8. Silver 1992

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CONTENTS

INTRODUCTION

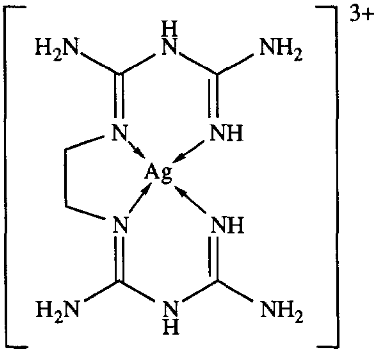
This review surveys the coordination chemistry of silver reported during the year 1992 and is similar in format to the corresponding review dealing with the 1991 literature [1]. The literature has been searched by using both *Current Contents* and the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2]. Structural figures have been redrawn using atomic coordinates; hydrogen atoms have been omitted for clarity.

Organometallic complexes have not been included in this survey, and this exclusion also covers low oxidation state transition metal cluster compounds which bear {AgL}-units where, for example, L is a phosphine ligand.

Two papers are relevant to the subject of extraction and analysis. Trace quantities of silver, for example in geological samples, can be analysed by using sodium 2-(8-hydroxyquinolin-5-ylazo)benzoate in aqueous solution in the presence of sodium/potassium tartrate (pH 5.2-6.1). With silver present, a purple coloration which lasts for up to 24 hr is obtained [3]. The relative effectiveness of Bu_2S, Bu_2Se and Bu_2Te in the extraction of gold and silver has been studied by using atomic absorption spectrometry. For the extraction of silver(I) ions, Bu_2Se and Bu_2Te prove to be better than the sulfur analogue; for gold(I), Bu_2S and Bu_2Se are preferred. The efficiency of the extraction process is dependent upon the solution pH [4].

8.1 SILVER(III)

The oxidation of cyanide ion by silver(III) in alkaline media has been investigated [5]. The silver(III) cation (1) has been isolated as the perchlorate salt. The acyclic tetra-aza-ligand stabilises the system (log $K \approx 52$). The report of this complex cation forms part of an investigation of the silver(I) catalysed oxidation of H_3PO_2 using (**1**). The silver(III) complex oxidises H_3PO_2 and the reaction is catalysed by silver(I) ions. The products are silver(I) ions [formed from (**1**)], the free acyclic ligand, and phosphite ion. The kinetics of the reaction have been discussed and a mechanism proposed [6].



(1)

8.2 SILVER(II)

The silver(II) complex $[Ag(py)_4][S_2O_8]$ has been prepared from silver(I) nitrate, potassium peroxodisulfate and pyridine. Its uses as an oxidation reagent have been studied, for example in the oxidation of aromatic aldehydes to acids, benzylic alcohols to carbonyls, and aryl thiols to sulfonic acids [7].

8.3 SILVER(I)

8.3.1 Complexes with halide and pseudo-halide ligands

The crystal structure of the bis(dimethylenedithio)tetrathiafulvalene salt of $[Ag(CN)_2]^-$ has been determined [8]. The salt $[PPN][Ag(CN)_2]$ may be prepared by metathesis from [PPN]Cl and $K[Ag(CN)_2]$. The infrared spectrum of $[PPN][Ag(CN)_2]$ shows two absorptions at 2131 and 2138 cm^{-1} which are characteristic of the cyano ligands. The salt reacts with Ph_3SnCl to give $[PPN][ClPh_3Sn(\mu\text{-}NC)AgCN]$, the IR spectrum of which exhibits bands at 2131 and 2143 cm^{-1}.

The new compound has also been characterised by ^{119}Sn NMR spectroscopy and X-ray diffraction methods. For comparison, the crystal structure of $[PPN][Ag(CN)_2]$ has also been determined. In both anions, the silver centre is close to being in a linear environment: in $[Ag(CN)_2]^-$, ∠C-Ag-C = 176(1)°, and in $[ClPh_3Sn(\mu\text{-}NC)AgCN]^-$, ∠C-Ag-C = 177.0(3)°. In the latter species, the environment of the nitrogen atom in the cyano bridge also approaches linearity (∠C≡N-Sn = 167.7(5)°) [9].

In the solid state, the salt $[Ph_2I][Ag(CN)_2]$ resists decomposition up to 160°C. Above this temperature, the volatiles PhI, PhNC and $(CN)_2$ are observed, and above 500°C, solid silver is present. Thermodynamic data provide a value for $\Delta H_{\text{melting}}$ of -28 kJ mol^{-1} for $[Ph_2I][Ag(CN)_2]$ [10].

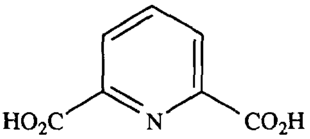
The unusual iodo species $[Ag_5I_7]^{2-}$ [structure (**25**)] is described in section 8.3.5.

