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Review

ORGANOMETALLIC COMPOUNDS CONTAINING NITROGEN, PHOSPHORUS, ARSENIC AND SULFUR *

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Phosphorus compounds

The chemistry of phosphorus compounds with low coordination numbers has grown dramatically in recent years [1–3]. We, however, were interested in compounds containing a phosphorus–phosphorus bond and having higher coordination numbers at the phosphorus atoms. In 1979 we obtained the first compound containing a λ^3-λ^5-phosphorus–phosphorus bond by the reaction of a substituted urea with $C_6F_5PCl_2$. It is a spirocyclic phosphorane containing a five-membered and a four-membered ring (Fig. 1).

The structure was established by X-ray analysis. The λ^3-phosphorus adopts an equitorial position in the larger ring of the spirobicyclic phosphorane. The coordination at the λ^5-phosphorus shows a 21 percent distortion from an idealised trigonal bipyramid towards a square pyramidal geometry. The very different axial P–N bond lengths of 186.7(3) and 174.3(2) pm in the four- and five-membered rings, respectively, are indicative of a significant degree of ring strain in the four-membered ring. The P–P bond length of 219.5 pm is slightly shorter than that which has been observed in diphosphanes with the coordination numbers 3 [4].

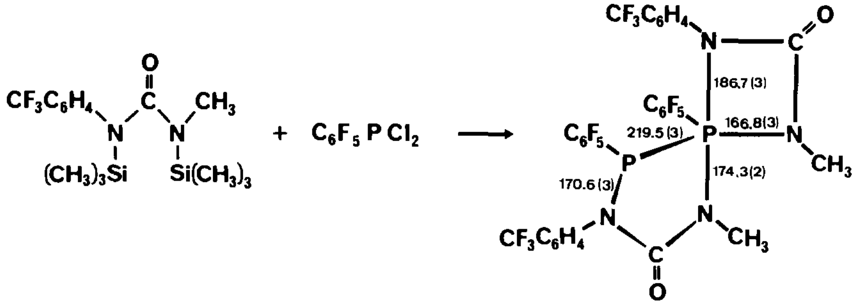

Fig. 1. Spirocyclic phosphorane with a five- and four-membered ring.

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The pyrolysis of the spiro compound (Fig. 2) having methyl groups bonded to nitrogen and phenyl groups bonded to phosphorus leads to elemination of carbodiamide, and a monocyclic compound containing a λ^3–λ^4-phosphorus–phosphorus bond [5] is formed (Fig. 3).

The reaction of *N*,*N*′-bissilylated ureas with PCl_3 in a 1/1 molar ratio results in the formation of new bicyclic compounds containing phosphorus–phosphorus bonds, depending not on the substituents at the nitrogen atoms but on the reaction conditions. The compounds contain a λ^3P–λ^3P or a λ^3P–λ^4P bond [6] (Fig. 4 and Fig. 5).

Richman et al. have reported the synthesis and X-ray structure analysis of the first diphosphorane to contain a λ^5P–λ^5P bond; in this dicyclenephosphorane the phosphorus atoms are surrounded by tetrakis(substituted amino) groups. A 33 per cent distortion of the trigonal bipyramid at phosphorus towards a rectangular pyramidal geometry was observed [7]. We were able to show that the oxidation of 2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1λ^3,5λ^3-diphosphabicyclo[3.3.0]octane-3,7-dione with tetrachloro-*o*-benzoquinone gives the corresponding diphosphorane without

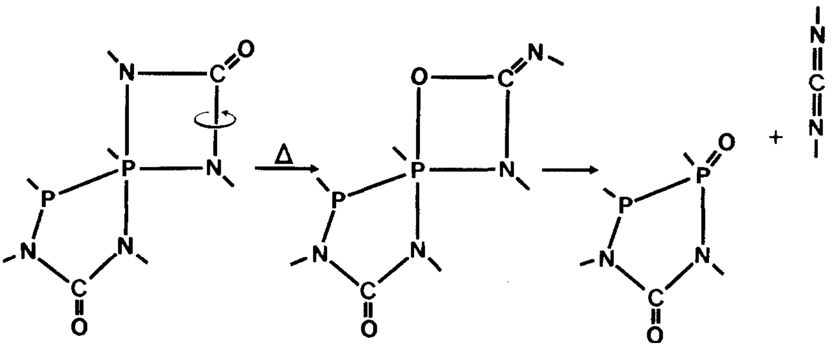


Fig. 2. Reaction pathway to λ^3 – λ^4-phosphorus–phosphorus compound (the methyl and phenyl groups are omitted for clarity).

