.4784(4)
c(Å)	13.140(3)	8.703(2)	25.413(3)
α (°)	90.00	67.309(18)	90.00
β (°)	99.547(17)	73.55(2)	93.441(12)
γ (°)	90.00	85.73(2)	90.00
Z	4	2	4
D_{calc}(Mg/m^3)	1.624	1.594	2.171
μ (mm^{-1})	0.136	0.139	2.228
F(000)	328	208	580
Crystal size (mm^3)	0.3 x 0.07 x 0.05	0.2 x 0.1 x 0.05	0.50 x 0.05 x 0.01
θ Range (°)	3.14-26.71	6.98-26.37	3.21- 26.72
Index range (h, k, l)	-13/12, -5/6, -16/16	-8/8, -10/10, -10/10	-10/10, -5/5, -32/32
Reflections collected	8878	5798	11804
Independent reflections	1359 (R_{int} = 0.0551)	1654 (R_{int} = 0.0612)	1909 (R_{int} = 0.0975)
Data / parameters	1359/ 128	1654/ 167	1909/ 167
Goodness-of-fit on F^2	1.186	1.139	1.085
Final R indices [I>2σ(I)]	0.0459	0.0488	0.0235
R_{wF}	0.1040	0.1092	0.0590
Largest diff. peak / hole (eÅ^{-3})	0.166/ -0.236	0.321/ -0.197	0.671/ -0.838

Table 26. Crystallographic data and structure refinement parameters for 22, 23, 24.

	22	**23**	**24**
Empirical formula	$C_{12}H_{20}N_8O_6Zn$	$C_{16}H_{36}N_{12}NiO_6$	$C_6H_{10}CuN_{10}O_6$
Formula mass	437.73	551.28	496.00
Temperature	213(2) K	173(2) K	173(2) K
Crystal system, space group	orthorhombic *P*bca	monoclinic *C2/* c	triclinic $P\bar{1}$
a(Å)	9.9867(8)	14.6461(9)	6.8351(8)
b(Å)	11.4329(6)	8.1146(10)	10.8806(13)
c(Å)	29.925(2)	20.317(2)	13.9186(16)
α (°)	90.00	89.994(10)	96.599(10)
β (°)	90.051(6)	104.474(9)	97.646(10)
γ (°)	90.00	90.039(9)	98.501(10)
Z	8	4	2
D_{calc}(Mg/m^3)	1.702	1.566	1.639
μ (mm^{-1})	1.490	0.891	1.144
F(000)	1808	1168	518
Crystal size (mm^3)	0.25 x 0.2 x 0.2	0.25 x 0.1 x 0.1	0.25 x 0.15 x 0.1
θ Range (°)	3.03-26.71	3.19-26.75	3.18- 26.71
Index range (h, k, l)	-12/12, -14/14, -37/36	-18/18, -10/10, -25/25	-10/8, -13/13, -17/17
Reflections collected	40761	16716	15124
Independent reflections	3618 (R_{int} = 0.0652)	2484 (R_{int} = 0.0557)	4254 (R_{int} = 0.0684)
Data / parameters	3618/ 324	2484/ 223	4254/ 392
Goodness-of-fit on F^2	1.124	1.187	1.085
Final *R* indices [I>2σ(I)]	0.0312	0.0303	0.0277
R_{wF}	0.0719	0.0699	0.0724
Largest diff. peak / hole (eÅ^{-3})	0.307/ -0.298	0.281/ -0.288	0.429/ -0.358

Table 27. Crystallographic data and structure refinement parameters for 26, 27a, 27c.

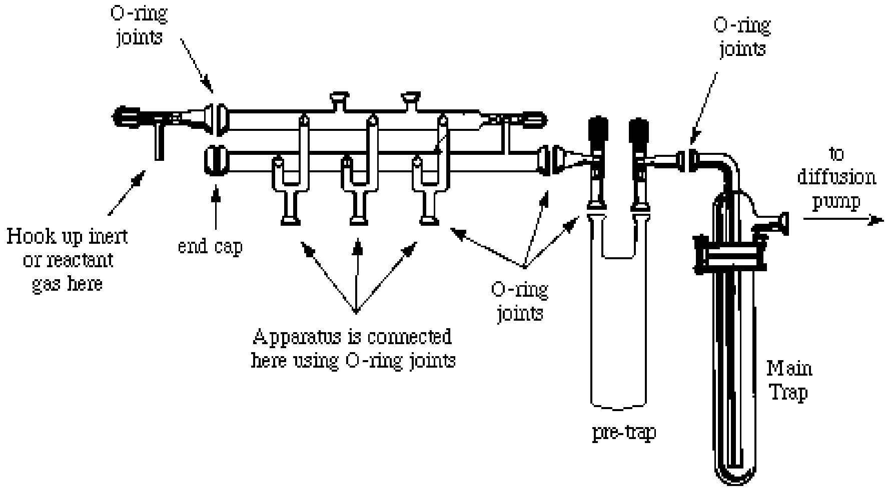
	26	**27a**	**27c**
Empirical formula	$C_{29}H_{26}N_3O_3P$	$C_{36}H_{30}Cl_4CrN_3O_8P$	$C_{36}H_{30}Cl_4N_3O_8PW$
Formula mass	495.50	857.40	989.25
Temperature	293(2) K	173(2) K	173(2) K
Crystal system, space group	monoclinic $P2_1$/c	monoclinic $P2_1$/n	monoclinic $P2_1$/n
a(Å)	7.7168(6)	14.8310(8)	14.8902(8)
b(Å)	13.6876(10)	15.2519(9)	15.3520(6)
c(Å)	23.896(2)	17.2594(10)	17.3543(10)
α (°)	90.00	90.00	90.00
β (°)	96.765(7)	96.120(4)	96.699(5)
γ (°)	90.00	90.00	90.00
Z	4	4	4
D_{calc}(Mg/m^3)	1.313	1.467	1.668
μ (mm^{-1})	0.146	0.665	3.297
F(000)	1040	1752	1952
Crystal size (mm^3)	0.3 x 0.3x 0.05	0.5 x 0.2 x 0.1	0.35 x 0.2 x 0.1
θ Range (°)	3.05-26.37	3.07-26.73	2.99-29.21
Index range (h, k, l)	-9/9, -17/16, -29/29	-17/18, -19/19, -21/21	-20/20, -21/21, -23/23
Reflections collected	29178	56747	72835
Independent reflections	5125 (R_{int} = 0.1164)	8217 (R_{int} = 0.0766)	10612 (R_{int} = 0.0676)
Data / parameters	5125/ 418	8217/ 578	10612/ 578
Goodness-of-fit on F^2	1.143	1.072	1.107
Final R indices [I>2σ(I)]	0.0634	0.0603	0.0412
R_{wF}	0.1108	0.1504	0.0904
Largest diff. peak / hole (eÅ^{-3})	0.353/ -0.293	1.091/ -1.018	1.066/ -1.313

Table 28. Crystallographic data and structure refinement parameters for 28, 29, 30.

	28	**29**	**30**
Empirical formula	$C_{19}H_{27}N_2O_3$	$C_{12}H_{22}N_2O_2$	$C_{12}H_{22}N_2O_3$
Formula mass	331.43	226.32	242.32
Temperature	173(2) K	173(2) K	150 K
Crystal system, space group	orthorhombic *P*bca	Tetragonal $P4_12_12$	orthorhombic *P*bca
a(Å)	8.6035(6)	7.8302(6)	8.536(2)
b(Å)	16.2003(13)	7.8302(6)	16.682(3)
c(Å)	25.671(2)A	20.957(2)	18.927(4)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
Z	8	4	8
D_{calc}(Mg/m^3)	1.231	1.170	1.194
μ (mm^{-1})	0.083	0.080	0.086
F(000)	1432	496	1056
Crystal size (mm^3)	0.6 x 0.6 x 0.4	0.25 x 0.15 x 0.1	0.31 x 0.22 x 0.19
θ Range (°)	6.84-24.71	3.25-26.73	3.21-29.27
Index range (h, k, l)	-10/10,-19/19, -30/30	-9/9, -9/9, -26/26	-10/11, -22/22, -25/25
Reflections collected	36834	18187	23723
Independent reflections	2979 (R_{int} = 0.1151)	1355 (R_{int} = 0.1019)	3644 (R_{int} = 0.1207)
Data / parameters	2979/ 313	1355/ 118	3644/ 243
Goodness-of-fit on F^2	1.056	1.231	1.156
Final R indices [I>2σ(I)]	0.0717	0.0527	0.0648
R_{wF}	0.0914	0.0613	0.1382
Largest diff. peak / hole (eÅ^{-3})	0.416/ -0.291	0.135/ -0.127	0.353/ -0.195

Table 29. Crystallographic data and structure refinement parameters for 31, 32, 33.

	31	**32**	**33**
Empirical formula	$C_{13}H_{22}N_2O_4$	$C_{16}H_{28}N_2O_2$	$C_{11}H_{21}Ag_{2.50}I_{3.50}N_2$
Formula mass	270.33	280.40	895.12
Temperature	223(2) K	173(2) K	173(2) K
Crystal system, space group	monoclinic *C*2/c	monoclinic $P2_1$/c	orthorhombic *P*bna
a(Å)	11.780(5)	11.928(2)	18.3099(2)
b(Å)	11.460(3)	10.379(2)	12.1757(3)
c(Å)	10.772(2)	13.615(3)	18.1450(3)
α (°)	90	90	90
β (°)	105.69(3)	102.87(3)	90
γ (°)	90	90	90
Z	4	4	8
D_{calc}(Mg/m^3)	1.283	1.133	2.940
μ (mm^{-1})	0.095	0.074	7.739
F(000)	584	616	3232
Crystal size (mm^3)	0.80 x 0.25 x 0.25	0.20 x 0.20 x 0.40	0.29 x 0.26 x 0.17
θ Range (°)	3.49-31.11	3.07 to 26.37	3.16-29.17
Index range (h, k, l)	-17/16, -1/16, -1/15	-14/14, -11/12, -17/17	-25/25, -16/16, -24/24
Reflections collected	2769	23116	69507
Independent reflections	1148 (R_{int} = 0.0476)	3348 (R_{int} = 0.0944)	69507 (R_{int} = 0.0689)
Data / parameters	2548/ 260	3348/ 294	5448/ 257
Goodness-of-fit on F^2	1.025	1.063	1.392
Final R indices [I>2σ(I)]	0.0531	0.0507	0.0357
R_{wF}	0.1555	0.1192	0.0718
Largest diff. peak / hole (eÅ^{-3})	0.362/ -0.334	0.330/ -0.312	1.063/ -1.540



Experimental 4

Section

4. General remarks

4.1 Methods of analysis

4.1.1 Elemental analysis

The elemental analyses were measured by an elemental analyzer from Carlo Erba Company, Model 1106. The accuracy was attached:

Carbon:	± 0.5%
Hydrogen:	± 0.3%
Nitrogen:	± 0.3%

4.1.2 Mass spectra

Mass spectra were recorded on a Finnigan Triple-Stage-Quadrupol spectrometer (TSQ-70) from Finnigan-Mat. High-resolution mass spectra were measured on a modified AMD Inectra MAT 711 A and reported as mass / charge (*m/z*). The used mass spectrometric ionization methods were electron-impact (EI) by 70 eV at 200°C or Fast-atom bombardment (FAB) by 70 eV in Nitrobenzylalcohol-Matrix at 60°C.

4.1.3 NMR spectra

The high resolution NMR spectra were acquired by a Bruker DRX 400 NMR spectrometer which operated at 400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C and 161.98 MHz for ^{31}P nuclei, respectively. The spectra were measured relative to TMS (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) as internal standard. All experiments were performed at 25 ºC. Data are reported as follows: chemical shift (multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broadened, *J* = coupling constant (Hz) in italic form).

4.1.4 IR spectra

The FT-IR spectra were acquired by a VERTEX 70 FT-IR Spectrometer. The measuring range was from 4000 to 300 cm^{-1}. The samples were measured using Drift spectroscopy method (Diffuse Reflectance Infrared Fourier Transform), the advantage of this method is the short time needed for preparing the samples.

4.2 Solvents

The solvents needed for the reactions were dried by conventional procedures and were stored over molecular sieves under argon.

4.3 Starting materials

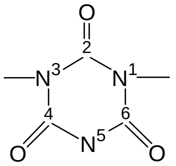
Air sensitive compounds were prepared and handled under argon by Schlenk techniques. The chemicals were purchased from the firms Adrich, Alfa Aesar, Fluka, Sigma-Aldrich and Merck. All chemicals were of reagent grade quality from commercial sources and were used without further purification. Compounds that are not described in the experimental part were synthesized according to a literature**.**

4.4 Synthesis of the compounds

4.4.1 Synthesis of 1,3-Dimethylcyanuric acid [DMCH]**(14)**

In open schlenk flask 20 g (270 mmol) g of N-methylurea was heated at 234 °C in oil bath for 5h. When the Schlenk flask was cooled to room temperature, NH_3 (75 mL, 2M) was added with stirring to dissolve the solid. H_2SO_4 (150 mL, 1M) was added in portions with continuous stirring at room temperature, after the addition was completed DMCH was precipitated. The crude product was collected by suction filtration, washed with cold water and air-dried. Colourless crystals were formed as needles by slow evaporation of a boiling methanol-water solution at room temperature. Yield 7.1 g (50%).

Anal. Calcd. for $C_5H_7N_3O_3$ (157.13 g/ mol): C 38.22, H 4.49, N 26.74; **Found**: C 37.64, H 4.54, N 26.12 %.



^{1}H NMR (DMSO-d_6): δ = 3.09 (s, 6H, NMe), 11.60 (s, 1H, NH).

^{13}C{^{1}H} NMR (DMSO-d_6): δ = 28.02 (Me), 148.90 ($C^{4,6}$), 150.38 (C^2).

IR (DRIFT): ν_{CO} = 1764 (vs), 1750 (vs), 1689 (vs) cm^{-1}.

MS (EI): m/z (%) = 157.0 (100) [M^+], 128 (17) [M^+-NMe] and further fragments.

4.4.2 Synthesis of 1,3-Dimethyl-O-lithiumcyanurate dihydrate [LiDMC.2H_2O] **(20)**

A suspension of DMCH (**14**) (0.400 g, 2.55 mmol) in ethanol (30 mL) was treated with Lithium (0.018 g, 2.55 mmol) with stirring at 25 °C. After the solution was stirred for 2h a clear solution was obtained, the reaction mixture was filtered and evaporated to dryness. The white solid obtained was washed with acetone (5 mL) and Et_2O (5 mL) and dried *in vacuo*. Colourless plates suitable for X-ray were formed by slow evaporation of a boiling methanol at room temperature. Yield 0.472 g (93%).

Anal. Calcd. for $C_{10}H_{20}Li_2N_6O_{10}$ (398.19 g/ mol): C 30.16, H 5.06, N 21.11; **Found**: C 30.08, H 5.14, N 21.03 %.

^{1}H NMR (DMSO-d_6): δ = 3.08 (s, 12H, NMe), 3.50 (br s, 8H, H_2O).

^{13}C{^{1}H} NMR (DMSO-d_6): δ = 27.85 (Me), 153.61(C^2), 156.39 ($C^{4,6}$).

IR (DRIFT): ν_{CO} = 1729 (vs), 1651 (vs), 1635 (sh) cm^{-1}.

MS (FAB neg.): m/z (%) = 155.8 [65].

4.4.3 Synthesis of Bis(1,3-dimethyl-N-silvercyanurate)(ethylenediamine) [$(AgDMC)_2$(en)**](21)**

A solution of $AgNO_3$ (0.118 g, 0.695 mmol) in distilled water (4 mL) was mixed with a solution of **20** (0.276 g, 0.693 mmol) in distilled water (6 mL) with continuous stirring at room temperature. The solution immediately became milky. The addition of ethylenediamine (en) (0.05 mL) dissolved in 2-propanol (6 mL) to the milky suspension resulted in a clear solution. The resulting solution was protected from light, stirred for 20 min, allowed to stand in darkness at room temperature and colourless crystals of **21** were obtained after 3 days. Yield 0.12 g (60 %).

Anal. Calcd. for $C_{12}H_{20}Ag_2N_8O_6$ (588.08 g/ mol): C 24.49, H 3.43, N 19.05; **Found**: C 24.33, H 3.51, N 18.67 %.

^{1}H NMR (DMSO-*d*$_6$): δ = 2.84 (s, 4H, CH_2), 3.20 (s, 12H, Me), 3.42 (s, 4H, NH_2).

^{13}C{^{1}H} NMR (DMSO-*d*$_6$): δ = 28.68 (Me), 43.86 (CH_2), 152.20 (C^2), 154.88 ($C^{4,6}$).

IR (DRIFT): ν_{CO} = 1728 (vs), 1716 (s), 1696 (s) cm^{-1}.

4.4.4 Synthesis of Bis(1,3-dimethylcyanurate)(ethylenediamine)Zinc(II) [$Zn(DMC)_2$(en)] **(22)**

A solution of $ZnCl_2.6H_2O$ (0.300 g, 1.23 mmol) in distilled water (10 mL) was mixed with a solution of **20** (0.978 g, 2.45 mmol) in distilled water (10 mL) with continuous stirring at room temperature. The solution immediately became milky. The addition of ethylenediamine (en) (0.08 mL) dissolved in 2-propanol (10 mL) to the milky suspension resulted in a clear solution. The resulting solution was stirred for 30 min and was allowed to stand at room temperature. Colorless block crystals were obtained after 3 days. These crystals were washed with acetone and dried. Yield 0.32 g (60 %).

Anal. Calcd. for $C_{12}H_{20}N_8O_6Zn$ (437.72 g/ mol): C 32.93, H 4.61, N 25.60; **Found**: C 32.80, H 4.56, N 25.59 %.

^{13}C-NMR(MAS): δ 30.90, 30.95 (NMe), 42.29, 43.74 ($2CH_2$), 148.60, 153.59, 155.85 (CO).

IR (DRIFT): ν_{CO} = 1727 (vs), 1701 (sh), 1632 (vs) cm^{-1}.

4.4.5 Synthesis of Tris(ethylenediamine)Nickel(II) Bis(1,3-dimethylcyanurate) $[Ni(en)_3][DMC]_2$ **(23)**

A solution of $Ni(NO_3)_2.6H_2O$ (0.351 g, 1.21 mmol) in distilled water (10 mL) was mixed with a solution of **20** (0.963 g, 2.41 mmol) in distilled water (10 mL) with continuous stirring at room temperature. Then ethylenediamine (en) (0.16 mL, 2.42 mmol) was added drop-wise. The solution was stirred for 30 min. and evaporated slowly at room temperature. Purple plates were obtained after 3 days. The crystals were washed with methanol to remove side products and dried. Yield 0.321 g (48 %).

Anal. Calcd. for $C_{16}H_{36}N_{12}NiO_6$ (551.23 g/ mol): C 34.86, H 6.58, N 30.49; **Found**: C 34.86, H 6.72, N 30.37 %.

IR (DRIFT): ν_{CO} = 1701 (vs), 1632 (vs) cm^{-1}.

4.4.6 Synthesis of (1,3-Dimethylcyanurate)bis(ethylenediamine)Copper(II) (1,3-dimethylcyanurato) $[Cu(DMC)(en)_2][DMC]$ (**24**)

A solution of $CuSO_4.5H_2O$ (1.03 g, 4.10 mmol) in distilled water (10 mL) was mixed with a solution of **20** (3.26 g, 8.19 mmol) in distilled water (40 mL) with continuous stirring at room temperature. The polycrystalline solid $[Cu(DMC)_2(H_2O)_3]$ was removed by suction filtration, washed with water and methanol several times, and dried in an oven at 50 ºC.

The en ligand (0.134 g, 2.23 mmol) was added drop-wise to an aqueous suspension (20 mL) of $[Cu(DMC)_2(H_2O)_3]$ (0.50 g, 1.12 mmol) with continuous stirring at room temperature for 30 min. and a dark blue solution was obtained. Light blue plates were obtained by slow evaporation of the resulting solution at room temperature within 4 days. Yield 0.250 g (45 %).

Anal. Calcd. for $C_{14}H_{28}CuN_{10}O_6$ (495.99 g/ mol): C 33.90, H 5.69, N 28.24; **Found**: C 33.80, H 5.59, N 28.04 %.

IR (DRIFT): ν_{CO} = 1706 (vs), 1668 (sh), 1621 (vs) cm^{-1}**.**

4.4.7 Synthesis of Thallium (1,3-dimethylcyanurate) Tl[DMC] **(25)**

0.646 g (3.96 mmol) **20** was dissolved in a minimum amount of water, and then 0.885 g (3.96 mmol) TlF was added with stirring at 25 °C for 10 min. The resulting precipitate was isolated, washed with cold water and methanol, and dried for 1 h at 80 °C. Yield: 0.900 g (63 %), colorless crystals.

Anal. Calcd. for $C_5H_6N_3O_3Tl$ (360.50 g/ mol): C 16.66, H 1.68, N 11.66; **Found** C 14.39, H 1.59, N 10.07 %.

^{1}H NMR (DMSO-d_6): $\delta = 3.11$ (s, 6 H, NMe).

^{13}C{^{1}H} NMR (DMSO-d_6): $\delta = 27.85$ (Me), 153.11 (C^2), 156.33 ($C^{4,6}$).

IR (DRIFT): $\nu_{CO} = 1724$ (vs), 1690 (sh), 1659 (s) cm^{-1}.

4.4.8 Synthesis of Tetraphenylphosphonium **(**1,3-dimethylcyanurate) [PPh$_4$][DMC] **(26)**

0.518 g (1.11 mmol) [PPh$_4$]I was dissolved in 20 mL of methanol, and then 0.400 g (1.11 mmol) **25** was added with stirring at 45 °C for 40 min. The filtered solution was evaporated to dryness, and the resulting solid was washed with Et$_2$O (2x 10 mL). Yield after recrystallisation from chloroform/ diethylether: 0.500 g (90 %), colorless crystals.