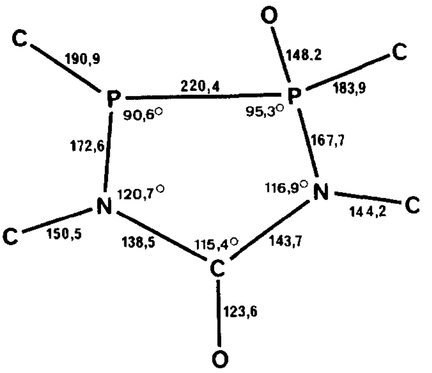


Fig. 3. λ^3 – λ^4-phosphorus–phosphorus compound (the hydrogen and further carbon atoms are omitted for clarity).

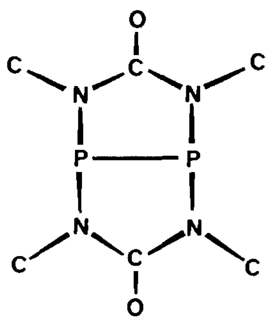


Fig. 4. λ^3P – λ^3P bicyclic phosphorus compound (the hydrogen atoms are omitted for clarity).

cleavage of the P–P bond. It is the first compound known to contain an axial λ^5P–λ^5P bond.

The molecular structure was confirmed by X-ray structural analysis. As would be expected on the basis of the relative electronegativities of the substituents at phosphorus, the five-membered ring of the tetrachloro-*o*-benzoquinone system adopts the preferred axial–equatorial placement. This forces the bicyclic component to take up the less favourable facial arrangement, with an axial P–P bridgehead and equatorial N-substituents. This compound has a λ^5P–λ^5P distance of 225.6(3) pm [8].

The reaction of the spirocyclic compound (Fig. 6) of composition $[OC(NCH_3)NC_6H_5]_2PCl$ with $NaP(O)(OC_2H_5)_2$ results in a phosphorus–phosphorus-bonded product. In this compound one phosphorus atom does not belong to a cyclic ring system, and the phosphorus atoms have coordination numbers of 5 and 4. Proof for the presence of the P–P bond is given by the ^{31}P NMR; the spin–spin coupling constant between the two phosphorus atoms is 708.9 Hz [9].

The preparation of polynuclear transition metal carbonyl complexes containing diphosphane ligands is of special interest, because such ligands may confer stability on the cluster unit and prevent it from fragmenting into monomeric units. The presence of more than one metal atom improves the catalytic potential in reactions in which multicentre interaction is important.

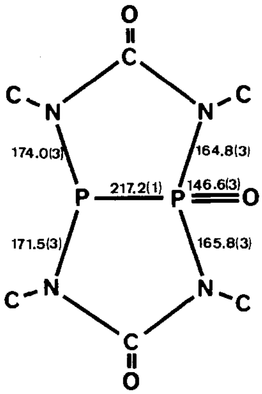


Fig. 5. λ^3P–λ^4P compound (the methyl groups are omitted for clarity).

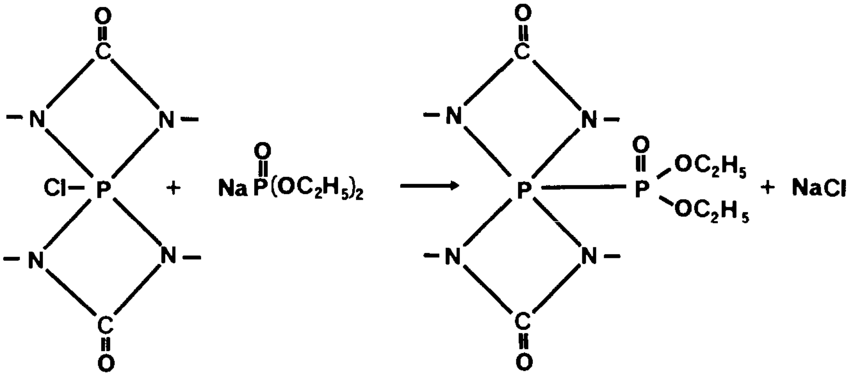


Fig. 6. $[CO(NCH_3)NC_6H_5]_2P–P(O)(OC_2H_5)_2$ (the methyl and phenyl groups are omitted for clarity).