Anal. Calcd. for $C_{29}H_{26}N_3O_3P$ (495.52 g/ mol): C 70.29, H 5.29, N 8.48; **Found** C 70.11, H 5.61, N 8.08 %.

^{1}H NMR (CDCl$_3$): $\delta = 3.11$ (s, 6 H, NMe), 7.56-7.85 (m, 20 H, Ph).

^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 28.4$ (Me), 116.3 (d, Ph C^1, $J = 89$ Hz), 129.8 (d, Ph $C^{3,5}$, $J = 12$ Hz), 133.4 (d, Ph $C^{2,6}$, $J = 11$ Hz), 134.9 (d, Ph C^4, $J = 3$ Hz), 154.8 (C^2_{DMC}), 157.8 ($C^{4,6}_{DMC}$).

^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 23.1$.

IR (DRIFT): $\nu_{CO} = 1704$ (vs), 1691 (s) cm^{-1}.

4.4.9 Synthesis of Tetraphenylphosphonium (1,3-dimethylcyanurate)(pentacarbonyl)Chromate $[PPh_4][Cr(DMC)(CO)_5]$ **(27a)**

A suspension of 0.400 g (0.807 mmol) **26** and 0.178 g (0.807 mmol) $Cr(CO)_6$ in 40 mL THF was refluxed for 4 h. The solvent was removed *in vacuo*, and the resulting solid was washed with *n*-hexane and dried *in vacuo*. Yield after recrystallisation from dichloromethane/*n*-hexane at -32 °C: 0.437 g (79 %), yellow needles.

Anal. Calcd. for $C_{34}H_{26}CrN_3O_8P$ (687.57 g/ mol): C 58.54, H 5.20, N 6.11; **Found** C 58.19, H 5.04, N 5.82 %.

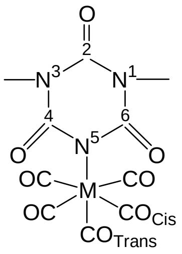
^{1}H NMR ($CDCl_3$): $\delta = 3.20$ (s, 6 H, NMe), 7.54-7.86 (m, 20 H, Ph).

^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 29.4$ (Me), 116.3 (d, Ph C^1, $J = 89$ Hz), 129.8 (d, Ph $C^{3,5}$, $J = 12$ Hz), 133.4 (d, Ph $C^{2,6}$, $J = 11$ Hz), 134.9 (d, Ph C^4, $J = 3$ Hz), 152.8 (C^2_{DMC}), 156.4 ($C^{4,6}_{DMC}$), 216.9 (CO_{cis}), 225.4 (CO_{trans}).

^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 23.3$.

IR (DRIFT): $\nu_{CO[DMC]} = 1740$ (sh), 1708 (s), 1675 (sh); $\nu_{CO[M-CO]} = 2053$ (w), 1971 (s), 1904 (vs), 1863 (sh), 1827 (vs) cm^{-1}.

MS (FAB neg.): m/z (%) = 347.9 [11], 319.9 [21, M-CO], 291.9 [100, M-2CO] and further fragments.



4.4.10 Synthesis of Tetraphenylphosphonium (1,3-dimethylcyanurate)(pentacarbonyl) Molybdate $[PPh_4][Mo(DMC)(CO)_5]$ **(27b)**

A suspension of 0.400 g (0.807 mmol) **26** and 0.213 g (0.807 mmol) $Mo(CO)_6$ in 40 mL THF was refluxed for 4 h. The solvent was removed *in vacuo*, and the resulting solid was washed with *n*-hexane and dried *in vacuo*. Yield after recrystallisation from dichloromethane/*n*-hexane at -32 °C: 0.480 g (81 %), yellow crystals.

Anal. Calcd. For $C_{34}H_{26}MoN_3O_8P$ (731.51 g/ mol): C 55.83, H 3.58, N 5.74; **Found** C 54.07, H 4.93, N 4.84 %.

^{1}H NMR ($CDCl_3$): $\delta = 3.17$ (s, 6 H, NMe), 7.54-7.85 (m, 20 H, Ph).

^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 28.4$ (Me), 116.4 (d, Ph C^1, $J = 89$ Hz), 129.8 (d, Ph $C^{3,5}$, $J = 12$ Hz), 133.3 (d, Ph $C^{2,6}$, $J = 11$ Hz), 134.8 (d, Ph C^4, $J = 3$ Hz), 152.0 (C^2_{DMC}), 155.4 ($C^{4,6}_{DMC}$), 205.7 (CO_{cis}), 217.2 (CO_{trans}).

^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 23.3$.

IR (DRIFT): $\nu_{CO[DMC]}$ = 1745 (sh), 1700 (s), 1640 (s); $\nu_{CO[M\text{-}CO]}$ = 2062 (w), 1963 (s), 1902 (vs), 1864 (sh), 1834 (vs) cm^{-1}.

MS (FAB neg.): m/z (%) = 391.8 [12], 363.9 [32, M-CO], 335.9 [88, M-2CO] and further fragments.

4.4.11 Synthesis of Tetraphenylphosphonium **(**1,3-dimethylcyanurate)(pentacarbonyl)Tungstate $[PPh_4][W(DMC)(CO)_5]$ **(27c)**

A suspension of 0.400 g (0.807 mmol) **26** and 0.284 g (0.807 mmol) $W(CO)_6$ in 40 mL THF was refluxed for 6 h. The solvent was removed *in vacuo*, and the resulting solid was washed with *n*-hexane and dried *in vacuo*. Yield after recrystallisation from dichloromethane/*n*-hexane at -32 °C: 0.476 g (72 %), yellow crystals.

Anal. Calcd. for $C_{34}H_{26}N_3O_8PW$ (819.42 g/ mol): C 49.84, H 3.20, N 5.53; **Found** C 49.18, H 3.48, N 4.91 %.

^{1}H NMR ($CDCl_3$): δ = 3.18 (s, 6 H, NMe), 7.54-7.86 (m, 20 H, Ph).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 28.6 (CH_3), 116.3 (d, Ph C^1, J = 89 Hz), 129.8 (d, Ph $C^{3,5}$, J = 12 Hz), 133.4 (d, Ph $C^{2,6}$, J = 11 Hz), 134.9 (d, Ph C^4, J = 3 Hz), 151.6 (C^{2}_{DMC}), 155.2 ($C^{4,6}_{DMC}$), 199.5 (CO_{cis}), 206.2 (CO_{trans}).

^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 23.3$.

IR (DRIFT): $\nu_{CO[DMC]}$ = 1708 (sh), 1679 (sh), 1642 (s); $\nu_{CO[M\text{-}CO]}$ = 2061 (w), 1942 (s), 1890 (vs), 1830 (sh), 1808 (vs) cm^{-1}.

MS (FAB neg.): m/z (%) = 479.8 [16], 451.9[44, M-CO], 423.9 [100, M-2CO] and further fragments.

4.4.12 Synthesis of 1,3-Diisopropyl-4,5-dimethylimidazolium-1,3-dimethylcyanurate (**28**)

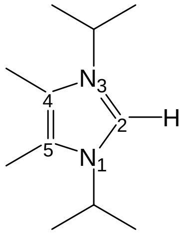
To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **9** (0.246 g, 1.37 mmol) in THF (25 mL) was added 1,3-dimethylcyanuric acid **14** (0.215 g, 1.37 mmol) at 0 °C and stirring for 24h at room temperature. After evaporation of the solvent, the product was washed with Et_2O (2 x 10 mL) and dried *in vacuo*. Yield after recrystallization from Acetone/ Et_2O: 0.350 g (76%) as block colourless crystals.

Anal. Calcd. for $C_{16}H_{27}N_5O_3$ (337.42 g/ mol): C 56.95, H 8.07, N 20.76; **Found**: C 56.20, H 6.74, N 20.31 %.

^{1}**H NMR** (DMSO-d_6): δ 1.49 (d, 12H, 1,3-CH*Me*$_2$, ^{3}J = 6.71 Hz), 2.29 (s, 6H, 4,5-Me), 3.02 (s, 6H, NMe_{DMC}), 4.56 (sept, 2H, *CH*Me_2), 9.23 (s, 1H, 2-H_{Im}).

^{13}**C{^{1}H} NMR** (DMSO-d_6): δ = 7.81 (4,5-Me), 22.14 (1,3-CH*Me*$_2$), 27.79 (Me_{DMC}), 49.61 (1,3-*C*HMe_2), 125.90 (C^{2}_{Im}), 130.64 ($C^{4,5}_{Im}$), 153.73 (C^{2}_{DMC}), 156.35 ($C^{4,6}_{DMC}$).

IR (DRIFT): ν_{CO} = 1703 (vs), 1674 (sh), 1631 (s) cm^{-1}.



4.4.13 Synthesis of 1,3-Diisopropyl-4,5-dimethylimidazolium formate (**29**)

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **9** (0.348 g, 1.93 mmol) in THF (25 mL) was added NH_4HCO_2 (0.122 g, 1.923 mmol) and reflux for 2h. After evaporation of the solvent, the product was washed with Et_2O (2 x 10 mL) and dried *in vacuo*. Yield after recrystallization from Acetone/ Et_2O: 0.350 g (80%) as colorless crystals.

Anal. Calcd. for $C_{12}H_{22}N_2O_2$ (226.32 g/ mol): C 63.68, H 9.80, N 12.38; **Found:** C 63.25, H 9.85, N 12.13 %.

^{1}**H NMR** (DMSO-d_6): δ = 1.50 (d, 12 H, 1,3-CH*Me*$_2$, ^{3}J = 6.72 Hz), 2.30 (s, 6 H, 4,5-Me), 4.58 (sept, 2 H, C*H*Me_2), 8.62 (s, 1 H, HCO_2), 9.54 (s, 1 H, 2-H_{Im}).

^{13}**C{^{1}H} NMR** (DMSO-d_6): δ = 7.82 (4,5-Me), 22.16 (1,3-CH*Me*$_2$), 49.59 (1,3-*C*HMe_2), 125.77 (C^{2}), 131.24 ($C^{4,5}$), 164.96 (HCO_2).

IR (DRIFT): ν_{CO} = 1632 (s) cm^{-1}.

4.4.14 Synthesis of 1,3-Diisopropyl-4,5-dimethylimidazolium bicarbonate (**30**)

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **9** (0.300 g, 1.66 mmol) in THF (25 mL) was added NH_4HCO_3 (0.132 g, 1.67 mmol) at 25 °C. After stirring overnight at room temperature, the insoluble crude product was filtered off washed with Et_2O and dried *in vacuo*. Yield after recrystallization from (DMSO-Acetone)/ Et_2O: 0.362 g (90%) as colorless crystals.

Anal. Calcd. for $C_{12}H_{22}N_2O_3$ (242.32 g/ mol): C 59.48, H 9.15, N 11.56; **Found**: C 59.30, H 8.82, N 11.23 %.

^{1}H NMR (DMSO-d_6): δ = 1.39 (d, 12H, 1,3-CH*Me*$_2$, ^{3}J = 6.6 Hz), 2.19 (s, 6H, 4,5-Me), 4.47 (sept, 2H, C*H*Me$_2$), 9.38 (s, 1H, 2-H$_{\mathrm{Im}}$), N/O (HCO_3).

^{13}C{^{1}H} NMR (DMSO-d_6): δ = 7.83 (4,5-Me), 22.13 (1,3-CH*Me*$_2$), 49.61 (1,3-*C*HMe$_2$), 125.75 (C^2), 131.36 ($C^{4,5}$), 158.18 (HCO_3).

IR (DRIFT): ν_{CO} = 1662 (s), 1624 (s) cm^{-1}.

4.4.15 Synthesis of 1,3-Diisopropyl-4,5-dimethylimidazolium hydrogenoxalate (**31**)

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **9** (0.398 g, 2.21 mmol) in THF (25 mL) was added $(NH_4)_2C_2O_4$ (0.314 g, 2.21 mmol) at room temperature and stirring overnight. The precipitate was filtered off, washed with Et_2O (2 x 10 mL) and dried *in vacuo*. Yield after recrystallization from CH_3CN/ Et_2O: 0.538 g (90 %) as colorless crystals.

Anal. Calcd. for $C_{13}H_{22}N_2O_4$ (270.33 g/ mol): C 57.76, H 8.20, N 10.36; **Found**. C 57.54, H 8.05, N 10.16.

^{1}H NMR (DMSO-d_6): δ = 1.62 (d, 12 H, 1,3-CH*Me$_2$*, ^{3}J = 6.72 Hz), 2.42 (s, 6 H, 4,5-Me), 4.58 (sept, 2 H, C*H*Me$_2$), 9.54 (s, 1 H, 2-H$_{\mathrm{Im}}$), N/O (HO).

^{13}C{^{1}H} NMR (DMSO-d_6): δ = 7.82 (4,5-Me), 22.16 (1,3-CH*Me*$_2$), 49.59 (1,3-*C*HMe$_2$), 125.77 (C^2), 131.24 ($C^{4,5}$), 164.96 (CO).

IR (DRIFT): ν_{CO} = 1679 (s), 1659 (s) cm^{-1}.

4.4.16 Synthesis of 1,3-Diisopropyl-4,5-dimethylimidazolium acetylacetonate (**32**)

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **9** (0.300 g, 1.67 mmol) in THF (25 mL) was added acetylacetone (0.334 g, 3.33 mmol) at -30 ^{o}C. After stirring for 2 hours at room temperature, the insoluble crude product was filtered off washed with Et_2O and dried *in vacuo*. Yield after recrystallization from Acetone/ Et_2O: 0.326 g (70%) as block colourless crystals.

Anal. Calcd. for $C_{16}H_{28}N_2O_3$ (280.41 g/ mol): C 68.53, H 10.06, N 9.99; **Found**: C 68.43, H 10.73, N 10.02 %.

^{13}C NMR (MAS): δ 9.82, 10.55 (4,5-Me), 23.59 (1,3-CH*Me*$_2$), 26.01, 30.94 (Me_{acac}), 51.74 (1,3-*C*HMe$_2$), 101.72 (CH_{acac}), 128.95 (C^2), 134.94 ($C^{4,5}$), 190.34 (CO).

MS (FAB neg.): m/z (%) = 98.9 [85].

IR (DRIFT): ν_{CO} = 1631 (s), 1585 (s) cm^{-1}.

4.4.17 Synthesis of Bis(1,3-Diisopropyl-4,5-dimethylimidazolium) heptaiodopentaargentate(I) (**33**)

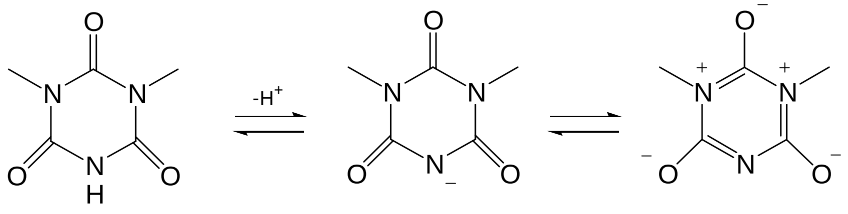
To a solution containing 1,3-diisopropyl-4,5-dimethylimidazolium iodide (0.120 g, 0.391 mmol) in acetonitrile (30 mL) was added AgI (0.091 g, 0.391 mmol) and reflux for 24h. The resulting mixture was filtered off and the solution was concentrated under vacuum to 15 mL and left to crystallise at -32 °C. Block colourless crystals were obtained. Yield 0.210 g (30%).

Anal. Calcd. for $C_{22}H_{42}Ag_5I_7N_4$ (1790.27 g/ mol): C 14.76, H 2.36, N 3.13; **Found**: C 14.72, H 2.30, N 3.11 %.

^{13}C NMR (MAS): δ 12.06 (4,5-Me), 26.93 (1,3-CH*Me*$_2$), 53.08 (1,3-*C*HMe$_2$), 128.13 (C^2_{Im}), 134.76 ($C^{4,5}_{Im}$).

5. Summary and Conclusions

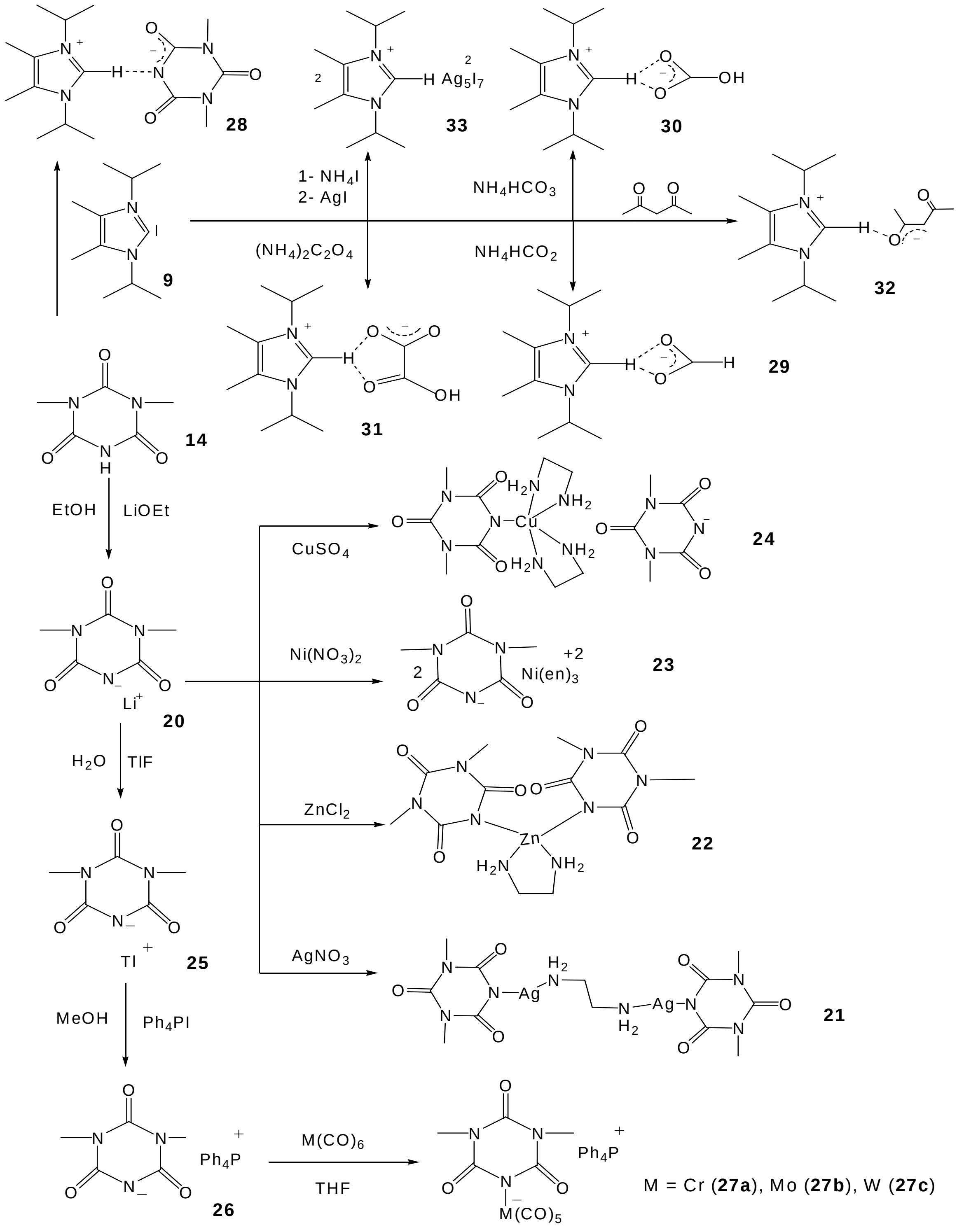
In summary, we have successfully synthesized new complexes containing DMC (1,3-dimethylcyanurate) ligand. The crystal structures of 1,3-dimethylcyanurato complexes of $Ag^{(I)}$ **21**, $Zn^{(II)}$ **22**, $Ni^{(II)}$ **23** and $Cu^{(II)}$ **24** formed by substituted en (ethylenediamine) have been determined by X-ray analyses. As shown in the present work, the DMC ligand coordinated to the central metal atom in a different structure types. The stereochemistry of these metals varies from a distorted linear AgN_2 coordination geometry **21**, where the metal-DMC bond ratio is 1:1, to a distorted tetrahedral ZnN_4 core **22** by 2:1 ratio, to octahedral NiN_6 core **23** occupied only by en ligands, while the DMC^{-1} anions remain as uncoordinated ions, and to a highly square-pyramidally distorted TBP CuN_5 core **24**, where the metal-DMC bond ratio is 1:1 with an extraordinary bond length of $Cu\text{-}N_{DMC}$ (2.382(1) Å). It is probably the longest among the five-coordinate copper(II) complexes characterized by X-ray analysis. The bidentate en co-ligand significantly contributes to the distortion of the coordination geometry around the central metal atom by forming interesting hydrogen bonds with DMC ligand around the coordination center. These cyanurate complexes showed that the DMC ligand coordinate through the negatively charged nitrogen atom in an obtuse angle to the central metal atom. On the other hand, the hard center $Li^{(I)}$ has found to be O-coordinated **20**. The tri-keto tautomer **14a** was found to be the only form in all of these cyanurato complexes.



14 **14a** **14b**

Stable tetraphenylphosphonium salts of pentacarbonylmetalate complexes have been synthesized in good yield from the reactions of $M(CO)_6$ with $[Ph_4P][DMC]$ **26**. The X-ray structures of the 1,3-dimethylcyanurate derivatives of chromium **27a** and tungsten **27c** carbonyls revealed a distorted octahedral geometry about the metal centers which were associated with five carbonyl ligands and a planar pseudoaromatic cyanurate ring. The DMC ligand was bound to the metal center through the deprotonated N_{31} atom. ^{13}C NMR and ν(M-CO) infrared spectroscopies indicated that the DMC ligand to possess significantly more electron donating ability as compared with the pyridine similarly bound to $M(CO)_5$ fragments.