Elegant syntheses of homobinuclear six-membered rings with diphosphane ligands were described by Vahrenkamp et al. [10]. The reaction of 2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1λ^3-5λ^3-diphosphabicyclo[3.3.0]octane-3,7-dione and $Cr(CO)_5THF$ results in the formation of the 1/1 and 2/1 metal diphosphane complexes without any oxidative cleavage of the phosphorus–phosphorus bond. The structure was confirmed by X-ray analysis. It crystallizes in the monoclinic space group $P2_1/c$ with unit cell constants a 1300.3(3), b 992.4(2), c 1457.7(3) pm, β 109.83(1)° and $Z = 4$. The λ^3P–λ^4P distance was found to be 221.7(4) pm (Fig. 7).

The bis(pentacarbonylchromium) complex can be vaporized without any noticeable decomposition. This compound can be stored in air without decomposition, is soluble in methylene chloride and ether, and can be recrystallized from THF.

Six-membered rings containing two metal and four phosphorus atoms were formed when the same ligand was treated with $Cr(CO)_4C_7H_8$, $Mo(CO)_4C_7H_8$ and $[Rh(CO)_2Cl]_2$ in equimolar stoichiometry. An unambiguously structural assignment

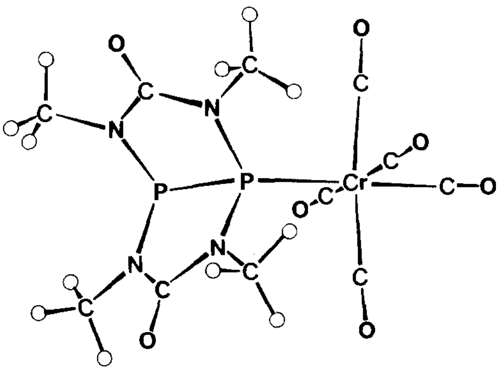


Fig. 7. $(CH_3N)_4(CO)_2P_2Cr(CO)_5$.

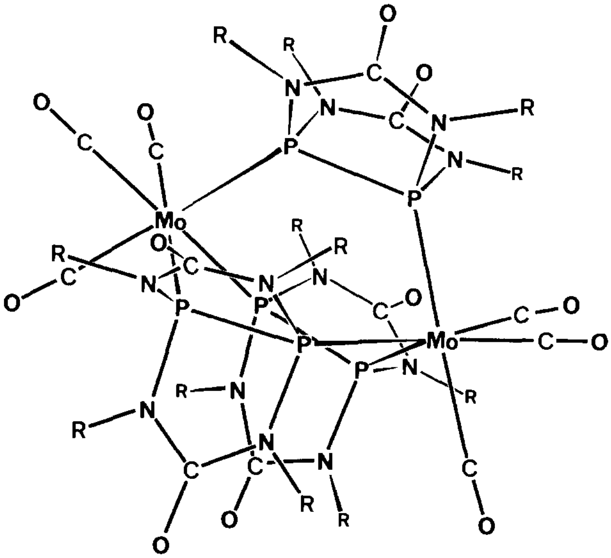


Fig. 8. $[(CH_3)_4(CO)_2P_2]_3Mo_2(CO)_6$.

could only be made by an X-ray structural analysis. The bicyclic phosphane ligands display an "open book" arrangement of the two five-membered P_2N_2C rings joined along the P–P bond. This complex displays crystallographic C_h-symmetry, with both chromium atoms and two of respective CO ligands lying in the mirror plane. A similar dimeric structure was observed for $[P_4(SiMe_2)_3Cr(CO)_4]_2$ [11]. A compound of composition $[(CO)_3Mo\{P_2[MeNC(O)NMe]_2\}_3Mo(CO)_3]$ was prepared from $Mo(CO)_3(C_7H_8)$ and the diphosphane ligand. The structure was investigated by X-ray analysis; the molecule possesses approximately 32 (D_3) symmetry, as can be seen from the figure in which the molecule is viewed along the Mo–Mo vector, which coincides with the pseudo-threefold axis (Fig. 8). There is no obvious explanation for the twist away from the idealised D_{3h} structure. The normal Mo–P and P–P distances result in Mo ··· Mo distance of 509.7(1) pm, too long for any bonding interaction [12]. In the course of our investigations on transition metal complexes of sulfur–nitrogen compounds we observed the enhanced oxidising capability of SO_2 in the presence of Zn^{2+}. Tetraphenyl diphosphane is smoothly oxidised and coordinated by $Zn(SO_2)_n(AsF_6)_2$ ($n = 2$–4) without rupture of the P–P bond. The ease of the oxygen transfer under zinc catalysis can be explained as due to the coordination of SO_2 via oxygen to the metal centre, which weakens the sulfur–oxygen bond.

$$Zn(SO_2)_n(AsF_6)_2 + 3\ P_2Ph_4 \rightarrow Zn[O_2P_2Ph_4]_3(AsF_6)_2 + S_n$$

Arsenic compounds

When the reaction of $(CF_3)_2AsN(SiMe_3)_2$ with chlorine is carried out in an exactly 1/1 molar ratio, $(CF_3)_2AsCl_2N(SiMe_3)_2$ is obtained. The compound possesses trigonal bipyramidal geometry with chlorine atoms occupying axial positions. The crystals are monoclinic $P2_1/m$ with a 929.8(4), b 1284.1(3), c 1509.0(2) pm, β 95.96(5)° and $Z = 4$. Both ^1H and ^{19}F NMR spectra in methylene chloride show one signal, virtually unchanged from 193 K to room temperature (Fig. 9).

When $(CF_3)_2AsN(SiMe_3)_2$ treated with excess of chlorine the dimer of

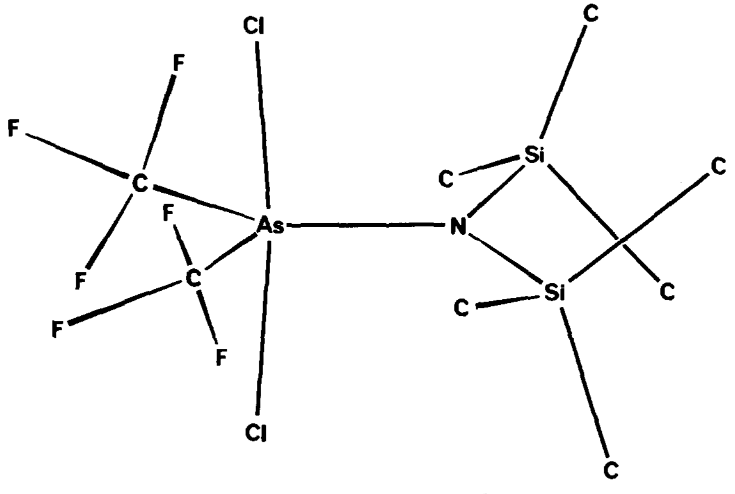


Fig. 9. Molecular structure of $(CF_3)_2AsCl_2N[SiMe_3]_2$.

$(CF_3)AsClNSiMe_3$ is formed. An X-ray structure analysis shows that this compound forms a planar four-membered arsenic-nitrogen ring (Fig. 10). A distorted trigonal bipyramidal geometry with axial and equitorial As–N distances of 193.3(7) and 176.8(7) pm were observed for the arsenic atoms. The difference between these bond lengths of 16.5 pm is somewhat larger than for the P–N distances in cyclodiphosphazanes. The axial As–Cl distance was found to be 229.6(4) pm. When this compound is refluxed in inert solvents or pyrolysed under vacuum, trimethylsilyl chloride and the trimeric and tetrameric bis(trifluoromethyl)arsazenes of composition $[(CF_3)_2AsN]_{3,4}$ are formed. The tetrameric bis(trifluoromethyl)arsazenes was investigated by an X-ray study. Figure 11 shows a view of the molecule (Fig. 11). The As and N atoms lie alternatively at ±38 and ±63 pm, respectively, from

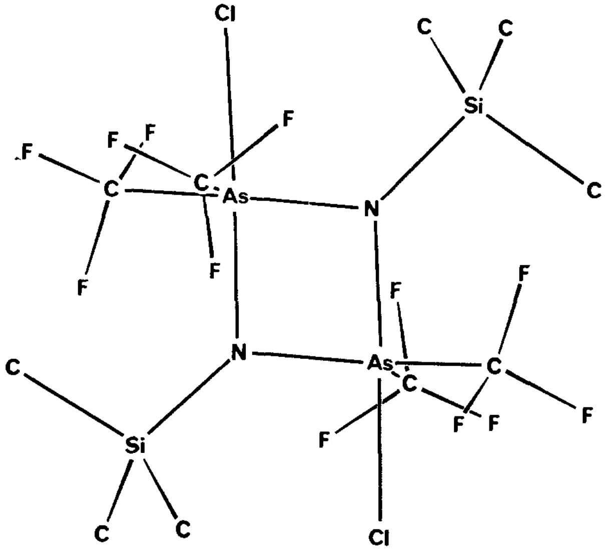


Fig. 10. Molecular structure of $[(CF_3)_2AsClNSiMe_3]_2$.