Owing to their strongly basic character of N-heterocyclic carbenes, the reaction of 2,3-dihydroimidazole-2-ylidene **9** either with compounds containing acidic hydrogen, or ammonium salts gives interesting results (scheme 12). The crystal structures of new imidazolium salts **28**, **29**, **30**, **31**, **32** and **33** have been determined by X-ray analyses. These imidazolium salts $[H(4,5\text{-}Me)(^iPr)_2Im][X]$, **15**, contain ion pairs held together either by a monofuctional (**28**, **32**) or a bifurcated (**29**, **30**, **31**) C-H…X (X = N, O) hydrogen bonds. We observe that the C-H…X hydrogen bonds may act as an additional stabilizing factor in their crystal structures. In the C-H…O hydrogen bonding, the C-H acts as the proton donor, this type of hydrogen-bonding interaction is, in general, rather weak compared to the conventional hydrogen bond. This study verifies also that the formation of the C-H…O interactions cause changes in the imidazolium C^2-H stretching frequency and bond length. Polymer **33** is a new example of a 1D Ag/I coordination polymer containing imidazolium cation that has argentophilic interactions. Compounds containing argentophilicity can be potentially used in silver-containing antibacterial agents.[71]



Scheme 12. The summary of all reactions.

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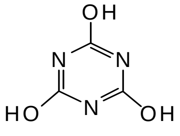
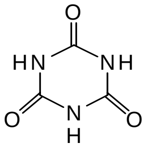
7.1 List of compounds



1

1) 2,4,6-Trihydroxy-1,3,5-triazine



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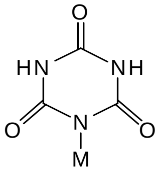
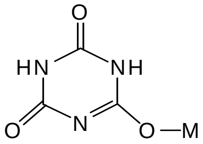
2) 2,4,6-Trione-1,3,5-triazine



3

3) N-Metal cyanurate



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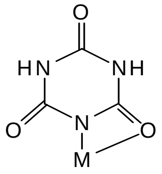
4) O-Metal cyanurate



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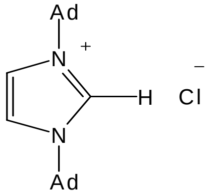
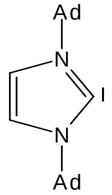
5) N-O-Metal cyanurate



6

6) 1,3-Diadamantylimidazolium chloride



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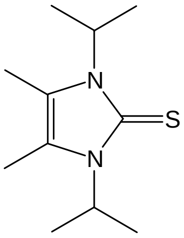
7) 1,3-Diadamantylimidazol-2-ylidene



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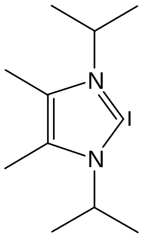
8) 1,3-Diisopropyl-4,5-dimethylimidazol-2-thione



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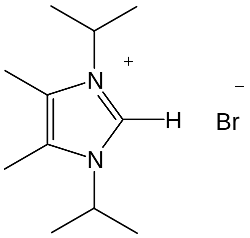
9) 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene



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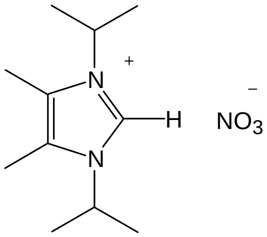
10) 1,3-Diisopropyl-4,5-dimethylimidazolium bromide



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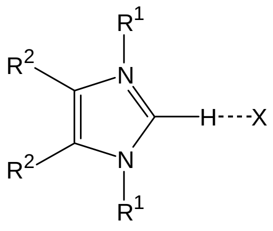
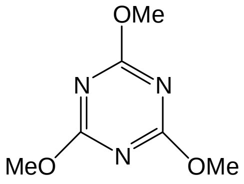
11) 1,3-Diisopropyl-4,5-dimethylimidazolium nitrate



12

12) Imidazolium salt



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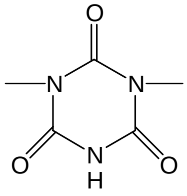
13) Trimethoxy-1,3,5-triazine



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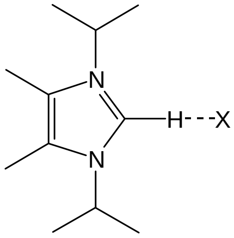
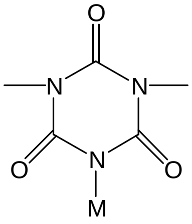
14) 1,3-Dimethyl-2,4,6-trioxo-1,3,5-triazine



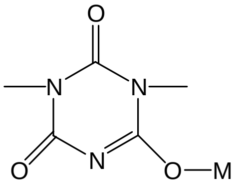
15

15) 1,3-Diisopropyl-4,5-dimethylimidazolium salt



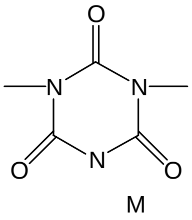
16

16) N-Metal (1,3-dimethylcyanurate)



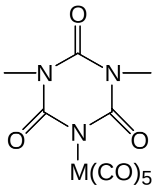
17

17) O-Metal (1,3-dimethylcyanurate)



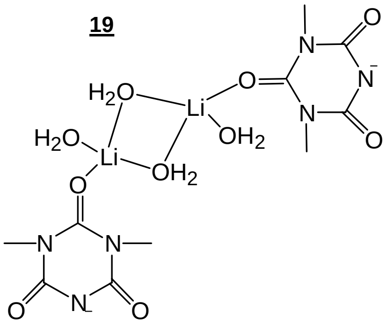
18

18) Metal (1,3-dimethylcyanurate)



19

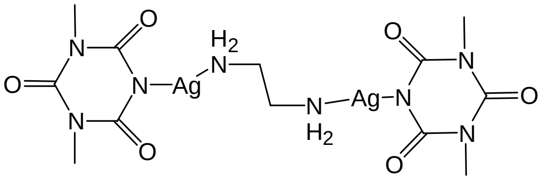
19) Pentacarbonylmetalate complex



20

20) 1,3-Dimethyl-O-lithiumcyanurate dihydrate

21) Bis(1,3-dimethyl-N-silvercyanurate)(ethylenediamine)



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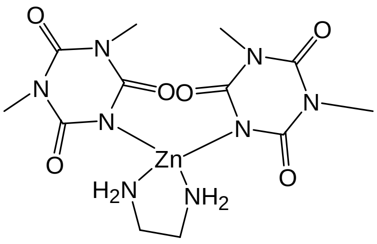
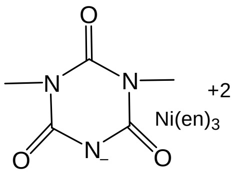


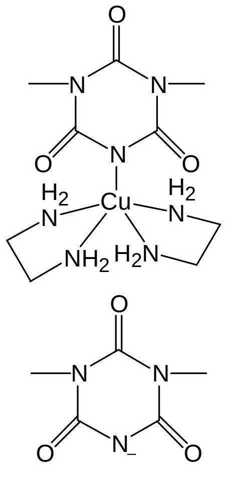
22

22) Bis(1,3-dimethylcyanurate)(ethylenediamine)Zinc(II)



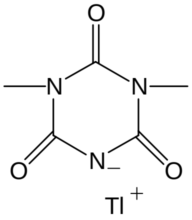
23

23) Tris(ethylenediamine)Nickel(II) Bis(1,3-dimethylcyanurate)



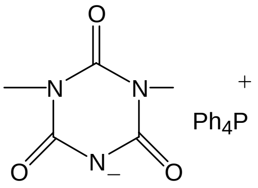
24

24) (1,3-Dimethylcyanurate)bis(ethylenediamine)Copper(II) (1,3-dimethylcyanurato)



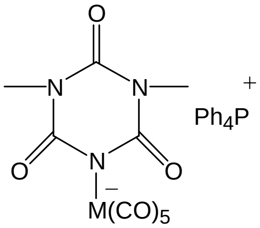
25

25) Thallium (1,3-dimethylcyanurate)



26

26) Tetraphenylphosphonium (1,3-dimethylcyanurate)

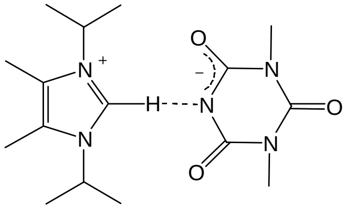


M = Cr(**27a**), Mo(**27b**), W(**27c**)

27a) Tetraphenylphosphonium (1,3-dimethylcyanurate)(pentacarbonyl)Chromate

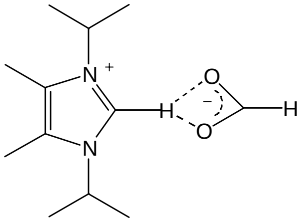
27b) Tetraphenylphosphonium (1,3-dimethylcyanurate)(pentacarbonyl)Molybdate

27c) Tetraphenylphosphonium (1,3-dimethylcyanurate)(pentacarbonyl)Tungstate



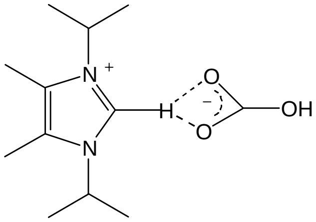
28

28) 1,3-Diisopropyl-4,5-dimethylimidazolium-1,3-dimethylcyanurate



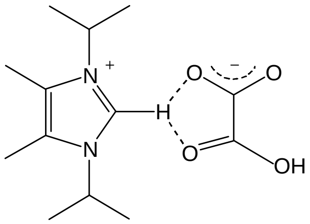
29

29) 1,3-Diisopropyl-4,5-dimethylimidazolium formate



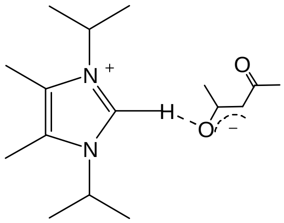
30

30) 1,3-Diisopropyl-4,5-dimethylimidazolium bicarbonate



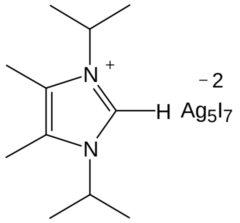
31

31) 1,3-Diisopropyl-4,5-dimethylimidazolium hydrogenoxalate



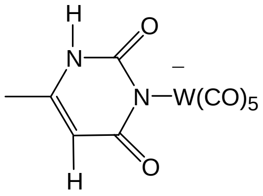
32

32) 1,3-Diisopropyl-4,5-dimethylimidazolium acetylacetonate



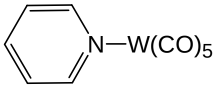
33

33) Bis(1,3-Diisopropyl-4,5-dimethylimidazolium) heptaiodopentaargentate



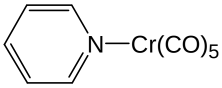
34

34) (6-methyluracilate)(pentacarbonyl)Tungstate



35

35) Pyridine-Tungstenpentacarbonyl



36

36) Pyridine-Chromiumpentacarbonyl

7.2 Crystal structure's tables

Table 30: Atomic coordinates and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_5H_7N_3O_3$ (**14**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

x	y	z	U(eq)	
C(1)	0.6345(2)	-0.1871(4)	0.8305(1)	20(1)
N(2)	0.5225(1)	-0.0213(3)	0.8277(1)	20(1)
C(3)	0.5137(2)	0.1913(3)	0.8957(1)	19(1)
N(4)	0.6207(1)	0.2253(3)	0.9716(1)	21(1)
C(5)	0.7341(2)	0.0683(4)	0.9849(1)	21(1)
N(6)	0.7364(1)	-0.1350(3)	0.9115(1)	20(1)
O(7)	0.6404(1)	-0.3670(3)	0.7674(1)	27(1)
C(8)	0.4064(2)	-0.0772(4)	0.7476(1)	27(1)
O(9)	0.4155(1)	0.3369(3)	0.8905(1)	24(1)
O(10)	0.8238(1)	0.1081(3)	1.0553(1)	28(1)
C(11)	0.8586(2)	-0.2973(4)	0.9180(2)	27(1)

Table 31. Anisotropic displacement parameters (A^2 x 10^3) for $C_5H_7N_3O_3$ (**14**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	23(1)	20(1)	19(1)	1(1)	7(1)	-1(1)
N(2)	21(1)	19(1)	19(1)	-1(1)	3(1)	0(1)
C(3)	22(1)	17(1)	19(1)	2(1)	7(1)	-1(1)
N(4)	24(1)	19(1)	21(1)	-4(1)	5(1)	-1(1)
C(5)	22(1)	20(1)	21(1)	1(1)	6(1)	-2(1)
N(6)	20(1)	20(1)	21(1)	1(1)	6(1)	2(1)
O(7)	31(1)	26(1)	25(1)	-8(1)	7(1)	3(1)
C(8)	26(1)	29(1)	23(1)	-2(1)	-1(1)	0(1)
O(9)	25(1)	22(1)	26(1)	-2(1)	4(1)	4(1)
O(10)	25(1)	31(1)	27(1)	-3(1)	0(1)	-1(1)
C(11)	23(1)	29(1)	29(1)	1(1)	6(1)	6(1)

Table 32. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_5H_7N_3O_3$ (**14**).

	x	y	z	U(eq)
H(4)	6170(2)	3530(5)	10141(18)	29(6)
H(8A)	3920(3)	670(6)	6960(2)	53(7)
H(8B)	4220(3)	-2390(7)	7110(2)	59(8)
H(8C)	3250(3)	-970(6)	7800(2)	50(7)
H(11A)	8390(2)	-4580(6)	8740(2)	47(7)
H(11B)	8810(3)	-3740(6)	9860(2)	51(7)
H(11C)	9290(3)	-1900(6)	8990(2)	55(8)

Table 33: Atomic coordinates and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_5H_{10}LiN_3O_5$ (**20**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	0.2475(3)	0.4714(2)	0.0064(2)	17(1)
N(2)	0.2987(3)	0.5897(2)	-0.1660(2)	18(1)
C(3)	0.3130(3)	0.7631(2)	-0.2067(3)	19(1)
N(4)	0.2748(3)	0.8162(2)	-0.0715(2)	19(1)
C(5)	0.2232(3)	0.6990(2)	0.1012(2)	18(1)
N(6)	0.2123(3)	0.5289(2)	0.1351(2)	19(1)
O(7)	0.2373(2)	0.3162(2)	0.0310(2)	26(1)
C(8)	0.3393(4)	0.5246(3)	-0.3056(3)	24(1)
O(9)	0.3595(3)	0.8677(2)	-0.3581(2)	32(1)
C(10)	0.2917(4)	1.0037(3)	-0.1132(3)	28(1)
O(11)	0.1886(2)	0.7550(2)	0.2178(2)	25(1)
Li	-0.1995(9)	0.9501(5)	0.4872(5)	48(1)
O(1)	0.1250(3)	1.0321(2)	0.3190(2)	29(1)
O(2)	-0.1563(3)	0.7107(2)	0.5208(2)	26(1)

Table 34. Anisotropic displacement parameters (A^2 x 10^3) for $C_5H_{10}LiN_3O_5$ (**20**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	16(1)	15(1)	16(1)	-3(1)	-3(1)	0(1)
N(2)	20(1)	17(1)	15(1)	-5(1)	-4(1)	1(1)
C(3)	18(1)	17(1)	17(1)	-3(1)	-3(1)	2(1)
N(4)	22(1)	13(1)	17(1)	-3(1)	-3(1)	0(1)
C(5)	16(1)	18(1)	18(1)	-6(1)	-3(1)	1(1)
N(6)	21(1)	16(1)	14(1)	-3(1)	-3(1)	0(1)
O(7)	37(1)	15(1)	21(1)	-5(1)	-4(1)	-2(1)
C(8)	30(1)	27(1)	18(1)	-11(1)	-5(1)	0(1)
O(9)	51(1)	19(1)	15(1)	0(1)	-1(1)	2(1)
C(10)	36(1)	16(1)	30(1)	-7(1)	-6(1)	1(1)
O(11)	37(1)	20(1)	18(1)	-9(1)	-4(1)	1(1)
Li	101(4)	19(2)	28(2)	-9(2)	-29(2)	19(2)
O(1)	53(1)	14(1)	15(1)	-4(1)	-4(1)	-2(1)
O(2)	36(1)	17(1)	17(1)	-2(1)	-4(1)	1(1)

Table 35. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_5H_{10}LiN_3O_5$ (**20**).

	x	y	z	U(eq)
H(8A)	4620(6)	4510(4)	-3000(4)	55(9)
H(8B)	2210(6)	4690(5)	-2990(5)	65(10)
H(8C)	3800(7)	6050(6)	-4060(6)	80(12)
H(10A)	4250(6)	10590(4)	-2160(5)	60(9)
H(10B)	3370(6)	10180(5)	-220(5)	72(11)
H(10C)	1670(7)	10650(5)	-1430(5)	83(12)
H(1A)	-1530(5)	8740(5)	7640(4)	51(9)
H(1B)	1660(5)	9470(5)	2760(4)	53(9)
H(2A)	-450(6)	6930(4)	4460(5)	47(8)
H(2B)	-1630(5)	6380(4)	6120(4)	36(8)

Table 36. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_6H_{10}AgN_4O_3$ (**21**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ag(1)	1754(1)	1832(1)	307(1)	25(1)
O(21)	-1545(3)	1266(4)	977(1)	30(1)
O(41)	95(3)	-5643(5)	2210(1)	32(1)
O(61)	3789(3)	-2414(5)	1032(1)	33(1)
N(3)	-758(3)	-2152(5)	1602(1)	23(1)
N(5)	1986(3)	-4059(5)	1631(1)	21(1)
N(1)	1112(3)	-588(5)	973(1)	22(1)
C(2)	-432(3)	-381(5)	1172(1)	21(1)
C(4)	416(3)	-4075(6)	1841(1)	22(1)
C(6)	2362(3)	-2336(6)	1199(1)	23(1)
C(31)	-2433(4)	-1983(9)	1816(1)	40(1)
C(51)	3317(4)	-5950(7)	1882(1)	29(1)
N(10)	2880(3)	4007(5)	-327(1)	23(1)
C(10)	4365(3)	5878(6)	-170(1)	21(1)

Table 37. Anisotropic displacement parameters (A^2 x 10^3) for $C_6H_{10}AgN_4O_3$ (**21**). The anisotropic displacement factor exponent takes the form:-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ag(1)	25(1)	26(1)	24(1)	6(1)	3(1)	1(1)
O(21)	28(1)	28(1)	33(1)	7(1)	-2(1)	5(1)
O(41)	34(1)	35(1)	27(1)	12(1)	-2(1)	-4(1)
O(61)	28(1)	43(1)	27(1)	2(1)	6(1)	9(1)
N(3)	20(1)	26(1)	22(1)	2(1)	1(1)	0(1)
N(5)	23(1)	20(1)	21(1)	0(1)	-2(1)	3(1)
N(1)	24(1)	23(1)	20(1)	2(1)	0(1)	-1(1)
C(2)	23(1)	18(1)	21(1)	-1(1)	-2(1)	-3(1)
C(4)	25(1)	21(1)	19(1)	0(1)	-3(1)	-3(1)
C(6)	25(1)	24(1)	20(1)	-2(1)	1(1)	-1(1)
C(31)	24(2)	62(2)	35(2)	13(2)	7(1)	3(1)
C(51)	29(1)	27(1)	28(1)	1(1)	-5(1)	9(1)
N(10)	23(1)	24(1)	21(1)	4(1)	-2(1)	1(1)
C(10)	23(1)	20(1)	21(1)	4(1)	4(1)	2(1)

Table 38. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_6H_{10}AgN_4O_3$ (**21**).

	x	y	z	U(eq)
H(31A)	-3250(11)	-3490(16)	1730(3)	140(3)
H(31B)	-3360(9)	-660(16)	1600(3)	140(2)
H(31C)	-2370(8)	-1790(12)	2140(3)	100(2)
H(51A)	4070(4)	-4750(8)	2127(14)	37(9)
H(51B)	3960(6)	-6820(9)	1671(18)	50(12)
H(10A)	3930(4)	7500(7)	6(12)	19(7)
H(10B)	4820(4)	6600(6)	-476(13)	22(7)
H(10C)	2290(5)	4970(9)	-514(16)	47(11)
H(10D)	3170(6)	2600(9)	-589(18)	50(11)
H(51C)	2910(6)	-7700(9)	1991(18)	52(12)

Table 39: Atomic coordinates and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_{12}H_{20}N_8O_6$ Zn (**22**). (U(eq) is defined as one third of the trace of the orthogonalized Uij tensor).

	x	y	z	U(eq)
Zn(1)	0.0664(1)	0.8553(1)	0.3610(1)	19(1)
N(1)	0.0937(2)	0.8882(2)	0.2970(1)	20(1)
C(2)	0.1885(2)	0.9656(2)	0.2834(1)	21(1)
O(02)	0.2552(2)	1.0229(2)	0.3098(1)	30(1)
N(3)	0.2097(2)	0.9777(2)	0.2376(1)	22(1)
C(03)	0.3117(2)	1.0612(2)	0.2223(1)	28(1)
C(4)	-0.3589(2)	0.9131(2)	0.2941(1)	21(1)
O(04)	-0.3345(2)	0.9189(1)	0.3339(1)	28(1)
N(5)	0.0410(2)	0.8418(2)	0.2222(1)	21(1)
C(05)	-0.0399(3)	0.7780(2)	0.1893(1)	29(1)
C(6)	0.0163(2)	0.8264(2)	0.2676(1)	21(1)
O(06)	-0.0713(2)	0.7599(2)	0.2802(1)	34(1)
N(7)	0.1099(2)	0.9653(2)	0.4108(1)	19(1)
C(8)	0.0221(2)	1.0556(2)	0.4142(1)	19(1)
O(08)	-0.0636(2)	1.0728(1)	0.3858(1)	28(1)
N(9)	0.0315(2)	1.1286(2)	0.4515(1)	22(1)
C(09)	-0.0567(3)	1.2310(2)	0.4548(1)	29(1)
C(10)	0.1189(2)	1.1086(2)	0.4862(1)	21(1)
O(010)	0.1211(2)	1.1695(1)	0.5196(1)	29(1)
N(11)	0.2033(2)	1.0141(2)	0.4807(1)	22(1)
C(011)	0.2985(3)	0.9885(2)	0.5167(1)	32(1)
C(12)	0.2005(2)	0.9405(2)	0.4433(1)	21(1)
O(012)	0.2778(2)	0.8579(2)	0.4410(1)	33(1)
N(13)	0.1481(2)	0.6937(2)	0.3773(1)	27(1)
C(14)	0.0401(3)	0.6298(2)	0.4011(1)	31(1)
C(15)	-0.0934(3)	0.6579(2)	0.3796(1)	29(1)
N(16)	-0.1130(2)	0.7861(2)	0.3804(1)	23(1)

Table 40. Anisotropic displacement parameters (A^2 x 10^3) for $C_{12}H_{20}N_8O_6$ Zn (**22**).The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Zn(1)	23(1)	20(1)	14(1)	-2(1)	1(1)	0(1)
N(1)	23(1)	22(1)	15(1)	-1(1)	2(1)	-2(1)
C(2)	24(1)	18(1)	19(1)	-2(1)	1(1)	2(1)
O(02)	31(1)	30(1)	27(1)	-7(1)	-2(1)	-8(1)
N(3)	24(1)	21(1)	21(1)	0(1)	5(1)	-2(1)
C(03)	25(1)	27(1)	31(1)	4(1)	6(1)	-4(1)
C(4)	24(1)	18(1)	19(1)	-2(1)	-3(1)	6(1)
O(04)	36(1)	31(1)	17(1)	-3(1)	-6(1)	3(1)
N(5)	26(1)	21(1)	15(1)	-2(1)	0(1)	-1(1)
C(05)	34(1)	31(1)	21(1)	-4(1)	-5(1)	-4(1)
C(6)	25(1)	23(1)	17(1)	-1(1)	1(1)	-1(1)
O(06)	39(1)	41(1)	21(1)	-1(1)	3(1)	-18(1)
N(7)	21(1)	21(1)	15(1)	-3(1)	-1(1)	0(1)
C(8)	21(1)	19(1)	18(1)	0(1)	1(1)	-4(1)
O(08)	31(1)	28(1)	26(1)	-2(1)	-11(1)	4(1)
N(9)	21(1)	22(1)	22(1)	-5(1)	0(1)	1(1)
C(09)	26(1)	26(1)	36(1)	-7(1)	0(1)	3(1)
C(10)	23(1)	22(1)	17(1)	-1(1)	3(1)	-6(1)
O(010)	38(1)	30(1)	20(1)	-8(1)	1(1)	-3(1)
N(11)	24(1)	25(1)	17(1)	-1(1)	-3(1)	-1(1)
C(011)	36(1)	34(1)	27(1)	-1(1)	-15(1)	0(1)
C(12)	20(1)	24(1)	20(1)	-2(1)	-1(1)	-1(1)
O(012)	30(1)	34(1)	36(1)	-9(1)	-9(1)	11(1)
N(13)	30(1)	26(1)	25(1)	-4(1)	1(1)	6(1)
C(14)	43(2)	26(1)	25(1)	4(1)	2(1)	3(1)
C(15)	39(1)	24(1)	25(1)	2(1)	2(1)	-9(1)
N(16)	22(1)	29(1)	17(1)	-1(1)	-2(1)	0(1)

Table 41. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_{12}H_{20}N_8O_6$ Zn (**22**).

	x	y	z	U(eq)
H(03A)	3870(3)	10570(3)	2413(10)	47(9)
H(03B)	2760(3)	11400(3)	2219(10)	48(9)
H(03C)	3390(3)	10380(3)	1931(11)	52(9)
H(05A)	120(3)	7230(3)	1730(10)	45(8)
H(05B)	-1040(3)	7360(3)	2034(11)	53(9)
H(05C)	-810(3)	8250(3)	1704(11)	46(9)
H(09A)	-1150(3)	12240(3)	4808(12)	60(10)
H(09B)	-1090(4)	12330(3)	4307(13)	73(12)
H(09C)	-50(3)	12990(3)	4590(10)	47(9)
H(11A)	2620(3)	10050(3)	5455(11)	59(9)
H(11B)	3850(4)	10320(3)	5115(11)	63(10)
H(11C)	3220(3)	9070(3)	5154(9)	35(7)
H(13A)	2170(3)	7060(3)	3951(10)	41(8)
H(13B)	1740(3)	6520(3)	3547(11)	49(9)

H(14A)	400(2)	6590(2)	4305(9)	24(6)
H(14B)	540(3)	5450(3)	4012(10)	47(8)
H(15A)	-1650(3)	6170(2)	3939(9)	35(7)
H(15B)	-930(3)	6300(2)	3485(10)	31(7)
H(16A)	-1760(3)	8040(2)	3638(9)	25(7)
H(16B)	-1360(3)	8060(2)	4083(10)	32(7)

Table 42: Atomic coordinates and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_{16}H_{36}N_{12}NiO_6$ (**23**). (U(eq) is defined as one third of the trace of the orthogonalized Uij tensor).

	x	y	z	U(eq)
Ni(1)	0.5000	0.5849(1)	0.7500	15(1)
N(1)	0.4054(1)	0.3868(2)	0.7164(1)	22(1)
C(2)	0.4595(1)	0.2341(2)	0.7183(1)	23(1)
N(3)	0.6049(1)	0.7668(2)	0.7828(1)	18(1)
C(4)	0.6289(1)	0.8385(2)	0.7227(1)	22(1)
C(5)	0.3647(1)	0.6995(2)	0.8259(1)	24(1)
N(6)	0.5472(1)	0.6031(2)	0.6593(1)	21(1)
C(10)	0.1574(1)	0.6881(2)	0.5976(1)	20(1)
N(11)	0.0954(1)	0.6796(2)	0.5321(1)	19(1)
C(12)	0.6197(1)	0.8920(2)	0.9779(1)	18(1)
N(13)	0.7072(1)	0.9649(2)	0.9923(1)	20(1)
C(14)	0.2680(1)	0.5348(2)	0.5582(1)	20(1)
N(15)	0.2409(1)	0.6105(2)	0.6089(1)	22(1)
O(16)	0.3677(1)	0.2676(2)	0.8583(1)	27(1)
C(17)	0.5024(1)	0.2565(3)	0.5206(1)	26(1)
O(18)	0.5671(1)	0.8931(2)	0.9205(1)	25(1)
C(19)	0.7363(2)	1.0479(3)	0.9369(1)	26(1)
O(20)	0.3447(1)	0.4639(2)	0.5664(1)	31(1)

Table 43. Anisotropic displacement parameters (A^2 x 10^3) for $C_{16}H_{36}N_{12}NiO_6$ (**23**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
Ni(1)	15(1)	14(1)	13(1)	0	2(1)	0
N(1)	21(1)	20(1)	22(1)	-1(1)	1(1)	-3(1)
C(2)	28(1)	19(1)	22(1)	-3(1)	6(1)	-4(1)
N(3)	17(1)	20(1)	17(1)	-1(1)	3(1)	1(1)
C(4)	22(1)	22(1)	24(1)	1(1)	8(1)	-4(1)
C(5)	25(1)	28(1)	23(1)	0(1)	12(1)	-1(1)
N(6)	24(1)	20(1)	17(1)	-2(1)	4(1)	3(1)
C(10)	20(1)	19(1)	18(1)	0(1)	4(1)	-1(1)
N(11)	17(1)	21(1)	18(1)	0(1)	4(1)	4(1)
C(12)	19(1)	16(1)	19(1)	-2(1)	4(1)	0(1)
N(13)	19(1)	23(1)	16(1)	2(1)	4(1)	-3(1)
C(14)	19(1)	22(1)	19(1)	0(1)	3(1)	1(1)

N(15)	20(1)	26(1)	17(1)	-2(1)	1(1)	2(1)
O(16)	28(1)	31(1)	22(1)	7(1)	9(1)	-4(1)
C(17)	20(1)	31(1)	28(1)	1(1)	5(1)	8(1)
O(18)	24(1)	31(1)	16(1)	-1(1)	1(1)	-5(1)
C(19)	27(1)	31(1)	21(1)	5(1)	7(1)	-5(1)
O(20)	22(1)	42(1)	28(1)	-4(1)	1(1)	13(1)

Table 44. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_{16}H_{36}N_{12}NiO_6$ (**23**).

	x	y	z	U(eq)
H(1A)	3756(18)	4050(3)	6757(15)	36(7)
H(1B)	3671(18)	3760(3)	7422(13)	28(6)
H(2A)	4209(15)	1430(3)	7173(11)	21(5)
H(2B)	4841(16)	2290(3)	6791(12)	24(6)
H(3A)	5893(17)	8510(3)	8080(13)	33(6)
H(3B)	6510(19)	7270(3)	8073(13)	31(7)
H(4A)	5787(15)	9150(3)	7007(11)	21(5)
H(4B)	6877(18)	9020(3)	7346(13)	33(6)
H(5A)	3547	7444	8677	29
H(5B)	3118	6286	8057	29
H(6A)	5575(15)	5080(3)	6433(11)	18(5)
H(6B)	5047(19)	6520(3)	6278(14)	37(7)
H(17A)	4792(18)	2360(3)	5591(14)	41(7)
H(17B)	4624(18)	2100(3)	4823(14)	37(7)
H(17C)	5090(2)	3750(5)	5198(17)	66(10)
H(19A)	7280(2)	9740(4)	8985(18)	65(10)
H(19B)	7950(2)	10750(4)	9523(17)	60(9)
H(19C)	7020(2)	11440(5)	9269(17)	68(10)

Table 45: Atomic coordinates and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_{14}H_{28}CuN_{10}O_6$(**24**).(U(eq) is defined as one third of the trace of the orthogonalized Uij tensor).

	x	y	z	U(eq)
Cu(1)	0.2191(1)	0.7687(1)	0.7353(1)	19(1)
N(1)	0.2300(2)	0.9041(1)	0.6125(1)	17(1)
C(2)	0.1570(2)	0.8526(2)	0.5194(1)	17(1)
N(3)	0.1845(2)	0.9245(1)	0.4429(1)	17(1)
C(4)	0.2672(2)	1.0494(2)	0.4596(1)	17(1)
N(5)	0.3305(2)	1.0982(1)	0.5560(1)	18(1)
C(6)	0.3221(2)	1.0251(2)	0.6332(1)	18(1)
N(7)	0.2689(2)	0.3777(1)	1.1395(1)	22(1)
C(8)	0.2628(2)	0.5012(2)	1.1606(1)	21(1)
N(9)	0.2632(2)	0.5755(1)	1.0843(1)	21(1)
C(10)	0.2486(2)	0.5263(2)	0.9875(1)	20(1)
N(11)	0.2461(2)	0.3985(1)	0.9707(1)	21(1)

C(12)	0.2651(2)	0.3246(2)	1.0470(1)	22(1)
N(13)	-0.0127(2)	0.8379(1)	0.7837(1)	22(1)
C(14)	0.0660(3)	0.9492(2)	0.8578(1)	26(1)
C(15)	0.2525(3)	0.9233(2)	0.9174(1)	31(1)
N(16)	0.3892(2)	0.8865(1)	0.8491(1)	24(1)
N(17)	0.0472(2)	0.6089(1)	0.6631(1)	24(1)
C(18)	0.1803(3)	0.5150(2)	0.6494(1)	30(1)
C(19)	0.3703(3)	0.5788(2)	0.6197(1)	26(1)
N(20)	0.4489(2)	0.6922(1)	0.6919(1)	21(1)
O(21)	0.0682(2)	0.7438(1)	0.4968(1)	24(1)
C(22)	0.1208(3)	0.8646(2)	0.3414(1)	23(1)
O(23)	0.2841(2)	1.1131(1)	0.3929(1)	24(1)
C(24)	0.4105(3)	1.2329(2)	0.5781(1)	24(1)
O(25)	0.3956(2)	1.0756(1)	0.7163(1)	25(1)
O(26)	0.2606(2)	0.5515(1)	1.2444(1)	30(1)
C(27)	0.2829(3)	0.7125(2)	1.1063(1)	28(1)
O(28)	0.2387(2)	0.5902(1)	0.9214(1)	28(1)
C(29)	0.2264(3)	0.3417(2)	0.8687(1)	28(1)
O(30)	0.2743(2)	0.2122(1)	1.0263(1)	31(1)

Table 46. Anisotropic displacement parameters (A^2 x 10^3) for $C_{14}H_{28}CuN_{10}O_6$(**24**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cu(1)	20(1)	17(1)	17(1)	1(1)	0(1)	-1(1)
N(1)	20(1)	17(1)	16(1)	5(1)	1(1)	2(1)
C(2)	15(1)	19(1)	19(1)	6(1)	2(1)	4(1)
N(3)	18(1)	18(1)	15(1)	5(1)	1(1)	3(1)
C(4)	13(1)	20(1)	21(1)	7(1)	3(1)	4(1)
N(5)	19(1)	14(1)	20(1)	5(1)	2(1)	1(1)
C(6)	16(1)	18(1)	20(1)	5(1)	3(1)	3(1)
N(7)	22(1)	22(1)	22(1)	11(1)	2(1)	2(1)
C(8)	17(1)	25(1)	21(1)	9(1)	2(1)	0(1)
N(9)	23(1)	19(1)	22(1)	8(1)	3(1)	3(1)
C(10)	17(1)	24(1)	21(1)	9(1)	2(1)	2(1)
N(11)	23(1)	22(1)	19(1)	7(1)	1(1)	3(1)
C(12)	19(1)	22(1)	24(1)	10(1)	0(1)	1(1)
N(13)	24(1)	23(1)	19(1)	8(1)	3(1)	2(1)
C(14)	35(1)	23(1)	22(1)	4(1)	6(1)	7(1)
C(15)	45(1)	29(1)	17(1)	-1(1)	-3(1)	10(1)
N(16)	29(1)	19(1)	23(1)	2(1)	-6(1)	4(1)
N(17)	27(1)	22(1)	20(1)	3(1)	4(1)	-4(1)
C(18)	41(1)	15(1)	31(1)	2(1)	1(1)	-2(1)
C(19)	32(1)	21(1)	26(1)	1(1)	2(1)	5(1)
N(20)	22(1)	19(1)	22(1)	8(1)	1(1)	1(1)
O(21)	31(1)	17(1)	22(1)	4(1)	0(1)	-3(1)
C(22)	25(1)	27(1)	16(1)	4(1)	1(1)	4(1)
O(23)	26(1)	24(1)	22(1)	12(1)	4(1)	2(1)
C(24)	25(1)	15(1)	30(1)	6(1)	2(1)	1(1)
O(25)	32(1)	22(1)	19(1)	2(1)	-1(1)	-2(1)
O(26)	39(1)	31(1)	20(1)	6(1)	7(1)	2(1)

C(27)	33(1)	20(1)	32(1)	7(1)	7(1)	5(1)
O(28)	35(1)	27(1)	24(1)	14(1)	2(1)	4(1)
C(29)	30(1)	31(1)	21(1)	4(1)	0(1)	5(1)
O(30)	39(1)	20(1)	32(1)	6(1)	1(1)	6(1)

Table 47. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_{14}H_{28}CuN_{10}O_6$(**24**).

	x	y	z	U(eq)
H(13A)	-920(4)	8550(2)	7344(18)	30(6)
H(13B)	-760(4)	7830(2)	8079(17)	31(6)
H(14A)	1000(3)	10180(2)	8232(15)	22(5)
H(14B)	-270(3)	9680(2)	8987(15)	24(5)
H(15A)	3150(4)	9950(3)	9630(2)	45(7)
H(15B)	2200(3)	8510(2)	9519(17)	32(6)
H(16A)	4860(4)	8540(2)	8795(18)	33(6)
H(16B)	4430(3)	9500(2)	8239(16)	22(5)
H(17A)	40(4)	6310(2)	6070(2)	40(7)
H(17B)	-470(4)	5800(2)	6904(17)	32(6)
H(18A)	2110(3)	4850(2)	7103(17)	32(6)
H(18B)	1100(4)	4430(2)	5998(18)	38(6)
H(19A)	4710(3)	5220(2)	6192(16)	30(6)
H(19B)	3430(3)	6030(2)	5571(16)	26(5)
H(20A)	5190(3)	7420(2)	6670(15)	21(5)
H(20B)	5250(4)	6750(2)	7372(18)	29(6)
H(22A)	1300(4)	7790(2)	3365(18)	39(6)
H(22B)	-140(4)	8710(2)	3200(19)	44(7)
H(22C)	2040(4)	9020(2)	3005(19)	43(7)
H(24A)	4130(4)	12600(3)	6450(2)	59(8)
H(24B)	5410(5)	12500(3)	5600(2)	56(8)
H(24C)	3300(4)	12780(2)	5412(19)	40(6)
H(27A)	1550(4)	7380(2)	10893(16)	28(5)
H(27B)	3840(4)	7540(2)	10759(19)	44(7)
H(27C)	3240(4)	7380(2)	11780(2)	47(7)
H(29A)	1050(3)	3594(19)	8349(16)	24(5)
H(29B)	3420(4)	3720(2)	8399(18)	39(6)
H(29C)	2280(4)	2560(2)	8686(18)	39(6)

Table 48. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $C_{29}H_{26}N_3O_3P$ (**26**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	9903(1)	6449(1)	3057(1)	22(1)
C(1)	8347(3)	7417(2)	2915(1)	24(1)
C(2)	7655(3)	7632(2)	2365(1)	29(1)
C(3)	6395(4)	8352(2)	2263(1)	35(1)
C(4)	5815(4)	8853(2)	2707(1)	37(1)
C(5)	6503(4)	8644(2)	3257(1)	36(1)
C(6)	7770(4)	7935(2)	3366(1)	30(1)
C(7)	10922(3)	6183(2)	2435(1)	24(1)
C(8)	9948(4)	5713(2)	1982(1)	31(1)
C(9)	10672(4)	5594(2)	1481(1)	34(1)
C(10)	12339(4)	5929(2)	1434(1)	33(1)
C(11)	13314(4)	6370(2)	1885(1)	32(1)
C(12)	12605(3)	6510(2)	2387(1)	27(1)
C(13)	8820(3)	5380(2)	3276(1)	24(1)
C(14)	7310(4)	5466(2)	3540(1)	31(1)
C(15)	6583(4)	4654(2)	3757(1)	37(1)
C(16)	7333(4)	3747(2)	3713(1)	35(1)
C(17)	8824(4)	3649(2)	3446(1)	35(1)
C(18)	9576(4)	4463(2)	3226(1)	32(1)
C(19)	11526(3)	6821(2)	3618(1)	25(1)
C(20)	12028(4)	7802(2)	3667(1)	30(1)
C(21)	13258(4)	8087(2)	4106(1)	39(1)
C(22)	13970(4)	7412(3)	4490(1)	45(1)
C(23)	13511(4)	6441(3)	4439(1)	44(1)
C(24)	12280(4)	6135(2)	4004(1)	31(1)
N(50)	3492(3)	2155(2)	4017(1)	29(1)
C(51)	3288(3)	1260(2)	4225(1)	29(1)
N(52)	2402(3)	1156(2)	4709(1)	30(1)
C(53)	1570(3)	1916(2)	4938(1)	32(1)
N(54)	1768(3)	2806(2)	4690(1)	31(1)
C(55)	2818(3)	2935(2)	4251(1)	30(1)

O(56)	3842(3)	509(2)	4024(1)	41(1)
C(57)	2342(5)	191(3)	4971(2)	43(1)
O(58)	728(3)	1811(2)	5337(1)	48(1)
C(59)	984(5)	3664(3)	4928(1)	50(1)
O(60)	3043(3)	3787(1)	4098(1)	42(1)

Table 49. Bond lengths [Å] and angles [°] for $C_{29}H_{26}N_3O_3P$ (**26**).