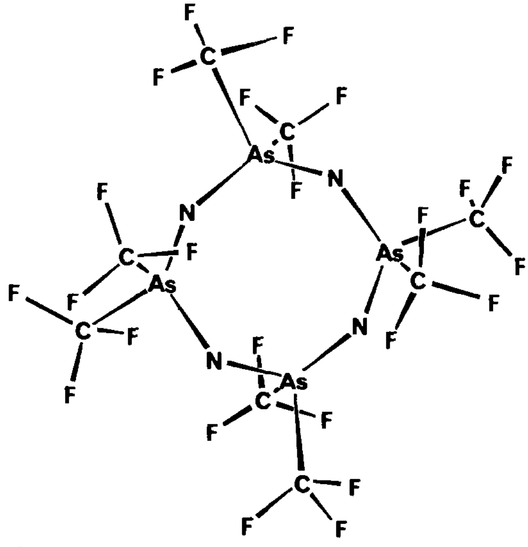


Fig. 11. Molecular structure of $[(CF_3)_2AsN]_4$.

the mean plane through the eight ring atoms. There is a barely significant alternation of the As–N bond lengths, the bonds in which both atoms are on the same side of the mean plane being slightly shorter (mean 171.6(7) pm) than those which cross the mean plane (mean 173.2(9) pm). A much more pronounced bond length alternation was observed in $(Ph_2AsN)_4$ [14–16].

Coordination compounds

The influence of the coinage metals in catalytic reactions can be shown. Reaction of $AgAsF_6$ with S_8 in liquid sulfur dioxide gives $Ag(S_8)_2AsF_6$, which contains cyclooctasulfur ligands (Fig. 12). The X-ray structure shows that the silver atoms achieve distorted four-coordination by 1,3-linkages to two S_8 rings. The silver atom is loosely coordinated with an irregular geometry to the two S_8 rings related by a twofold axis. The S_8 rings retain the usual crown conformation with S–S 204.0–206.4(3) pm. S–S–S 104.4–109.2(2)°, torsion angles 93.0–104.1(4)°. This wider spread of bond angles and torsion angles is the main difference between the S_8 ligand and S_8 in elemental sulfur. The torsion angle irregularities are not directly associated with the atoms bound to silver.

Cyanogen reacts with elemental sulfur in the presence of copper powder and dimethylformamide at 120°C to yield $S(CN)_4$. According to an X-ray structure analysis this molecule is an 1,2,4-thiadiazole-3,5-dicarbonitrile [17,18] (Fig. 13).

$S(CN)_4$ reacts with various reagents to yield imidic esters, thioimides and dicarboximides by using the different reactivities of the two nitrile groups. The first attack occurs at the nitrile group adjacent to sulfur [19].

Dichloro- or monochloro-phenylisocyanate dichloride reacts with elemental sulfur in the presence of iron powder to yield the thiazole in a 70% yield (Fig. 14).

Crown-ether complexes are formed when $AgAsF_6$ in liquid sulfur dioxide is treated with ethylene oxide, a crystalline complex of composition $[Ag(OCH_2\text{-}CH_2)_8][AsF_6]$ was obtained (Fig. 15). According to the X-ray structural investigation two ligands of 12-crown-4 are coordinated to silver. Silver(I) has coordination