P(1)-C(13)	1.793(3)
P(1)-C(1)	1.793(3)
P(1)-C(19)	1.795(3)
P(1)-C(7)	1.800(2)
C(1)-C(2)	1.390(4)
C(1)-C(6)	1.406(3)
C(2)-C(3)	1.386(4)
C(3)-C(4)	1.381(4)
C(4)-C(5)	1.390(4)
C(5)-C(6)	1.380(4)
C(7)-C(12)	1.391(4)
C(7)-C(8)	1.400(4)
C(8)-C(9)	1.388(4)
C(9)-C(10)	1.382(4)
C(10)-C(11)	1.380(4)
C(11)-C(12)	1.388(4)
C(13)-C(14)	1.394(4)
C(13)-C(18)	1.395(4)
C(14)-C(15)	1.374(4)
C(15)-C(16)	1.380(4)
C(16)-C(17)	1.386(4)
C(17)-C(18)	1.388(4)
C(19)-C(24)	1.395(4)
C(19)-C(20)	1.399(4)
C(20)-C(21)	1.384(4)
C(21)-C(22)	1.372(5)
C(22)-C(23)	1.377(5)

C(23)-C(24)	1.387(4)
N(50)-C(51)	1.338(3)
N(50)-C(55)	1.338(4)
C(51)-O(56)	1.231(3)
C(51)-N(52)	1.419(3)
N(52)-C(53)	1.370(4)
N(52)-C(57)	1.464(4)
C(53)-O(58)	1.225(3)
C(53)-N(54)	1.371(4)
N(54)-C(55)	1.410(3)
N(54)-C(59)	1.466(4)
C(55)-O(60)	1.240(3)

C(13)-P(1)-C(1)	109.45(12)
C(13)-P(1)-C(19)	108.82(12)
C(1)-P(1)-C(19)	108.98(12)
C(13)-P(1)-C(7)	109.83(12)
C(1)-P(1)-C(7)	109.89(12)
C(19)-P(1)-C(7)	109.84(12)
C(2)-C(1)-C(6)	119.8(2)
C(2)-C(1)-P(1)	120.67(19)
C(6)-C(1)-P(1)	119.5(2)
C(3)-C(2)-C(1)	120.0(3)
C(4)-C(3)-C(2)	120.1(3)
C(3)-C(4)-C(5)	120.2(3)
C(6)-C(5)-C(4)	120.4(3)
C(5)-C(6)-C(1)	119.4(3)
C(12)-C(7)-C(8)	120.3(2)
C(12)-C(7)-P(1)	120.42(19)
C(8)-C(7)-P(1)	119.1(2)
C(9)-C(8)-C(7)	119.1(3)
C(10)-C(9)-C(8)	120.3(3)
C(11)-C(10)-C(9)	120.6(3)
C(10)-C(11)-C(12)	120.0(3)
C(11)-C(12)-C(7)	119.6(2)
C(14)-C(13)-C(18)	119.6(2)

C(14)-C(13)-P(1)	120.4(2)
C(18)-C(13)-P(1)	119.72(19)
C(15)-C(14)-C(13)	120.2(3)
C(14)-C(15)-C(16)	120.3(3)
C(15)-C(16)-C(17)	120.1(3)
C(16)-C(17)-C(18)	120.2(3)
C(17)-C(18)-C(13)	119.5(3)
C(24)-C(19)-C(20)	120.0(2)
C(24)-C(19)-P(1)	120.2(2)
C(20)-C(19)-P(1)	119.8(2)
C(21)-C(20)-C(19)	119.5(3)
C(22)-C(21)-C(20)	120.2(3)
C(21)-C(22)-C(23)	120.8(3)
C(22)-C(23)-C(24)	120.3(3)
C(23)-C(24)-C(19)	119.2(3)
C(51)-N(50)-C(55)	120.5(2)
O(56)-C(51)-N(50)	124.0(2)
O(56)-C(51)-N(52)	117.2(2)
N(50)-C(51)-N(52)	118.9(2)
C(53)-N(52)-C(51)	122.9(2)
C(53)-N(52)-C(57)	118.3(2)
C(51)-N(52)-C(57)	118.8(2)
O(58)-C(53)-N(52)	122.6(3)
O(58)-C(53)-N(54)	122.6(3)
N(52)-C(53)-N(54)	114.9(2)
C(53)-N(54)-C(55)	122.4(2)
C(53)-N(54)-C(59)	118.2(2)
C(55)-N(54)-C(59)	119.2(2)
O(60)-C(55)-N(50)	123.6(2)
O(60)-C(55)-N(54)	116.7(3)
N(50)-C(55)-N(54)	119.7(2)

Symmetry transformations used to generate equivalent atoms:

Table 50. Anisotropic displacement parameters (A^2 x 10^3) for $C_{29}H_{26}N_3O_3P$ (**26**). The anisotropic displacement factor exponent takes the form: -2pi^2 [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	22(1)	25(1)	21(1)	-2(1)	4(1)	-3(1)
C(1)	23(1)	23(1)	28(1)	0(1)	6(1)	-2(1)
C(2)	25(1)	33(2)	29(1)	-2(1)	4(1)	-3(1)
C(3)	28(2)	39(2)	36(2)	6(1)	-2(1)	1(1)
C(4)	28(2)	30(2)	54(2)	1(1)	4(1)	3(1)
C(5)	37(2)	31(2)	42(2)	-6(1)	16(1)	-3(1)
C(6)	36(2)	29(2)	27(1)	-2(1)	8(1)	-3(1)
C(7)	24(1)	25(1)	22(1)	-3(1)	5(1)	1(1)
C(8)	27(2)	37(2)	31(1)	-8(1)	3(1)	-2(1)
C(9)	34(2)	40(2)	26(1)	-10(1)	2(1)	3(1)
C(10)	41(2)	34(2)	27(1)	-3(1)	13(1)	5(1)
C(11)	31(1)	28(1)	41(2)	0(1)	14(1)	1(1)
C(12)	26(1)	26(1)	29(1)	-4(1)	4(1)	-2(1)
C(13)	23(1)	27(1)	23(1)	-3(1)	3(1)	-5(1)
C(14)	30(2)	32(2)	33(2)	-6(1)	8(1)	-3(1)
C(15)	32(2)	41(2)	39(2)	-5(1)	13(1)	-10(1)
C(16)	37(2)	32(2)	36(2)	-1(1)	3(1)	-14(1)
C(17)	34(2)	26(2)	44(2)	-1(1)	3(1)	-4(1)
C(18)	26(1)	31(2)	37(2)	-3(1)	6(1)	-4(1)
C(19)	22(1)	30(1)	23(1)	-5(1)	5(1)	-3(1)
C(20)	31(2)	30(2)	31(1)	-3(1)	6(1)	-6(1)
C(21)	33(2)	41(2)	45(2)	-16(2)	8(1)	-13(1)
C(22)	29(2)	61(2)	41(2)	-15(2)	-7(1)	-8(2)
C(23)	32(2)	58(2)	38(2)	2(2)	-7(1)	3(2)
C(24)	29(2)	31(2)	33(1)	-3(1)	2(1)	0(1)
N(50)	26(1)	35(1)	28(1)	6(1)	9(1)	-1(1)
C(51)	21(1)	40(2)	26(1)	4(1)	4(1)	0(1)
N(52)	27(1)	37(1)	24(1)	9(1)	3(1)	-6(1)
C(53)	25(1)	50(2)	22(1)	-1(1)	1(1)	-7(1)
N(54)	28(1)	40(1)	26(1)	-2(1)	7(1)	-2(1)
C(55)	22(1)	43(2)	26(1)	4(1)	1(1)	-6(1)

O(56)	39(1)	39(1)	49(1)	5(1)	18(1)	5(1)
C(57)	39(2)	51(2)	40(2)	19(2)	5(2)	-2(2)
O(58)	49(1)	70(2)	29(1)	0(1)	20(1)	-12(1)
C(59)	53(2)	55(2)	44(2)	-13(2)	15(2)	3(2)
O(60)	39(1)	34(1)	56(1)	8(1)	14(1)	-2(1)

Table 51. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_{29}H_{26}N_3O_3P$ (**26**).

	x	y	z	U(eq)
H(2)	8010(40)	7270(20)	2049(13)	39(8)
H(3)	5970(40)	8530(20)	1876(13)	41(8)
H(4)	4940(40)	9350(20)	2628(11)	32(8)
H(5)	6150(40)	9000(20)	3561(13)	38(8)
H(6)	8250(40)	7774(19)	3742(12)	28(7)
H(8)	8780(40)	5500(20)	2009(12)	35(8)
H(9)	9960(40)	5295(19)	1158(12)	28(7)
H(10)	12860(40)	5840(20)	1105(12)	33(8)
H(11)	14490(40)	6580(20)	1858(12)	39(8)
H(12)	13230(30)	6833(19)	2701(11)	21(6)
H(14)	6800(30)	6060(20)	3583(11)	23(7)
H(15)	5560(40)	4710(20)	3934(13)	42(9)
H(16)	6800(40)	3180(20)	3851(12)	39(8)
H(17)	9350(40)	3000(20)	3394(13)	41(8)
H(18)	10640(40)	4410(20)	3026(13)	46(9)
H(20)	11510(40)	8270(20)	3389(12)	34(8)
H(21)	13550(40)	8750(20)	4126(13)	41(9)
H(22)	14780(50)	7620(20)	4809(14)	56(10)
H(23)	13960(50)	5970(30)	4695(15)	60(11)
H(24)	11980(40)	5480(20)	3976(12)	32(8)
H(57A)	1740(50)	270(30)	5321(17)	68(11)
H(57B)	1640(50)	-290(30)	4699(16)	69(12)
H(57C)	3490(50)	-90(30)	5059(15)	62(11)

H(59A)	1221	4234	4715	75
H(59B)	1473	3747	5313	75
H(59C)	-254	3573	4910	75

Table 52: Atomic coordinates and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_{36}H_{30}C_{l4}CrN_{3}O_{8}P$ (**27a**). (U(eq) is defined as one third of the trace of the orthogonalized Uij tensor).

	x	y	z	U(eq)
Cr(1)	0.1585(1)	0.1574(1)	0.0908(1)	24(1)
N(31)	0.0413(2)	0.2431(2)	0.0873(1)	27(1)
C(32)	0.0166(2)	0.2934(2)	0.0234(2)	32(1)
N(33)	-0.0604(2)	0.3470(2)	0.0237(2)	34(1)
C(34)	-0.1132(2)	0.3512(2)	0.0846(2)	31(1)
N(35)	-0.0824(2)	0.3011(2)	0.1475(1)	30(1)
C(36)	-0.0064(2)	0.2464(2)	0.1503(2)	30(1)
O(37)	0.0571(2)	0.2933(2)	-0.0350(1)	47(1)
C(38)	-0.0883(3)	0.4002(3)	-0.0462(2)	51(1)
O(39)	-0.1817(2)	0.3955(2)	0.0824(2)	43(1)
C(40)	-0.1298(3)	0.3069(3)	0.2176(2)	44(1)
O(41)	0.0137(2)	0.2035(2)	0.2098(1)	44(1)
C(42)	0.1313(2)	0.1255(2)	-0.0157(2)	30(1)
O(43)	0.1231(2)	0.1012(2)	-0.0788(1)	42(1)
C(44)	0.2249(2)	0.2559(2)	0.0609(2)	33(1)
O(45)	0.2668(2)	0.3135(2)	0.0421(2)	52(1)
C(46)	0.0884(2)	0.0604(2)	0.1220(2)	31(1)
O(47)	0.0501(2)	0.0009(2)	0.1404(2)	47(1)
C(48)	0.1981(2)	0.1782(2)	0.1983(2)	32(1)
O(49)	0.2291(2)	0.1841(2)	0.2615(1)	49(1)
C(50)	0.2592(2)	0.0882(2)	0.0907(2)	31(1)
O(51)	0.3241(2)	0.0457(2)	0.0901(2)	48(1)
P(1)	-0.4146(1)	0.2545(1)	0.0120(1)	23(1)
C(1)	-0.4983(2)	0.1838(2)	-0.0380(2)	25(1)
C(2)	-0.5869(2)	0.2148(2)	-0.0538(2)	30(1)
C(3)	-0.6537(2)	0.1603(2)	-0.0890(2)	35(1)
C(4)	-0.6322(3)	0.0756(2)	-0.1093(2)	39(1)
C(5)	-0.5445(3)	0.0452(2)	-0.0951(2)	39(1)
C(6)	-0.4768(2)	0.0986(2)	-0.0588(2)	32(1)
C(7)	-0.4394(2)	0.2682(2)	0.1112(2)	27(1)
C(8)	-0.5175(2)	0.2319(2)	0.1365(2)	31(1)
C(9)	-0.5352(2)	0.2447(3)	0.2133(2)	41(1)
C(10)	-0.4761(3)	0.2924(3)	0.2643(2)	47(1)
C(11)	-0.3984(3)	0.3275(3)	0.2392(2)	45(1)
C(12)	-0.3790(2)	0.3148(2)	0.1631(2)	35(1)
C(13)	-0.3047(2)	0.2047(2)	0.0127(2)	27(1)
C(14)	-0.2695(2)	0.1532(2)	0.0751(2)	33(1)
C(15)	-0.1869(2)	0.1112(2)	0.0730(2)	41(1)
C(16)	-0.1400(2)	0.1203(2)	0.0087(2)	44(1)
C(17)	-0.1748(2)	0.1711(3)	-0.0536(2)	44(1)

C(18)	-0.2569(2)	0.2140(2)	-0.0523(2)	36(1)
C(19)	-0.4179(2)	0.3574(2)	-0.0387(2)	27(1)
C(20)	-0.4476(2)	0.3598(2)	-0.1177(2)	35(1)
C(21)	-0.4499(3)	0.4392(2)	-0.1572(2)	42(1)
C(22)	-0.4224(3)	0.5153(2)	-0.1187(2)	41(1)
C(23)	-0.3928(3)	0.5128(2)	-0.0406(2)	47(1)
C(24)	-0.3901(2)	0.4344(2)	0.0004(2)	40(1)
Cl(11)	0.6910(1)	0.5970(1)	0.1622(1)	82(1)
Cl(12)	0.8773(1)	0.5731(1)	0.2246(1)	92(1)
C(01)	0.8044(3)	0.5932(3)	0.1406(2)	52(1)
Cl(21)	0.0738(1)	0.4675(1)	0.2170(1)	102(1)
Cl(22)	0.2647(1)	0.4151(1)	0.2403(1)	118(1)
C(02)	0.1545(4)	0.3990(4)	0.2625(3)	78(1)

Table 53: Full bond lengths [Å] and angles [º] for $C_{36}H_{30}Cl_4CrN_3O_8P$ (**27a**).

Cr(1)-C(50)	1.829(3)
Cr(1)-C(44)	1.898(3)
Cr(1)-C(42)	1.904(3)
Cr(1)-C(48)	1.911(3)
Cr(1)-C(46)	1.918(3)
Cr(1)-N(31)	2.170(2)
N(31)-C(36)	1.361(4)
N(31)-C(32)	1.362(4)
C(32)-O(37)	1.226(4)
C(32)-N(33)	1.406(4)
N(33)-C(34)	1.376(4)
N(33)-C(38)	1.476(4)
C(34)-O(39)	1.218(4)
C(34)-N(35)	1.367(4)
N(35)-C(36)	1.398(4)
N(35)-C(40)	1.464(4)
C(36)-O(41)	1.228(4)
C(42)-O(43)	1.144(4)
C(44)-O(45)	1.143(4)
C(46)-O(47)	1.134(4)
C(48)-O(49)	1.141(4)
C(50)-O(51)	1.161(4)
P(1)-C(1)	1.793(3)
P(1)-C(19)	1.795(3)
P(1)-C(13)	1.796(3)
P(1)-C(7)	1.802(3)
C(1)-C(6)	1.395(4)
C(1)-C(2)	1.397(4)
C(2)-C(3)	1.383(4)
C(3)-C(4)	1.384(5)
C(4)-C(5)	1.378(5)
C(5)-C(6)	1.389(5)
C(7)-C(12)	1.394(4)
C(7)-C(8)	1.395(4)
C(8)-C(9)	1.393(4)
C(9)-C(10)	1.381(5)
C(10)-C(11)	1.382(5)
C(11)-C(12)	1.387(5)
C(13)-C(14)	1.389(4)

C(13)-C(18)	1.396(4)
C(14)-C(15)	1.387(5)
C(15)-C(16)	1.378(5)
C(16)-C(17)	1.381(6)
C(17)-C(18)	1.385(5)
C(19)-C(20)	1.388(4)
C(19)-C(24)	1.396(4)
C(20)-C(21)	1.389(5)
C(21)-C(22)	1.378(5)
C(22)-C(23)	1.373(6)
C(23)-C(24)	1.386(5)
Cl(11)-C(01)	1.761(5)
Cl(12)-C(01)	1.741(4)
Cl(21)-C(02)	1.714(6)
Cl(22)-C(02)	1.735(6)

C(50)-Cr(1)-C(44)	90.56(14)
C(50)-Cr(1)-C(42)	86.59(13)
C(44)-Cr(1)-C(42)	90.14(13)
C(50)-Cr(1)-C(48)	86.02(13)
C(44)-Cr(1)-C(48)	91.00(14)
C(42)-Cr(1)-C(48)	172.54(13)
C(50)-Cr(1)-C(46)	91.24(13)
C(44)-Cr(1)-C(46)	178.12(13)
C(42)-Cr(1)-C(46)	90.52(13)
C(48)-Cr(1)-C(46)	88.58(13)
C(50)-Cr(1)-N(31)	177.57(11)
C(44)-Cr(1)-N(31)	87.28(11)
C(42)-Cr(1)-N(31)	92.31(11)
C(48)-Cr(1)-N(31)	95.12(11)
C(46)-Cr(1)-N(31)	90.93(11)
C(36)-N(31)-C(32)	120.6(3)
C(36)-N(31)-Cr(1)	118.93(19)
C(32)-N(31)-Cr(1)	120.48(19)
O(37)-C(32)-N(31)	123.6(3)
O(37)-C(32)-N(33)	118.2(3)
N(31)-C(32)-N(33)	118.2(3)
C(34)-N(33)-C(32)	124.0(3)
C(34)-N(33)-C(38)	117.8(3)
C(32)-N(33)-C(38)	118.2(3)
O(39)-C(34)-N(35)	122.8(3)
O(39)-C(34)-N(33)	122.9(3)
N(35)-C(34)-N(33)	114.3(3)
C(34)-N(35)-C(36)	124.1(3)
C(34)-N(35)-C(40)	118.3(3)
C(36)-N(35)-C(40)	117.6(3)
O(41)-C(36)-N(31)	123.2(3)
O(41)-C(36)-N(35)	118.0(3)
N(31)-C(36)-N(35)	118.8(3)
O(43)-C(42)-Cr(1)	172.8(3)
O(45)-C(44)-Cr(1)	177.8(3)
O(47)-C(46)-Cr(1)	177.2(3)
O(49)-C(48)-Cr(1)	172.4(3)
O(51)-C(50)-Cr(1)	178.5(3)
C(1)-P(1)-C(19)	108.03(13)
C(1)-P(1)-C(13)	109.29(13)
C(19)-P(1)-C(13)	110.52(13)

C(1)-P(1)-C(7)	108.97(13)
C(19)-P(1)-C(7)	111.34(13)
C(13)-P(1)-C(7)	108.65(14)
C(6)-C(1)-C(2)	120.0(3)
C(6)-C(1)-P(1)	121.3(2)
C(2)-C(1)-P(1)	118.7(2)
C(3)-C(2)-C(1)	119.8(3)
C(2)-C(3)-C(4)	119.9(3)
C(5)-C(4)-C(3)	120.5(3)
C(4)-C(5)-C(6)	120.4(3)
C(5)-C(6)-C(1)	119.3(3)
C(12)-C(7)-C(8)	119.9(3)
C(12)-C(7)-P(1)	119.2(2)
C(8)-C(7)-P(1)	120.9(2)
C(9)-C(8)-C(7)	119.4(3)
C(10)-C(9)-C(8)	120.6(3)
C(9)-C(10)-C(11)	119.9(3)
C(10)-C(11)-C(12)	120.5(3)
C(11)-C(12)-C(7)	119.7(3)
C(14)-C(13)-C(18)	120.0(3)
C(14)-C(13)-P(1)	120.6(2)
C(18)-C(13)-P(1)	119.3(2)
C(15)-C(14)-C(13)	120.1(3)
C(16)-C(15)-C(14)	119.8(3)
C(15)-C(16)-C(17)	120.3(3)
C(16)-C(17)-C(18)	120.6(3)
C(17)-C(18)-C(13)	119.2(3)
C(20)-C(19)-C(24)	120.0(3)
C(20)-C(19)-P(1)	119.4(2)
C(24)-C(19)-P(1)	120.6(2)
C(19)-C(20)-C(21)	119.5(3)
C(22)-C(21)-C(20)	120.5(3)
C(23)-C(22)-C(21)	119.8(3)
C(22)-C(23)-C(24)	120.9(3)
C(23)-C(24)-C(19)	119.2(3)
Cl(12)-C(01)-Cl(11)	110.6(2)
Cl(21)-C(02)-Cl(22)	116.2(3)

Table 54. Anisotropic displacement parameters (A^2 x 10^3) for $C_{36}H_{30}Cl_4CrN_3O_8P$ (**27a**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
Cr(1)	25(1)	25(1)	23(1)	0(1)	5(1)	2(1)
N(31)	27(1)	30(1)	24(1)	3(1)	6(1)	4(1)
C(32)	32(2)	34(2)	31(2)	5(1)	4(1)	5(1)
N(33)	37(1)	33(1)	32(1)	8(1)	3(1)	9(1)
C(34)	30(2)	29(2)	33(2)	-5(1)	-1(1)	2(1)
N(35)	28(1)	35(1)	27(1)	-2(1)	4(1)	5(1)
C(36)	29(1)	33(2)	27(1)	0(1)	5(1)	3(1)
O(37)	52(2)	57(2)	35(1)	18(1)	18(1)	18(1)
C(38)	56(2)	53(2)	42(2)	18(2)	0(2)	17(2)
O(39)	38(1)	45(1)	46(1)	-2(1)	1(1)	17(1)

C(40)	40(2)	59(2)	34(2)	-5(2)	12(2)	13(2)
O(41)	47(1)	59(2)	29(1)	15(1)	13(1)	23(1)
C(42)	28(1)	31(1)	31(2)	3(1)	5(1)	-1(1)
O(43)	50(1)	48(1)	28(1)	-4(1)	2(1)	-2(1)
C(44)	31(2)	34(2)	35(2)	-4(1)	9(1)	3(1)
O(45)	54(2)	38(1)	68(2)	-3(1)	25(1)	-12(1)
C(46)	30(2)	36(2)	26(1)	-3(1)	4(1)	1(1)
O(47)	52(2)	41(1)	48(1)	1(1)	13(1)	-13(1)
C(48)	31(2)	33(2)	32(2)	-2(1)	5(1)	2(1)
O(49)	49(2)	64(2)	31(1)	-8(1)	-3(1)	2(1)
C(50)	34(2)	33(2)	27(1)	1(1)	5(1)	2(1)
O(51)	39(1)	50(2)	56(2)	4(1)	10(1)	19(1)
P(1)	25(1)	22(1)	23(1)	-2(1)	4(1)	0(1)
C(1)	30(1)	23(1)	22(1)	-1(1)	5(1)	-3(1)
C(2)	31(2)	32(2)	27(1)	-2(1)	5(1)	-1(1)
C(3)	30(2)	46(2)	29(2)	2(1)	3(1)	-8(1)
C(4)	47(2)	38(2)	32(2)	2(1)	-1(1)	-19(2)
C(5)	57(2)	24(2)	35(2)	-2(1)	0(2)	-7(1)
C(6)	40(2)	24(1)	31(2)	1(1)	1(1)	3(1)
C(7)	29(1)	28(1)	24(1)	-2(1)	6(1)	2(1)
C(8)	31(2)	36(2)	26(1)	3(1)	4(1)	-2(1)
C(9)	37(2)	56(2)	32(2)	1(2)	13(1)	-3(2)
C(10)	48(2)	67(2)	27(2)	-4(2)	12(2)	0(2)
C(11)	44(2)	62(2)	29(2)	-12(2)	5(1)	-6(2)
C(12)	34(2)	44(2)	28(2)	-6(1)	5(1)	-5(1)
C(13)	25(1)	25(1)	31(1)	-4(1)	5(1)	0(1)
C(14)	34(2)	29(2)	36(2)	0(1)	5(1)	1(1)
C(15)	39(2)	31(2)	51(2)	-2(2)	-3(2)	6(1)
C(16)	28(2)	39(2)	63(2)	-16(2)	2(2)	5(1)
C(17)	35(2)	53(2)	48(2)	-10(2)	17(2)	0(2)
C(18)	34(2)	40(2)	35(2)	-1(1)	9(1)	1(1)
C(19)	26(1)	24(1)	30(1)	-1(1)	6(1)	0(1)
C(20)	52(2)	28(2)	28(2)	-2(1)	8(1)	-2(1)
C(21)	60(2)	37(2)	31(2)	5(1)	10(2)	1(2)
C(22)	47(2)	27(2)	53(2)	9(2)	18(2)	0(1)
C(23)	57(2)	27(2)	57(2)	-1(2)	3(2)	-10(2)
C(24)	46(2)	31(2)	40(2)	-1(1)	-3(2)	-7(1)
Cl(11)	72(1)	96(1)	79(1)	-6(1)	14(1)	26(1)
Cl(12)	89(1)	94(1)	84(1)	19(1)	-35(1)	-10(1)
C(01)	66(3)	44(2)	46(2)	5(2)	2(2)	7(2)
Cl(21)	95(1)	96(1)	108(1)	32(1)	-24(1)	-5(1)
Cl(22)	73(1)	135(2)	155(2)	-46(1)	51(1)	-32(1)
C(02)	89(4)	64(3)	81(4)	-2(3)	13(3)	2(3)

Table 55. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_{36}H_{30}Cl_4CrN_3O_8P$ (**27a**).

	x	y	z	U(eq)
H(38A)	-462	3913	-840	76
H(38B)	-889	4610	-321	76
H(38C)	-1479	3828	-680	76
H(40A)	-900(3)	3120(3)	2600(3)	68(14)
H(40B)	-1700(3)	2640(3)	2200(3)	58(14)

H(40C)	-1610(3)	3590(3)	2160(3)	66(14)
H(2)	-6000(2)	2750(2)	-390(2)	31(9)
H(3)	-7130(3)	1780(3)	-990(2)	42(10)
H(4)	-6780(3)	400(3)	-1360(2)	48(11)
H(5)	-5280(3)	-140(3)	-1110(2)	45(10)
H(6)	-4210(2)	800(2)	-510(2)	28(9)
H(8)	-5560(3)	2010(3)	1050(2)	42(10)
H(9)	-5850(3)	2190(2)	2310(2)	37(9)
H(10)	-4880(3)	3040(3)	3190(3)	68(14)
H(11)	-3560(4)	3610(3)	2740(3)	77(15)
H(12)	-3280(3)	3390(3)	1460(2)	45(11)
H(14)	-2960(2)	1460(2)	1170(2)	32(9)
H(15)	-1620(3)	780(3)	1160(2)	48(11)
H(16)	-840(3)	930(3)	80(2)	54(12)
H(17)	-1410(3)	1800(3)	-930(3)	52(12)
H(18)	-2810(2)	2510(2)	-890(2)	33(9)
H(20)	-4690(3)	3080(3)	-1420(2)	43(10)
H(21)	-4700(3)	4370(3)	-2110(3)	52(11)
H(22)	-4240(3)	5700(3)	-1430(2)	39(10)
H(23)	-3750(3)	5640(3)	-130(3)	65(13)
H(24)	-3750(3)	4310(2)	520(2)	38(10)
H(06A)	8070(3)	5450(3)	1050(3)	61(13)
H(06B)	8220(3)	6520(3)	1210(3)	73(15)
H(03A)	1373	3391	2493	93
H(03B)	1539	4055	3183	93

Table 56: Atomic coordinates and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_{36}H_{30}Cl_4N_3O_8PW$ (**27c**). (U(eq) is defined as one third of the trace of the orthogonalized Uij tensor).

	x	y	z	U(eq)
P(1)	0.9180(1)	1.2462(1)	-0.0112(1)	27(1)
C(1)	0.9426(3)	1.2325(3)	-0.1095(2)	31(1)
C(2)	1.0197(3)	1.2681(3)	-0.1346(3)	38(1)
C(3)	1.0375(3)	1.2558(4)	-0.2108(3)	47(1)
C(4)	0.9774(4)	1.2084(4)	-0.2618(3)	53(1)
C(5)	0.9006(4)	1.1739(4)	-0.2375(3)	50(1)
C(6)	0.8816(3)	1.1859(3)	-0.1618(3)	42(1)
C(7)	0.9209(3)	1.1442(2)	0.0396(2)	31(1)
C(8)	0.9501(3)	1.1416(3)	0.1181(3)	41(1)
C(9)	0.9514(4)	1.0627(3)	0.1578(3)	49(1)
C(10)	0.9241(4)	0.9876(3)	0.1193(3)	50(1)
C(11)	0.8954(4)	0.9899(3)	0.0414(4)	54(1)
C(12)	0.8928(3)	1.0674(3)	0.0000(3)	45(1)
C(13)	0.8090(3)	1.2965(2)	-0.0129(2)	30(1)
C(14)	0.7736(3)	1.3473(3)	-0.0754(3)	36(1)
C(15)	0.6914(3)	1.3888(3)	-0.0735(3)	44(1)
C(16)	0.6447(3)	1.3807(3)	-0.0103(3)	46(1)
C(17)	0.6796(3)	1.3301(3)	0.0523(3)	49(1)
C(18)	0.7613(3)	1.2877(3)	0.0515(3)	39(1)
C(19)	1.0022(3)	1.3159(2)	0.0390(2)	29(1)
C(20)	0.9817(3)	1.4009(3)	0.0589(2)	35(1)
C(21)	1.0500(4)	1.4532(3)	0.0951(3)	43(1)

C(22)	1.1368(3)	1.4229(3)	0.1104(3)	43(1)
C(23)	1.1575(3)	1.3382(3)	0.0906(2)	39(1)
C(24)	1.0901(3)	1.2846(3)	0.0556(2)	33(1)
W(30)	0.6597(1)	0.6562(1)	0.0914(1)	28(1)
N(31)	0.5358(2)	0.7432(2)	0.0871(2)	32(1)
C(32)	0.4885(3)	0.7454(3)	0.1499(2)	35(1)
N(33)	0.4133(2)	0.8000(2)	0.1476(2)	35(1)
C(34)	0.3821(3)	0.8497(3)	0.0847(3)	38(1)
N(35)	0.4337(3)	0.8467(2)	0.0240(2)	40(1)
C(36)	0.5101(3)	0.7934(3)	0.0228(2)	38(1)
O(37)	0.5094(2)	0.7021(3)	0.2083(2)	52(1)
C(38)	0.3669(4)	0.8049(4)	0.2171(3)	49(1)
O(39)	0.3136(2)	0.8945(2)	0.0830(2)	49(1)
C(40)	0.4053(4)	0.9005(4)	-0.0448(3)	59(1)
O(41)	0.5503(2)	0.7935(2)	-0.0344(2)	53(1)
C(42)	0.7022(3)	0.6789(3)	0.2057(2)	37(1)
O(43)	0.7326(3)	0.6862(3)	0.2690(2)	56(1)
C(44)	0.5890(3)	0.5516(3)	0.1257(2)	35(1)
O(45)	0.5529(3)	0.4919(2)	0.1450(2)	55(1)
C(46)	0.7271(3)	0.7625(3)	0.0577(3)	38(1)
O(47)	0.7657(3)	0.8207(2)	0.0381(2)	59(1)
C(48)	0.6303(3)	0.6220(3)	-0.0223(2)	34(1)
O(49)	0.6222(2)	0.5986(2)	-0.0853(2)	47(1)
C(50)	0.7688(3)	0.5847(3)	0.0914(2)	36(1)
O(51)	0.8344(2)	0.5440(2)	0.0910(2)	53(1)
Cl(11)	0.1937(2)	0.0957(2)	0.1621(1)	104(1)
Cl(12)	0.3796(2)	0.0715(2)	0.2245(2)	120(1)
C(01)	0.3055(5)	0.0922(5)	0.1414(4)	68(2)
Cl(21)	0.7607(2)	0.9159(2)	0.2343(2)	154(1)
Cl(22)	0.5708(2)	0.9651(2)	0.2145(2)	134(1)
C(02)	0.6437(9)	0.8968(6)	0.2606(5)	129(4)

Table 57: Full bond lengths [Å] and angles [º] for $C_{36}H_{30}Cl_4N_3O_8PW$ (**27c**)

P(1)-C(19)	1.794(4)
P(1)-C(7)	1.795(4)
P(1)-C(13)	1.795(4)
P(1)-C(1)	1.799(4)
C(1)-C(2)	1.387(6)
C(1)-C(6)	1.403(6)
C(2)-C(3)	1.391(6)
C(3)-C(4)	1.390(7)
C(4)-C(5)	1.371(7)
C(5)-C(6)	1.388(6)
C(7)-C(8)	1.381(6)
C(7)-C(12)	1.404(6)
C(8)-C(9)	1.392(6)
C(9)-C(10)	1.369(7)
C(10)-C(11)	1.371(8)
C(11)-C(12)	1.387(7)
C(13)-C(14)	1.389(6)
C(13)-C(18)	1.398(6)
C(14)-C(15)	1.385(6)
C(15)-C(16)	1.371(7)

C(16)-C(17)	1.386(8)
C(17)-C(18)	1.381(6)
C(19)-C(24)	1.393(6)
C(19)-C(20)	1.393(5)
C(20)-C(21)	1.388(6)
C(21)-C(22)	1.370(7)
C(22)-C(23)	1.389(7)
C(23)-C(24)	1.382(6)
W(30)-C(50)	1.960(4)
W(30)-C(46)	2.037(4)
W(30)-C(48)	2.039(4)
W(30)-C(42)	2.042(4)
W(30)-C(44)	2.046(4)
W(30)-N(31)	2.273(3)
N(31)-C(32)	1.364(5)
N(31)-C(36)	1.373(5)
C(32)-O(37)	1.222(5)
C(32)-N(33)	1.395(5)
N(33)-C(34)	1.367(5)
N(33)-C(38)	1.460(6)
C(34)-O(39)	1.227(5)
C(34)-N(35)	1.377(6)
N(35)-C(36)	1.404(5)
N(35)-C(40)	1.472(6)
C(36)-O(41)	1.218(5)
C(42)-O(43)	1.143(5)
C(44)-O(45)	1.133(5)
C(46)-O(47)	1.136(5)
C(48)-O(49)	1.144(5)
C(50)-O(51)	1.161(5)
Cl(11)-C(01)	1.744(8)
Cl(12)-C(01)	1.740(7)
Cl(21)-C(02)	1.874(13)
Cl(22)-C(02)	1.649(9)

C(19)-P(1)-C(7)	107.88(19)
C(19)-P(1)-C(13)	109.32(18)
C(7)-P(1)-C(13)	110.69(18)
C(19)-P(1)-C(1)	108.80(18)
C(7)-P(1)-C(1)	111.59(18)
C(13)-P(1)-C(1)	108.51(18)
C(2)-C(1)-C(6)	119.7(4)
C(2)-C(1)-P(1)	121.2(3)
C(6)-C(1)-P(1)	119.0(3)
C(1)-C(2)-C(3)	120.1(4)
C(4)-C(3)-C(2)	119.8(4)
C(5)-C(4)-C(3)	120.3(4)
C(4)-C(5)-C(6)	120.7(5)
C(5)-C(6)-C(1)	119.4(4)
C(8)-C(7)-C(12)	120.0(4)
C(8)-C(7)-P(1)	119.7(3)
C(12)-C(7)-P(1)	120.2(3)
C(7)-C(8)-C(9)	119.8(4)
C(10)-C(9)-C(8)	120.4(5)
C(9)-C(10)-C(11)	119.9(4)
C(10)-C(11)-C(12)	121.3(5)
C(11)-C(12)-C(7)	118.5(5)

C(14)-C(13)-C(18)	119.8(4)
C(14)-C(13)-P(1)	120.9(3)
C(18)-C(13)-P(1)	119.2(3)
C(15)-C(14)-C(13)	119.7(4)
C(16)-C(15)-C(14)	120.7(5)
C(15)-C(16)-C(17)	120.0(4)
C(18)-C(17)-C(16)	120.4(5)
C(17)-C(18)-C(13)	119.5(5)
C(24)-C(19)-C(20)	119.9(4)
C(24)-C(19)-P(1)	118.8(3)
C(20)-C(19)-P(1)	121.2(3)
C(21)-C(20)-C(19)	118.9(4)
C(22)-C(21)-C(20)	121.2(4)
C(21)-C(22)-C(23)	120.1(4)
C(24)-C(23)-C(22)	119.7(4)
C(23)-C(24)-C(19)	120.2(4)
C(50)-W(30)-C(46)	90.76(17)
C(50)-W(30)-C(48)	86.63(17)
C(46)-W(30)-C(48)	89.20(17)
C(50)-W(30)-C(42)	86.14(17)
C(46)-W(30)-C(42)	92.00(18)
C(48)-W(30)-C(42)	172.68(16)
C(50)-W(30)-C(44)	90.90(17)
C(46)-W(30)-C(44)	178.33(16)
C(48)-W(30)-C(44)	91.15(16)
C(42)-W(30)-C(44)	87.87(17)
C(50)-W(30)-N(31)	177.32(14)
C(46)-W(30)-N(31)	86.83(14)
C(48)-W(30)-N(31)	92.16(15)
C(42)-W(30)-N(31)	95.11(15)
C(44)-W(30)-N(31)	91.52(14)
C(32)-N(31)-C(36)	120.9(3)
C(32)-N(31)-W(30)	118.8(3)
C(36)-N(31)-W(30)	120.3(3)
O(37)-C(32)-N(31)	122.8(4)
O(37)-C(32)-N(33)	118.5(4)
N(31)-C(32)-N(33)	118.7(3)
C(34)-N(33)-C(32)	123.7(3)
C(34)-N(33)-C(38)	118.7(4)
C(32)-N(33)-C(38)	117.6(4)
O(39)-C(34)-N(33)	122.5(4)
O(39)-C(34)-N(35)	122.4(4)
N(33)-C(34)-N(35)	115.1(4)
C(34)-N(35)-C(36)	123.8(4)
C(34)-N(35)-C(40)	118.0(4)
C(36)-N(35)-C(40)	118.2(4)
O(41)-C(36)-N(31)	123.2(4)
O(41)-C(36)-N(35)	119.1(4)
N(31)-C(36)-N(35)	117.7(4)
O(43)-C(42)-W(30)	173.4(4)
O(45)-C(44)-W(30)	177.3(4)
O(47)-C(46)-W(30)	178.5(4)
O(49)-C(48)-W(30)	172.9(4)
O(51)-C(50)-W(30)	178.5(4)
Cl(12)-C(01)-Cl(11)	111.3(4)
Cl(22)-C(02)-Cl(21)	111.1(6)

Table 58. Anisotropic displacement parameters (A^2 x 10^3) for $C_{36}H_{30}Cl_4N_3O_8PW$ (**27c**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
P(1)	28(1)	25(1)	28(1)	-2(1)	5(1)	0(1)
C(1)	33(2)	32(2)	28(2)	-4(1)	7(1)	2(2)
C(2)	36(2)	43(2)	34(2)	1(2)	4(2)	-5(2)
C(3)	39(2)	67(3)	37(2)	0(2)	13(2)	-6(2)
C(4)	57(3)	73(4)	32(2)	-9(2)	13(2)	-1(3)
C(5)	48(3)	68(3)	35(2)	-18(2)	6(2)	-10(2)
C(6)	39(2)	51(2)	35(2)	-10(2)	7(2)	-8(2)
C(7)	31(2)	25(2)	38(2)	-1(1)	9(2)	-2(1)
C(8)	59(3)	32(2)	34(2)	0(2)	11(2)	-5(2)
C(9)	71(3)	40(2)	38(2)	7(2)	17(2)	1(2)
C(10)	56(3)	32(2)	64(3)	13(2)	19(2)	-1(2)
C(11)	63(3)	29(2)	71(4)	-2(2)	5(3)	-9(2)
C(12)	48(3)	35(2)	52(3)	-1(2)	-3(2)	-8(2)
C(13)	30(2)	29(2)	32(2)	-5(1)	6(2)	-2(1)
C(14)	37(2)	31(2)	42(2)	0(2)	7(2)	0(2)
C(15)	42(2)	33(2)	55(3)	-5(2)	-3(2)	6(2)
C(16)	31(2)	43(2)	66(3)	-13(2)	6(2)	5(2)
C(17)	40(2)	52(3)	57(3)	-6(2)	19(2)	-1(2)
C(18)	35(2)	44(2)	40(2)	-1(2)	10(2)	1(2)
C(19)	32(2)	30(2)	27(2)	-1(1)	8(1)	-4(1)
C(20)	43(2)	27(2)	35(2)	-2(2)	4(2)	-1(2)
C(21)	61(3)	27(2)	42(2)	-4(2)	2(2)	-6(2)
C(22)	47(2)	43(2)	36(2)	1(2)	0(2)	-18(2)
C(23)	35(2)	47(2)	35(2)	2(2)	4(2)	-9(2)
C(24)	35(2)	33(2)	31(2)	-2(2)	6(2)	-1(2)
W(30)	28(1)	29(1)	28(1)	0(1)	5(1)	2(1)
N(31)	34(2)	33(2)	30(2)	7(1)	9(1)	6(1)
C(32)	35(2)	39(2)	33(2)	5(2)	7(2)	6(2)
N(33)	32(2)	40(2)	32(2)	-1(1)	5(1)	7(1)
C(34)	37(2)	35(2)	41(2)	-5(2)	0(2)	4(2)
N(35)	44(2)	37(2)	38(2)	7(2)	2(2)	10(2)
C(36)	41(2)	39(2)	34(2)	7(2)	6(2)	5(2)
O(37)	53(2)	71(2)	35(2)	16(2)	16(2)	23(2)
C(38)	43(3)	67(3)	38(2)	-2(2)	13(2)	15(2)
O(39)	42(2)	49(2)	53(2)	-3(2)	0(2)	17(2)
C(40)	69(4)	58(3)	48(3)	22(2)	1(2)	25(3)
O(41)	58(2)	64(2)	40(2)	19(2)	18(2)	19(2)
C(42)	41(2)	42(2)	30(2)	-3(2)	7(2)	4(2)
O(43)	59(2)	72(2)	37(2)	-9(2)	-1(2)	2(2)
C(44)	36(2)	36(2)	33(2)	-2(2)	5(2)	-2(2)
O(45)	65(2)	45(2)	58(2)	1(2)	15(2)	-14(2)
C(46)	35(2)	38(2)	42(2)	-4(2)	12(2)	-1(2)
O(47)	61(2)	41(2)	80(3)	-3(2)	30(2)	-14(2)
C(48)	33(2)	37(2)	31(2)	3(2)	2(2)	-2(2)
O(49)	53(2)	56(2)	31(2)	-1(1)	1(1)	-5(2)
C(50)	37(2)	35(2)	35(2)	-2(2)	5(2)	1(2)
O(51)	47(2)	53(2)	59(2)	1(2)	10(2)	19(2)
Cl(11)	105(2)	115(2)	96(2)	-2(1)	22(1)	39(1)
Cl(12)	126(2)	120(2)	101(2)	29(1)	-49(1)	-30(2)

C(01)	92(5)	52(3)	57(3)	1(3)	-2(3)	7(3)
Cl(21)	98(2)	178(3)	200(3)	-86(2)	76(2)	-60(2)
Cl(22)	127(2)	117(2)	145(2)	43(2)	-34(2)	-14(2)
C(02)	249(14)	73(5)	64(5)	-4(4)	8(6)	50(7)

Table 59. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3)for $C_{36}H_{30}C_{l4}N_{3}O_{8}PW$ (**27c**).

	x	y	z	U(eq)
H(2)	10580(4)	12990(4)	-1010(3)	51(15)
H(3)	10880(4)	12830(4)	-2280(3)	52(15)
H(4)	9900(4)	11990(4)	-3130(4)	61(17)
H(5)	8590(4)	11460(4)	-2710(3)	55(16)
H(6)	8300(3)	11580(3)	-1430(3)	39(13)
H(8)	9760(3)	11930(3)	1470(3)	45(14)
H(9)	9690(4)	10600(4)	2070(4)	70(2)
H(10)	9300(3)	9400(3)	1480(3)	42(13)
H(11)	8760(4)	9400(4)	110(3)	65(17)
H(12)	8790(4)	10690(4)	-560(4)	69(18)
H(14)	8080(4)	13510(3)	-1190(3)	46(14)
H(15)	6660(3)	14240(3)	-1160(3)	42(13)
H(16)	5850(4)	14070(3)	-110(3)	49(14)
H(17)	6500(4)	13110(4)	920(4)	70(2)
H(18)	7850(4)	12530(4)	920(4)	66(18)
H(20)	9190(3)	14220(3)	490(3)	37(12)
H(21)	10380(4)	15060(4)	1100(3)	62(17)
H(22)	11830(4)	14590(3)	1340(3)	49(14)
H(23)	12200(4)	13200(3)	1020(3)	42(13)
H(24)	11030(3)	12230(3)	450(2)	25(10)
H(38A)	4090(5)	8070(4)	2610(4)	71(19)
H(38B)	3390(4)	8560(4)	2180(3)	58(17)
H(38C)	3230(5)	7530(5)	2160(4)	90(2)
H(40A)	4468	8923	-826	89
H(40B)	4049	9607	-300	89
H(40C)	3457	8835	-667	89
H(01A)	3110(4)	440(4)	1050(4)	68(18)
H(01B)	3240(6)	1430(5)	1260(5)	100(3)
H(02A)	6255	8375	2476	155
H(02B)	6437	9042	3162	155

Table 60: Atomic coordinates and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_{19}H_{27}N_2O_3$ (**28**). (U(eq) is defined as one third of the trace of the orthogonalized Uij tensor).