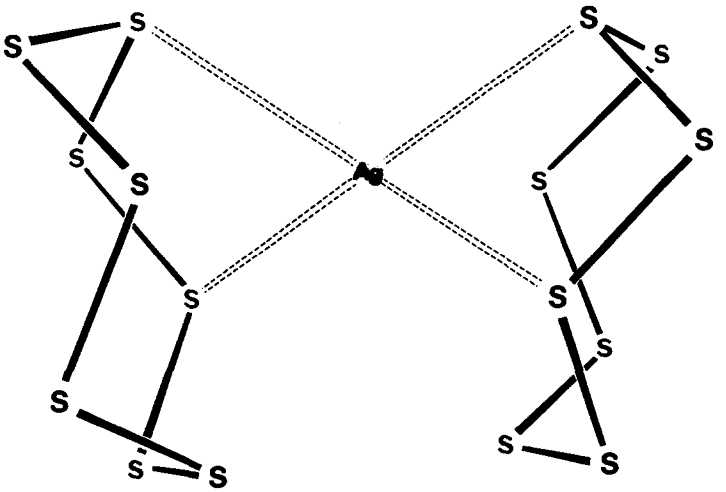


Fig. 12. Molecular structure of $Ag(S_8)_2{}^+$ $AsF_6{}^-$ (the anion AsF_6 is omitted for clarity).

number 8 in this complex. If instead of ethylene oxide the trimer of formaldehyde is used in the presence of silver(I), then a twelve-membered ring is formed. In contrast to crown-ethers this ring has the alternating elements carbon and oxygen (Fig. 16). The molecule forms three planes, one with three oxygen atoms. The oxygen atoms are coordinated to silver. The six carbon atoms are arranged in the second plane, and finally the third plane has three oxygen atoms coordinated to silver [20,21]. The structure of this molecule is similar to that of S_{12}.

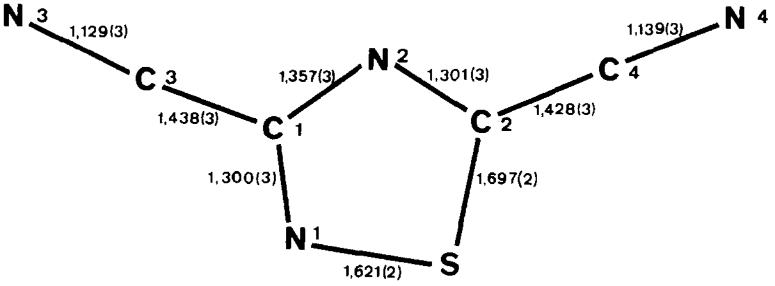


Fig. 13. Molecular structure of $S(CN)_4$.

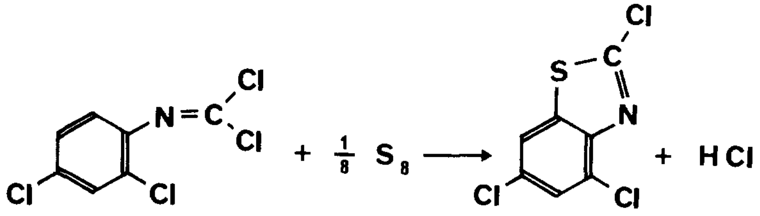
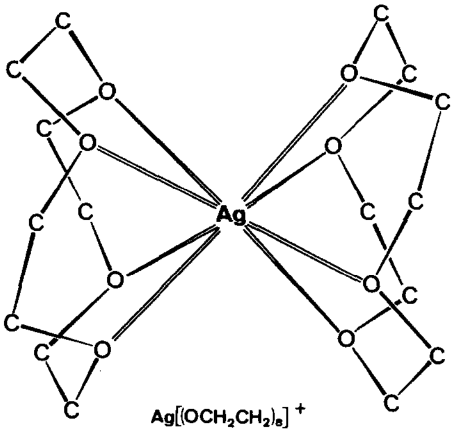


Fig. 14. The reaction of an isocyanate dichloride with elemental sulfur.



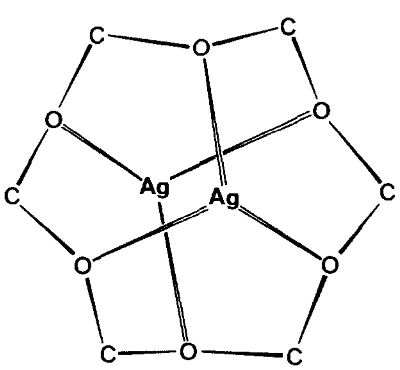


Fig. 15. Molecular structure of $[Ag(OCH_2CH_2)_8]^+$ AsF_6^- (the anion AsF_6 is omitted for clarity).

Fig. 16. Molecular structure of $[Ag_2(OCH_2)_6]^{2+}$ $2AsF_6^-$ (the hydrogen atoms and the anions AsF_6 are omitted for clarity).

Acknowledgement

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