	x	y	z	U(eq)
N(1)	-0.0131(3)	0.4228(2)	0.1154(1)	31(1)
C(2)	0.0750(4)	0.3725(2)	0.0873(1)	31(1)
N(3)	0.1539(3)	0.4165(2)	0.0524(1)	29(1)
C(4)	0.1167(3)	0.4997(2)	0.0592(1)	28(1)
C(5)	0.0118(4)	0.5039(2)	0.0987(1)	30(1)
C(6)	-0.1116(4)	0.3964(2)	0.1601(1)	38(1)
C(7)	-0.2175(5)	0.3267(3)	0.1435(2)	47(1)
C(8)	-0.0081(5)	0.3748(3)	0.2059(1)	45(1)
C(9)	-0.0705(4)	0.5756(2)	0.1224(2)	39(1)
C(10)	0.1861(4)	0.5661(2)	0.0265(1)	36(1)
C(11)	0.2676(4)	0.3824(2)	0.0146(1)	33(1)
C(12)	0.4286(4)	0.3820(3)	0.0390(2)	45(1)
C(13)	0.2173(5)	0.2981(2)	-0.0037(2)	42(1)
N(20)	-0.1430(3)	0.6890(2)	0.3790(1)	23(1)
C(21)	-0.2524(4)	0.7064(2)	0.3438(1)	40(1)
N(22)	-0.2770(3)	0.6518(2)	0.3014(1)	21(1)
C(23)	-0.2019(4)	0.5773(2)	0.2976(1)	32(1)
N(24)	-0.0982(3)	0.5604(2)	0.3368(1)	18(1)
C(25)	-0.0627(4)	0.6178(2)	0.3765(1)	35(1)
O(26)	-0.3327(3)	0.7701(2)	0.3449(1)	58(1)
C(27)	-0.3904(5)	0.6724(3)	0.2609(2)	55(1)
O(28)	-0.2240(3)	0.5295(2)	0.2614(1)	44(1)
C(29)	-0.0150(5)	0.4819(2)	0.3337(2)	43(1)
O(30)	0.0405(3)	0.5994(2)	0.4080(1)	50(1)

Table 61. Anisotropic displacement parameters (A^2 x 10^3) for $C_{19}H_{27}N_2O_3$ (**28**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
N(1)	33(1)	30(1)	29(1)	2(1)	5(1)	3(1)
C(2)	34(2)	28(2)	31(2)	6(1)	4(1)	2(1)
N(3)	30(1)	31(1)	25(1)	2(1)	0(1)	0(1)
C(4)	30(2)	27(2)	28(2)	2(1)	-8(1)	-1(1)
C(5)	30(2)	29(2)	32(2)	-2(1)	-5(1)	0(1)
C(6)	36(2)	38(2)	39(2)	-1(2)	12(2)	3(2)
C(7)	39(2)	52(2)	50(2)	4(2)	10(2)	-5(2)
C(8)	56(2)	50(2)	28(2)	-2(2)	9(2)	-2(2)
C(9)	39(2)	33(2)	45(2)	-6(2)	-3(2)	3(2)
C(10)	37(2)	35(2)	38(2)	2(2)	-2(2)	-8(2)
C(11)	38(2)	35(2)	24(2)	2(1)	5(1)	3(1)
C(12)	34(2)	62(3)	39(2)	-1(2)	7(2)	3(2)
C(13)	50(2)	39(2)	37(2)	-3(2)	9(2)	4(2)
N(20)	26(2)	22(1)	20(1)	-7(1)	1(1)	-5(1)

C(21)	41(2)	31(2)	48(2)	-5(2)	15(2)	-7(2)
N(22)	24(1)	20(1)	20(1)	1(1)	-3(1)	0(1)
C(23)	32(2)	37(2)	27(2)	-2(1)	3(1)	-8(1)
N(24)	19(1)	21(1)	13(1)	-1(1)	-1(1)	0(1)
C(25)	31(2)	51(2)	23(2)	-2(1)	3(1)	-13(2)
O(26)	61(2)	37(2)	75(2)	-9(1)	3(2)	10(1)
C(27)	59(3)	55(2)	51(2)	8(2)	-15(2)	6(2)
O(28)	53(2)	44(1)	34(1)	-12(1)	-10(1)	-3(1)
C(29)	48(2)	45(2)	36(2)	-2(2)	1(2)	10(2)
O(30)	42(2)	73(2)	34(1)	-8(1)	-11(1)	0(1)

Table 62. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_{19}H_{27}N_2O_3$ (**28**).

	x	y	z	U(eq)
H(2)	810(4)	3190(2)	927(12)	24(8)
H(6)	-1790(5)	4440(2)	1693(14)	44(10)
H(7A)	-2720(5)	3420(3)	1126(19)	58(12)
H(7B)	-1550(4)	2730(2)	1368(14)	43(10)
H(7C)	-2880(6)	3180(3)	1702(19)	69(14)
H(8A)	-790(5)	3650(3)	2341(18)	63(13)
H(8B)	590(5)	3190(3)	1960(17)	64(12)
H(8C)	670(5)	4250(3)	2128(17)	64(13)
H(9A)	-170(5)	6310(3)	1106(16)	58(12)
H(9B)	-700(4)	5720(2)	1634(15)	38(9)
H(9C)	-1850(5)	5740(3)	1110(17)	60(12)
H(10A)	1540(5)	6200(3)	398(17)	65(13)
H(10B)	1710(5)	5570(3)	-125(18)	63(12)
H(10C)	3010(6)	5640(3)	309(17)	64(13)
H(11)	2660(4)	4220(2)	-148(13)	32(8)
H(12A)	4590(6)	4400(3)	520(2)	79(15)
H(12B)	4280(4)	3430(2)	695(16)	47(10)
H(12C)	5010(5)	3600(2)	123(15)	45(10)
H(13A)	1070(6)	2960(3)	-188(18)	70(14)
H(13B)	2260(4)	2590(2)	252(15)	42(10)
H(13C)	2890(5)	2820(2)	-330(16)	52(11)
H(27A)	-4346	7256	2680	83
H(27B)	-4713	6316	2605	83
H(27C)	-3397	6734	2276	83
H(29A)	-850(5)	4330(3)	3307(15)	52(11)
H(29B)	480(6)	4700(3)	3720(2)	80(15)
H(29C)	470(5)	4770(3)	3014(18)	57(12)

Table 63: Atomic coordinates and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_{12}H_{22}N_2O_2$ (**29**). (U(eq) is defined as one third of the trace of the orthogonalized Uij tensor).

	x	y	z	U(eq)
N(1)	0.5719(2)	0.6937(2)	0.0402(1)	27(1)
C(2)	0.4743(2)	0.5509(2)	0.0254(1)	25(1)
C(3)	0.7029(3)	0.7029(3)	0.0000	32(1)
C(4)	0.5363(3)	0.8228(3)	0.0906(1)	31(1)
C(5)	0.4942(3)	0.9923(3)	0.0594(1)	38(1)
C(6)	0.6864(4)	0.8344(4)	0.1362(1)	39(1)
C(7)	0.3189(3)	0.5037(3)	0.0624(1)	36(1)
C(8)	0.0223(3)	1.0223(3)	0.0000	39(1)
O(9)	0.0543(3)	0.8947(2)	0.0324(1)	56(1)

Table 64: Full bond lengths [Å] and angles [º] for $C_{12}H_{22}N_2O_2$ (**29**).

N(1)-C(3)	1.329(2)
N(1)-C(2)	1.390(2)
N(1)-C(4)	1.489(3)
C(2)-C(2)#1	1.362(4)
C(2)-C(7)	1.489(3)
C(3)-N(1)#1	1.329(2)
C(4)-C(5)	1.515(3)
C(4)-C(6)	1.517(3)
C(8)-O(9)	1.233(2)
C(8)-O(9)#2	1.233(2)
C(3)-N(1)-C(2)	109.10(17)
C(3)-N(1)-C(4)	123.91(18)
C(2)-N(1)-C(4)	126.95(16)
C(2)#1-C(2)-N(1)	106.62(10)
C(2)#1-C(2)-C(7)	131.10(12)
N(1)-C(2)-C(7)	122.28(18)
N(1)#1-C(3)-N(1)	108.6(3)
N(1)-C(4)-C(5)	109.25(16)
N(1)-C(4)-C(6)	110.00(19)
C(5)-C(4)-C(6)	112.8(2)
O(9)-C(8)-O(9)#2	129.2(3)

Table 65. Anisotropic displacement parameters (A^2 x 10^3) for $C_{12}H_{22}N_2O_2$ (**29**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
N(1)	27(1)	32(1)	23(1)	-2(1)	5(1)	-5(1)
C(2)	25(1)	27(1)	22(1)	6(1)	-6(1)	-6(1)
C(3)	31(1)	31(1)	34(2)	-8(1)	8(1)	-9(2)
C(4)	32(1)	34(1)	26(1)	-5(1)	11(1)	-5(1)
C(5)	36(1)	40(1)	39(1)	-7(1)	-4(1)	8(1)
C(6)	55(2)	39(1)	24(1)	-7(1)	-3(1)	6(1)
C(7)	32(1)	47(1)	28(1)	5(1)	1(1)	-15(1)
C(8)	35(1)	35(1)	46(2)	-5(1)	5(1)	-11(2)
O(9)	57(1)	52(1)	58(1)	6(1)	-7(1)	-15(1)

Table 66. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_{12}H_{22}N_2O_2$ (**29**).

	x	y	z	U(eq)
H(3)	7890(3)	7890(3)	0	39(9)
H(4)	4400(3)	7800(3)	1128(10)	28(6)
H(5A)	3920(3)	9800(3)	355(12)	42(7)
H(5B)	5960(4)	10340(3)	337(12)	48(7)
H(5C)	4650(3)	10770(3)	925(12)	44(7)
H(6A)	7960(4)	8720(3)	1131(12)	48(7)
H(6B)	6610(3)	9170(3)	1668(11)	37(7)
H(6C)	7050(4)	7240(4)	1561(13)	60(8)
H(7A)	3490(3)	4780(3)	1066(11)	40(6)
H(7B)	2320(4)	6030(4)	625(12)	49(7)
H(7C)	2690(4)	4000(4)	446(13)	55(8)
H(8)	1140(5)	11140(5)	0	85(15)

Table 67. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $C_{24}H_{44}N_4O_6$ (**30**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	665(1)	1454(1)	3551(1)	22(1)
N(2)	-373(2)	2560(1)	3914(1)	26(1)
C(2)	1588(2)	2073(1)	3291(1)	24(1)
C(4)	977(2)	581(1)	3468(1)	26(1)
C(1)	-513(2)	1764(1)	3920(1)	26(1)
C(3)	935(2)	2767(1)	3520(1)	26(1)
O(1)	4378(2)	381(1)	4207(1)	53(1)
O(3)	6594(2)	596(1)	4793(1)	52(1)
C(6)	521(2)	151(1)	4143(1)	33(1)
C(7)	3017(2)	1925(1)	2860(1)	36(1)
C(12)	5754(2)	725(1)	4242(1)	34(1)
O(2)	6203(2)	1175(1)	3762(1)	53(1)
C(8)	1474(3)	3611(1)	3441(1)	47(1)
C(10)	-2008(3)	2789(2)	4965(1)	50(1)
C(9)	-1475(2)	3123(1)	4262(1)	39(1)
C(5)	125(3)	251(1)	2829(1)	46(1)
C(11)	-2840(4)	3284(2)	3770(2)	78(1)

Table 68. Bond lengths [Å] and angles [°] for $C_{24}H_{44}N_4O_6$ (**30**).

N(1)-C(1)	1.3285(19)
N(1)-C(2)	1.3891(19)
N(1)-C(4)	1.4886(19)
N(2)-C(1)	1.333(2)
N(2)-C(3)	1.386(2)
N(2)-C(9)	1.483(2)
C(2)-C(3)	1.358(2)
C(2)-C(7)	1.487(2)
C(4)-C(5)	1.516(2)
C(4)-C(6)	1.517(2)

C(3)-C(8)	1.488(2)
O(1)-C(12)	1.309(2)
O(3)-C(12)	1.284(2)
C(12)-O(2)	1.238(2)
C(10)-C(9)	1.512(3)
C(9)-C(11)	1.514(4)
C(1)-N(1)-C(2)	109.08(12)
C(1)-N(1)-C(4)	124.88(13)
C(2)-N(1)-C(4)	125.97(12)
C(1)-N(2)-C(3)	108.98(13)
C(1)-N(2)-C(9)	124.80(14)
C(3)-N(2)-C(9)	126.21(14)
C(3)-C(2)-N(1)	106.69(13)
C(3)-C(2)-C(7)	130.83(15)
N(1)-C(2)-C(7)	122.47(14)
N(1)-C(4)-C(5)	110.77(13)
N(1)-C(4)-C(6)	109.10(13)
C(5)-C(4)-C(6)	112.21(16)
N(1)-C(1)-N(2)	108.40(14)
C(2)-C(3)-N(2)	106.86(13)
C(2)-C(3)-C(8)	130.36(16)
N(2)-C(3)-C(8)	122.66(15)
O(2)-C(12)-O(3)	121.65(16)
O(2)-C(12)-O(1)	120.44(17)
O(3)-C(12)-O(1)	117.89(17)
N(2)-C(9)-C(10)	110.33(16)
N(2)-C(9)-C(11)	109.14(17)
C(10)-C(9)-C(11)	111.9(2)

Symmetry transformations used to generate equivalent atoms:

Table 69. Anisotropic displacement parameters ($Å^2 x 10^3$) for $C_{24}H_{44}N_4O_6$ (**30**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	21(1)	23(1)	21(1)	-2(1)	0(1)	1(1)
N(2)	29(1)	26(1)	24(1)	-5(1)	3(1)	2(1)
C(2)	26(1)	29(1)	19(1)	1(1)	0(1)	-1(1)
C(4)	27(1)	23(1)	27(1)	-2(1)	-2(1)	5(1)
C(1)	24(1)	26(1)	28(1)	-5(1)	2(1)	0(1)
C(3)	32(1)	27(1)	21(1)	-1(1)	1(1)	-2(1)
O(1)	38(1)	67(1)	53(1)	12(1)	-20(1)	-21(1)
O(3)	34(1)	75(1)	45(1)	11(1)	-16(1)	-12(1)
C(6)	35(1)	28(1)	36(1)	6(1)	0(1)	2(1)
C(7)	33(1)	43(1)	34(1)	4(1)	12(1)	3(1)
C(12)	25(1)	41(1)	37(1)	-6(1)	-4(1)	1(1)
O(2)	39(1)	71(1)	49(1)	16(1)	-7(1)	-14(1)
C(8)	63(1)	31(1)	46(1)	1(1)	11(1)	-10(1)
C(10)	55(1)	51(1)	44(1)	-14(1)	21(1)	6(1)
C(9)	46(1)	31(1)	41(1)	-10(1)	13(1)	10(1)
C(5)	71(2)	29(1)	38(1)	-11(1)	-22(1)	12(1)
C(11)	78(2)	90(2)	65(2)	-8(2)	-1(2)	61(2)

Table 70. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 x 10^3$) for $C_{24}H_{44}N_4O_6$ (**30**).

	x	y	z	U(eq)
H(4)	2110(20)	559(11)	3413(10)	25(4)
H(1)	-1330(30)	1474(13)	4129(11)	39(5)
H(7C)	3780(30)	1642(14)	3126(12)	49(6)
H(6B)	-620(30)	181(12)	4227(11)	37(5)
H(6A)	860(30)	-406(14)	4120(11)	43(6)
H(9A)	-910(30)	3615(15)	4346(12)	50(6)

H(7A)	3480(30)	2428(15)	2737(12)	51(6)
H(5B)	410(30)	-304(15)	2766(13)	53(6)
H(6C)	1090(30)	397(13)	4555(12)	42(6)
H(5C)	-1040(30)	293(14)	2907(12)	47(6)
H(8C)	1750(40)	3854(18)	3923(17)	78(9)
H(7B)	2730(30)	1630(14)	2412(13)	51(6)
H(5A)	440(30)	524(14)	2410(13)	50(6)
H(10B)	-1080(40)	2669(17)	5279(17)	76(9)
H(10C)	-2660(30)	2310(16)	4888(14)	57(7)
H(8B)	680(40)	3920(20)	3222(17)	86(10)
H(10A)	-2600(30)	3197(16)	5185(13)	60(7)
H(11B)	-3480(40)	3640(20)	3986(17)	86(10)
H(8A)	2380(30)	3614(16)	3113(14)	63(7)
H(11A)	-2380(40)	3540(20)	3336(19)	91(11)
H(11C)	-3370(50)	2790(20)	3650(20)	106(14)
H(1B)	4040(50)	-40(30)	4690(20)	146(16)

Table 71. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for $C_{13}H_{22}N_2O_4$ (**31**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	841(2)	9855(2)	8219(2)	50(1)
O(1)	4826(2)	25(2)	1147(2)	63(1)
O(2)	5609(4)	1778(3)	1541(3)	109(1)
C(1)	0	10526(4)	7500	52(1)
C(2)	525(3)	8696(3)	7956(3)	49(1)
C(3)	1242(3)	7705(3)	8637(4)	60(1)
C(4)	1923(3)	10272(3)	9178(3)	56(1)
C(5)	1635(4)	10530(7)	10430(4)	98(2)
C(6)	2449(4)	11290(4)	8667(4)	73(1)
C(7)	5146(2)	921(3)	1849(3)	51(1)

Table 72. Bond lengths [Å] and angles [°] for $C_{13}H_{22}N_2O_4$ (**31**).

N(1)-C(1)	1.323(4)
N(1)-C(2)	1.388(4)
N(1)-C(4)	1.482(4)
O(1)-C(7)	1.269(4)
O(2)-C(7)	1.211(4)
C(1)-N(1)#1	1.323(4)
C(2)-C(2)#1	1.351(6)
C(2)-C(3)	1.484(4)
C(4)-C(6)	1.493(5)
C(4)-C(5)	1.505(6)
C(7)-C(7)#2	1.531(6)
C(1)-N(1)-C(2)	108.7(3)
C(1)-N(1)-C(4)	125.7(3)
C(2)-N(1)-C(4)	125.6(3)
N(1)#1-C(1)-N(1)	109.0(4)
C(2)#1-C(2)-N(1)	106.80(16)
C(2)#1-C(2)-C(3)	129.99(19)
N(1)-C(2)-C(3)	123.2(3)
N(1)-C(4)-C(6)	110.9(3)
N(1)-C(4)-C(5)	109.2(3)
C(6)-C(4)-C(5)	113.1(4)
O(2)-C(7)-O(1)	125.1(3)
O(2)-C(7)-C(7)#2	118.6(2)
O(1)-C(7)-C(7)#2	116.2(2)

Symmetry transformations used to generate equivalent atoms:

#1: 1-x, y, z+ 3/2, #2: 1-x, y, 0.5-z

Table 73. Anisotropic displacement parameters (A^2x 10^3) for $C_{13}H_{22}N_2O_4$ (**31**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h2 a*2U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	44(1)	49(1)	55(2)	1(1)	10(1)	0(1)
O(1)	81(2)	54(1)	62(2)	-7(1)	31(1)	-13(1)
O(2)	168(3)	89(2)	87(2)	-23(2)	64(2)	-65(2)
C(1)	49(2)	46(2)	56(3)	0	7(2)	0
C(2)	45(1)	51(2)	51(2)	2(1)	15(1)	1(1)
C(3)	57(2)	53(2)	69(2)	9(2)	18(2)	8(1)
C(4)	43(2)	65(2)	58(2)	1(2)	8(1)	-5(1)

C(5)	66(3)	174(5)	54(2)	-19(3)	14(2)	-39(3)
C(6)	63(2)	71(2)	77(3)	6(2)	6(2)	-17(2)
C(7)	48(2)	50(2)	54(2)	-1(1)	11(1)	-6(1)

Table 74. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2x 10 ^{3}) for $C_{13}H_{22}N_2O_4$ (**31**).

	x	y	z	U(eq)
H(1)	0	11310(40)	7500	44(11)
H(3A)	880(40)	6980(40)	8310(40)	77(12)
H(4A)	2460(30)	9650(30)	9320(30)	54(9)
H(5A)	1170(60)	9850(50)	10750(60)	130(20)
H(6A)	1920(50)	11950(50)	8410(50)	97(14)
H(1B)	4910(140)	530(130)	390(150)	320(70)
H(3B)	2030(50)	7750(40)	8510(50)	99(14)
H(5B)	2380(40)	10740(40)	11070(50)	92(13)
H(6B)	3170(40)	11570(40)	9310(40)	82(12)
H(3C)	1290(40)	7680(40)	9610(40)	80(12)
H(5C)	940(70)	11160(60)	10180(60)	140(20)
H(6C)	2570(50)	11110(50)	7780(60)	116(18)
H(1)	0	11310(40)	7500	44(11)
H(3A)	880(40)	6980(40)	8310(40)	77(12)
H(4A)	2460(30)	9650(30)	9320(30)	54(9)
H(5A)	1170(60)	9850(50)	10750(60)	130(20)
H(6A)	1920(50)	11950(50)	8410(50)	97(14)
H(1B)	4910(140)	530(130)	390(150)	320(70)
H(3B)	2030(50)	7750(40)	8510(50)	99(14)
H(5B)	2380(40)	10740(40)	11070(50)	92(13)
H(6B)	3170(40)	11570(40)	9310(40)	82(12)

H(3C)	1290(40)	7680(40)	9610(40)	80(12)
H(5C)	940(70)	11160(60)	10180(60)	140(20)
H(6C)	2570(50)	11110(50)	7780(60)	116(18)

Table 75. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2x 10^3) for $C_{16}H_{28}N_2O_2$ (**32**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2244(1)	2481(1)	7156(1)	24(1)
N(4)	3912(1)	3144(1)	7962(1)	26(1)
O(20)	3023(1)	9353(1)	707(1)	35(1)
O(25)	1507(2)	5683(2)	940(1)	78(1)
C(2)	2554(1)	1714(1)	8013(1)	24(1)
C(3)	3602(1)	2138(1)	8524(1)	25(1)
C(5)	3073(1)	3335(1)	7146(1)	26(1)
C(6)	1107(1)	2431(2)	6432(1)	27(1)
C(7)	1193(2)	2975(2)	5419(1)	36(1)
C(8)	233(1)	3160(2)	6878(2)	40(1)
C(9)	1832(1)	627(2)	8230(1)	29(1)
C(10)	4335(1)	1691(2)	9498(1)	31(1)
C(11)	5008(1)	3876(2)	8203(1)	32(1)
C(12)	5563(2)	3886(3)	7318(2)	62(1)
C(13)	4810(3)	5227(4)	8501(4)	99(2)
C(21)	2491(1)	8328(2)	810(1)	26(1)
C(22)	2380(1)	7300(2)	127(1)	28(1)
C(23)	1859(2)	6090(2)	203(1)	38(1)
C(24)	1703(2)	5201(2)	-705(2)	51(1)
C(25)	1926(2)	8268(2)	1701(1)	42(1)

Table 76. Bond lengths [Å] and angles [°] for $C_{16}H_{28}N_2O_2$ (**32**).

N(1)-C(5)	1.330(2)
N(1)-C(2)	1.393(2)
N(1)-C(6)	1.489(2)
N(4)-C(5)	1.334(2)
N(4)-C(3)	1.392(2)
N(4)-C(11)	1.485(2)
O(20)-C(21)	1.263(2)
O(25)-C(23)	1.245(2)
C(2)-C(3)	1.361(2)
C(2)-C(9)	1.488(2)
C(3)-C(10)	1.490(2)
C(6)-C(7)	1.515(2)
C(6)-C(8)	1.521(2)
C(11)-C(13)	1.493(4)
C(11)-C(12)	1.499(3)
C(21)-C(22)	1.402(2)
C(21)-C(25)	1.515(2)
C(22)-C(23)	1.415(2)
C(23)-C(24)	1.521(3)
C(5)-N(1)-C(2)	109.27(12)
C(5)-N(1)-C(6)	125.87(12)
C(2)-N(1)-C(6)	124.56(12)
C(5)-N(4)-C(3)	109.12(12)
C(5)-N(4)-C(11)	124.68(13)
C(3)-N(4)-C(11)	126.18(12)
C(3)-C(2)-N(1)	106.61(12)
C(3)-C(2)-C(9)	130.50(14)
N(1)-C(2)-C(9)	122.84(13)
C(2)-C(3)-N(4)	106.69(12)
C(2)-C(3)-C(10)	130.12(14)
N(4)-C(3)-C(10)	123.19(13)
N(1)-C(5)-N(4)	108.30(13)
N(1)-C(6)-C(7)	110.69(12)

N(1)-C(6)-C(8)	108.78(13)
C(7)-C(6)-C(8)	111.71(15)
N(4)-C(11)-C(13)	110.82(16)
N(4)-C(11)-C(12)	110.54(14)
C(13)-C(11)-C(12)	109.7(3)
O(20)-C(21)-C(22)	122.89(14)
O(20)-C(21)-C(25)	116.60(15)
C(22)-C(21)-C(25)	120.48(15)
C(21)-C(22)-C(23)	127.20(15)
O(25)-C(23)-C(22)	126.36(17)
O(25)-C(23)-C(24)	116.56(16)
C(22)-C(23)-C(24)	117.08(16)

Table 77. Anisotropic displacement parameters (A^2x 10^3) for $C_{16}H_{28}N_2O_2$ (**32**). The anisotropic displacement factor exponent takes the form: -2pi^2 [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	21(1)	26(1)	24(1)	1(1)	4(1)	0(1)
N(4)	22(1)	29(1)	27(1)	5(1)	2(1)	-3(1)
O(20)	39(1)	30(1)	39(1)	-3(1)	13(1)	-4(1)
O(25)	137(2)	64(1)	33(1)	2(1)	18(1)	-57(1)
C(2)	25(1)	25(1)	23(1)	0(1)	8(1)	1(1)
C(3)	26(1)	24(1)	25(1)	2(1)	7(1)	1(1)
C(5)	23(1)	27(1)	27(1)	5(1)	3(1)	-2(1)
C(6)	22(1)	29(1)	29(1)	-1(1)	-1(1)	-3(1)
C(7)	35(1)	43(1)	27(1)	2(1)	-2(1)	-5(1)
C(8)	23(1)	50(1)	44(1)	-5(1)	3(1)	2(1)
C(9)	32(1)	30(1)	28(1)	0(1)	10(1)	-6(1)
C(10)	32(1)	33(1)	26(1)	5(1)	2(1)	1(1)
C(11)	22(1)	34(1)	35(1)	5(1)	-2(1)	-6(1)
C(12)	40(1)	84(2)	68(2)	-19(1)	24(1)	-32(1)
C(13)	49(2)	81(2)	171(4)	-85(2)	33(2)	-29(2)
C(21)	21(1)	32(1)	26(1)	4(1)	3(1)	2(1)
C(22)	27(1)	30(1)	25(1)	4(1)	4(1)	1(1)

C(23)	47(1)	35(1)	28(1)	6(1)	-1(1)	-9(1)
C(24)	70(2)	35(1)	47(1)	-5(1)	14(1)	-12(1)
C(25)	44(1)	54(1)	31(1)	-4(1)	14(1)	-10(1)

Table 78. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10 ^{3}) for $C_{16}H_{28}N_2O_2$ (**32**).

	x	y	z	U(eq)
H(5A)	3075(15)	4002(18)	6655(13)	31(4)
H(6A)	931(14)	1520(17)	6356(12)	25(4)
H(7A)	473(18)	2817(19)	4929(16)	45(5)
H(7B)	1829(18)	2540(20)	5178(16)	46(5)
H(7C)	1337(17)	3910(20)	5458(15)	43(5)
H(8A)	190(20)	2820(20)	7556(19)	61(7)
H(8B)	-510(20)	3070(20)	6440(17)	53(6)
H(8C)	454(18)	4080(20)	6961(16)	51(6)
H(9A)	1065(18)	950(19)	8316(15)	43(5)
H(9B)	2239(17)	178(19)	8829(16)	42(5)
H(9C)	1670(16)	41(18)	7670(15)	36(5)
H(10A)	3980(16)	963(19)	9754(14)	37(5)
H(10B)	4435(17)	2400(20)	10012(16)	45(5)
H(10C)	5086(18)	1419(19)	9419(15)	42(5)
H(11A)	5495(19)	3410(20)	8738(17)	53(6)
H(12A)	6320(20)	4270(20)	7516(18)	64(7)
H(12B)	5630(30)	3030(40)	7050(30)	120(13)
H(12C)	5090(30)	4380(40)	6750(30)	127(14)
H(13A)	4540(30)	5130(30)	9060(30)	92(11)
H(13B)	4310(50)	5620(50)	8230(40)	16(2)
H(13C)	5560(30)	5690(30)	8690(20)	95(9)
H(22A)	2679(15)	7441(18)	-486(14)	35(5)
H(24A)	950(20)	4810(30)	-800(20)	75(8)
H(24B)	2240(30)	4530(30)	-550(20)	81(9)
H(24C)	1820(30)	5640(30)	-1310(30)	95(10)
H(25A)	2340(30)	7730(30)	2190(30)	106(11)

H(25B)	1970(30)	9070(40)	2020(30)	120(12)
H(25C)	1260(30)	7750(30)	1610(30)	116(12)

Table 79. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_{11}H_{21}Ag_{2.50}I_{3.50}N_2$ (**33**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(2)	1895(3)	3341(4)	633(3)	21(1)
C(3)	1552(3)	3683(4)	11(3)	21(1)
C(5)	2633(3)	3035(4)	-310(3)	21(1)
C(11)	3119(3)	2415(4)	910(3)	21(1)
C(12)	3878(3)	2549(5)	609(3)	30(1)
C(13)	2920(4)	1221(5)	1026(4)	38(1)
C(21)	1661(3)	3352(5)	1421(3)	29(1)
C(31)	818(3)	4181(5)	-92(4)	31(1)
C(41)	1879(3)	3727(4)	-1359(3)	24(1)
C(42)	2224(4)	2884(6)	-1857(3)	35(1)
C(43)	2132(4)	4882(5)	-1529(4)	38(1)
Ag(1)	5000	6454(1)	2500	34(1)
Ag(2)	4945(1)	5880(1)	873(1)	35(1)
Ag(3)	5352(1)	3806(1)	1789(1)	39(1)
I(1)	5968(1)	4176(1)	425(1)	24(1)
I(2)	5000	1805(1)	2500	28(1)
I(3)	3875(1)	4976(1)	1987(1)	24(1)
I(4)	5550(1)	7821(1)	1403(1)	27(1)
N(1)	2576(2)	2941(3)	420(2)	18(1)
N(4)	2026(2)	3476(3)	-574(2)	20(1)

Table 80. Bond lengths [Å] and angles [°] for $C_{11}H_{21}Ag_{2.50}I_{3.50}N_2$ (**33**).

C(2)-C(3)	1.357(7)
C(2)-N(1)	1.394(6)
C(2)-C(21)	1.493(7)
C(3)-N(4)	1.394(6)
C(3)-C(31)	1.486(7)
C(5)-N(4)	1.325(6)
C(5)-N(1)	1.332(6)
C(5)-H(5)	0.98(5)
C(11)-N(1)	1.480(6)
C(11)-C(12)	1.501(7)
C(11)-C(13)	1.514(8)
C(11)-H(11)	0.92(6)
C(12)-H(12A)	1.00(6)
C(12)-H(12B)	0.94(6)
C(12)-H(12C)	0.91(8)
C(13)-H(13A)	0.91(7)

C(13)-H(13B)	0.90(8)
C(13)-H(13C)	1.03(10)
C(21)-H(21A)	0.96(6)
C(21)-H(21B)	0.94(8)
C(21)-H(21C)	0.86(7)
C(31)-H(31A)	0.85(7)
C(31)-H(31B)	1.04(7)
C(31)-H(31C)	0.99(7)
C(41)-N(4)	1.482(6)
C(41)-C(42)	1.506(8)
C(41)-C(43)	1.512(8)
C(41)-H(41)	1.03(7)
C(42)-H(42A)	0.92(6)
C(42)-H(42B)	0.99(7)
C(42)-H(42C)	0.93(9)
C(43)-H(43A)	1.03(7)
C(43)-H(43B)	0.98(7)
C(43)-H(43C)	0.76(9)
Ag(1)-I(4)	2.7833(5)
Ag(1)-I(4)#1	2.7834(5)
Ag(1)-I(3)	2.8890(5)
Ag(1)-I(3)#1	2.8890(5)
Ag(1)-Ag(2)	3.0360(5)
Ag(1)-Ag(2)#1	3.0361(5)
Ag(2)-I(4)	2.7822(6)
Ag(2)-I(1)#2	2.8883(5)
Ag(2)-I(1)	2.9102(5)
Ag(2)-I(3)	3.0233(6)
Ag(2)-Ag(3)	3.1139(7)
Ag(3)-I(1)	2.7561(5)
Ag(3)-I(2)	2.8309(6)
Ag(3)-Ag(3)#1	2.8851(8)
Ag(3)-I(3)#1	2.9945(6)
Ag(3)-I(3)	3.0772(6)
I(1)-Ag(2)#2	2.8883(5)
I(2)-Ag(3)#1	2.8308(6)
I(3)-Ag(3)#1	2.9945(6)

C(3)-C(2)-N(1)	106.9(4)
C(3)-C(2)-C(21)	131.4(5)
N(1)-C(2)-C(21)	121.7(4)
C(2)-C(3)-N(4)	106.8(4)
C(2)-C(3)-C(31)	130.4(5)
N(4)-C(3)-C(31)	122.7(5)
N(4)-C(5)-N(1)	109.2(4)
N(4)-C(5)-H(5)	129(3)
N(1)-C(5)-H(5)	121(3)
N(1)-C(11)-C(12)	110.9(4)
N(1)-C(11)-C(13)	109.7(4)
C(12)-C(11)-C(13)	112.2(5)
N(1)-C(11)-H(11)	108(4)
C(12)-C(11)-H(11)	106(4)
C(13)-C(11)-H(11)	110(4)
C(11)-C(12)-H(12A)	113(4)
C(11)-C(12)-H(12B)	106(4)
H(12A)-C(12)-H(12B)	112(5)
C(11)-C(12)-H(12C)	115(5)
H(12A)-C(12)-H(12C)	107(6)

H(12B)-C(12)-H(12C)	102(6)
C(11)-C(13)-H(13A)	110(4)
C(11)-C(13)-H(13B)	108(5)
H(13A)-C(13)-H(13B)	107(6)
C(11)-C(13)-H(13C)	112(5)
H(13A)-C(13)-H(13C)	116(6)
H(13B)-C(13)-H(13C)	104(7)
C(2)-C(21)-H(21A)	109(3)
C(2)-C(21)-H(21B)	120(5)
H(21A)-C(21)-H(21B)	104(6)
C(2)-C(21)-H(21C)	108(5)
H(21A)-C(21)-H(21C)	117(6)
H(21B)-C(21)-H(21C)	98(6)
C(3)-C(31)-H(31A)	111(5)
C(3)-C(31)-H(31B)	108(4)
H(31A)-C(31)-H(31B)	106(6)
C(3)-C(31)-H(31C)	111(4)
H(31A)-C(31)-H(31C)	110(6)
H(31B)-C(31)-H(31C)	111(6)
N(4)-C(41)-C(42)	111.1(4)
N(4)-C(41)-C(43)	109.4(4)
C(42)-C(41)-C(43)	112.6(5)
N(4)-C(41)-H(41)	102(4)
C(42)-C(41)-H(41)	111(4)
C(43)-C(41)-H(41)	110(4)
C(41)-C(42)-H(42A)	110(4)
C(41)-C(42)-H(42B)	106(4)
H(42A)-C(42)-H(42B)	115(6)
C(41)-C(42)-H(42C)	116(6)
H(42A)-C(42)-H(42C)	105(7)
H(42B)-C(42)-H(42C)	106(7)
C(41)-C(43)-H(43A)	111(4)
C(41)-C(43)-H(43B)	120(4)
H(43A)-C(43)-H(43B)	101(5)
C(41)-C(43)-H(43C)	116(7)
H(43A)-C(43)-H(43C)	114(8)
H(43B)-C(43)-H(43C)	93(8)
I(4)-Ag(1)-I(4)#1	106.52(3)
I(4)-Ag(1)-I(3)	113.606(10)
I(4)#1-Ag(1)-I(3)	110.170(10)
I(4)-Ag(1)-I(3)#1	110.168(10)
I(4)#1-Ag(1)-I(3)#1	113.606(10)
I(3)-Ag(1)-I(3)#1	102.94(2)
I(4)-Ag(1)-Ag(2)	56.924(11)
I(4)#1-Ag(1)-Ag(2)	145.19(2)
I(3)-Ag(1)-Ag(2)	61.304(13)
I(3)#1-Ag(1)-Ag(2)	101.16(2)
I(4)-Ag(1)-Ag(2)#1	145.19(2)
I(4)#1-Ag(1)-Ag(2)#1	56.923(11)
I(3)-Ag(1)-Ag(2)#1	101.16(2)
I(3)#1-Ag(1)-Ag(2)#1	61.305(12)
Ag(2)-Ag(1)-Ag(2)#1	153.40(3)
I(4)-Ag(2)-I(1)#2	122.21(2)
I(4)-Ag(2)-I(1)	116.48(2)
I(1)#2-Ag(2)-I(1)	97.333(15)
I(4)-Ag(2)-I(3)	109.63(2)
I(1)#2-Ag(2)-I(3)	99.31(2)
I(1)-Ag(2)-I(3)	110.11(2)

I(4)-Ag(2)-Ag(1)	56.959(15)
I(1)#2-Ag(2)-Ag(1)	144.85(2)
I(1)-Ag(2)-Ag(1)	114.46(2)
I(3)-Ag(2)-Ag(1)	56.950(12)
I(4)-Ag(2)-Ag(3)	114.15(2)
I(1)#2-Ag(2)-Ag(3)	123.64(2)
I(1)-Ag(2)-Ag(3)	54.325(13)
I(3)-Ag(2)-Ag(3)	60.163(14)
Ag(1)-Ag(2)-Ag(3)	70.10(2)
I(1)-Ag(3)-I(2)	130.03(2)
I(1)-Ag(3)-Ag(3)#1	170.370(14)
I(2)-Ag(3)-Ag(3)#1	59.363(11)
I(1)-Ag(3)-I(3)#1	113.24(2)
I(2)-Ag(3)-I(3)#1	100.29(2)
Ag(3)#1-Ag(3)-I(3)#1	63.08(2)
I(1)-Ag(3)-I(3)	112.88(2)
I(2)-Ag(3)-I(3)	98.34(2)
Ag(3)#1-Ag(3)-I(3)	60.19(2)
I(3)#1-Ag(3)-I(3)	96.21(2)
I(1)-Ag(3)-Ag(2)	59.067(14)
I(2)-Ag(3)-Ag(2)	152.49(2)
Ag(3)#1-Ag(3)-Ag(2)	111.77(2)
I(3)#1-Ag(3)-Ag(2)	97.07(2)
I(3)-Ag(3)-Ag(2)	58.459(14)
Ag(3)-I(1)-Ag(2)#2	119.42(2)
Ag(3)-I(1)-Ag(2)	66.61(2)
Ag(2)#2-I(1)-Ag(2)	82.666(15)
Ag(3)#1-I(2)-Ag(3)	61.27(2)
Ag(1)-I(3)-Ag(3)#1	73.77(2)
Ag(1)-I(3)-Ag(2)	61.746(11)
Ag(3)#1-I(3)-Ag(2)	111.30(2)
Ag(1)-I(3)-Ag(3)	72.530(15)
Ag(3)#1-I(3)-Ag(3)	56.72(2)
Ag(2)-I(3)-Ag(3)	61.378(13)
Ag(2)-I(4)-Ag(1)	66.117(15)
C(5)-N(1)-C(2)	108.4(4)
C(5)-N(1)-C(11)	125.5(4)
C(2)-N(1)-C(11)	125.9(4)
C(5)-N(4)-C(3)	108.7(4)
C(5)-N(4)-C(41)	125.7(4)
C(3)-N(4)-C(41)	125.6(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2 #2 -x+1,-y+1,-z

Table 81. Anisotropic displacement parameters (A^2 x 10^3) for $C_{11}H_{21}Ag_{2.50}I_{3.50}N_2$ (**33**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
C(2)	20(2)	18(2)	25(2)	-4(2)	4(2)	-3(2)
C(3)	21(2)	19(2)	24(2)	-3(2)	6(2)	-3(2)
C(5)	19(2)	24(2)	20(2)	0(2)	2(2)	-1(2)

C(11)	26(2)	24(2)	15(2)	1(2)	2(2)	1(2)
C(12)	23(2)	47(3)	21(2)	5(2)	-3(2)	1(2)
C(13)	41(3)	28(3)	45(4)	10(3)	1(3)	-1(2)
C(21)	32(3)	29(3)	26(2)	0(2)	10(2)	3(2)
C(31)	20(2)	34(3)	40(3)	3(2)	3(2)	4(2)
C(41)	22(2)	30(2)	20(2)	4(2)	-4(2)	1(2)
C(42)	42(3)	44(3)	20(2)	-4(2)	-7(2)	5(3)
C(43)	47(4)	34(3)	34(3)	14(3)	2(3)	0(3)
Ag(1)	44(1)	36(1)	22(1)	0	6(1)	0
Ag(2)	41(1)	34(1)	28(1)	-5(1)	-1(1)	1(1)
Ag(3)	46(1)	45(1)	26(1)	5(1)	10(1)	-2(1)
I(1)	26(1)	29(1)	18(1)	0(1)	2(1)	6(1)
I(2)	31(1)	30(1)	24(1)	0	2(1)	0
I(3)	22(1)	27(1)	24(1)	1(1)	0(1)	1(1)
I(4)	27(1)	30(1)	24(1)	2(1)	5(1)	-3(1)
N(1)	19(2)	19(2)	17(2)	0(1)	1(1)	-1(1)
N(4)	19(2)	22(2)	19(2)	1(1)	1(1)	0(1)

Table 82. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_{11}H_{21}Ag_{2.50}I_{3.50}N_2$ (**33**).

	x	y	z	U(eq)
H(5)	3077(29)	2803(43)	-571(29)	12(12)
H(11)	3112(33)	2784(49)	1352(34)	24(15)
H(12A)	3995(34)	3326(54)	468(33)	27(16)
H(12B)	4195(33)	2279(47)	971(33)	21(14)
H(12C)	3987(41)	2117(61)	213(42)	43(20)
H(13A)	2866(36)	873(53)	585(38)	28(16)
H(13B)	2483(46)	1200(64)	1255(43)	48(21)
H(13C)	3267(54)	845(72)	1396(51)	71(28)
H(21A)	2024(32)	3733(46)	1706(30)	17(13)
H(21B)	1588(42)	2689(63)	1677(40)	46(20)
H(21C)	1221(40)	3601(57)	1444(37)	34(17)
H(31A)	557(40)	3790(59)	-378(38)	36(19)
H(31B)	885(38)	4930(59)	-356(37)	37(18)
H(31C)	570(40)	4279(57)	388(39)	39(19)
H(41)	1320(36)	3685(54)	-1385(36)	32(17)
H(42A)	2721(34)	2955(47)	-1852(32)	19(14)
H(42B)	1990(38)	2985(55)	-2343(39)	37(18)
H(42C)	2139(50)	2154(76)	-1730(49)	68(27)
H(43A)	1899(35)	5440(53)	-1169(35)	29(16)
H(43B)	2647(39)	5078(55)	-1485(36)	33(17)
H(43C)	2113(51)	5059(75)	-1931(52)	67(29)

7.3 Bibliography

Personal Data

Name	Qutaiba Abu-Salem
Date of Birth	10.06.1975
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Family Status	Single

Education

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1981-1985	Primary schools, Kuwait.
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1997-2000	M.Sc. Study in "Jordan University Of Science & Technology" (J.U.S.T), Irbid, Jordan.
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