8.3.2 Complexes with oxygen donor ligands

An investigation of the solid state structure of $Ag_2H_2P_2O_7$ has revealed the presence of infinite $[H_2P_2O_7{}^{2-}]_n$ units which run parallel to the crystallographic *b* axis. Within this system, hydrogen bonding is an important structural feature [11]. Averbuch-Pouchet and coworkers have also presented data on $Ag_4K_6P_{10}O_{30}.10H_2O$. In the solid state, a $[P_{10}O_{30}]^{10-}$ structural motif is present — this is an unusual centrosymmetric, cyclic unit. Four-coordinate silver atoms are incorporated into Ag_4O_{10} clusters [12]. Another interesting structural study is that of $Ag_{20}O_{33}H_{22}(ClO_4)_4$, which is formed by the electrochemical oxidation of aqueous $AgClO_4$ ($[Ag]^+$ = 2 M). The solid state structure consists of $[H_{22}O_{17}]^{12-}$ clusters which are likened to gas hydrates. These units are linked together via Ag-O bonds; a three dimensional network results [13].

The preparation and crystal structural determination of a 1:1 silver(I) nitrate-urea complex have been described. The results confirm the polymeric nature of the complex which is formulated as $[(AgNO_3)_2\{OC(NH_2)_2\}_2]_n$. In the solid state, it contains two independent silver(I) centres. The first is three-coordinate (trigonal planar) with Ag-O bonds to two nitrate ions and the oxygen atom of one urea molecule. In the second site, a silver(I) ion is tetrahedrally coordinated to two nitrate ions and to a urea molecule which bonds in an *N,O*-mode [14].

The synthesis of $[(Ph_3P)_2AgL]$ where HL is 2,4,6-trichlorophenol has been reported. The product has been characterised by X-ray crystallographic and ^{35}Cl NQR spectroscopic studies. Related complexes have also been studied. In $[(Ph_3P)_2AgL]$, the silver(I) centre is three-coordinate, with one Ag-O and two Ag-P interactions. Within the crystal lattice, a further weak interaction is observed to a chlorine atom of the ligand L$^-$ in the next molecule (Ag----Cl = 3.160(2) Å) [15].



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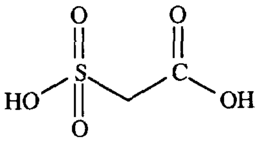
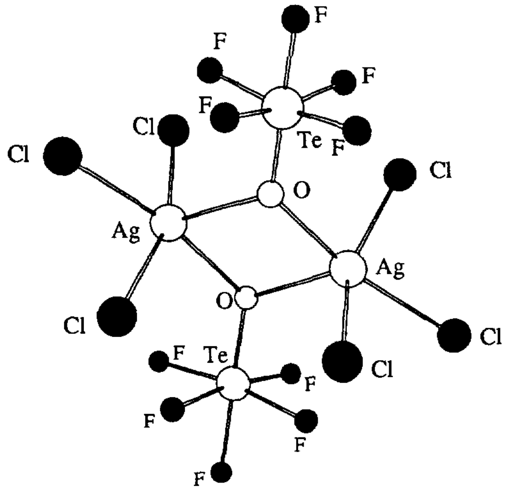


(3)

The complex [Ag(HL)(H_2L)].H_2O in which H_2L is ligand (**2**), reacts with $Gd(NO_3)_3$ in aqueous MeOH to generate [Ag{$GdL_2(H_2O)_3$}].$3H_2O$. Structural characterisation of this complex reveals a nine-coordinate Gd(III) centre. The silver(I) ion is coordinated by two CO_2^- groups of the conjugate base of ligand (**2**). The net result is a polymeric structure in the solid state [16].

The crystal structure of disilver(I) sulfoacetate monohydrate has been determined. The ligand, L^{2-} where H_2L = (**3**), is involved in a chelate ring to one silver(I) centre. This metal centre is octahedrally coordinated with Ag-O distances lying between 2.393(4) and 2.671(5)Å. The lattice contains a second silver(I) environment, which is distorted tetrahedral with Ag-O distances of 2.222(3) to 2.587(4)Å. This forms part of a centrosymmetric 8-membered ring consisting of two carboxylate groups and two of the 4-coordinate silver centres [17].

A series of papers deals with salts involving the $[OTeF_5]^-$ ion. The reactions of $B(OTeF_5)_3$ with $[AgOTeF_5]$ in weakly coordinating solvents, solv, lead to the formation of $[Ag(solv)_x][B(OTeF_5)_4]$. For solv = 1,1,2-trichlorotrifluoroethane, a crystallographic study of the complex reveals that the Ag^+ ion is weakly coordinated by three $[B(OTeF_5)_4]^-$ ligands via Ag-O (2.500-2.756Å) and Ag-F (2.644-3.017Å) interactions [18]. Treatment of $NbCl_5$ and $TiCl_4$ with an excess of $[AgOTeF_5]$ leads to the formation of the complexes $[AgNb(OTeF_5)_6]$ and $[AgTi(OTeF_5)_6]$, respectively. The silver-titanium complex has been crystallographically characterised. Dichloromethane solvent molecules are incorporated into the lattice to give a system which is formulated as $[Ag(CH_2Cl_2)]_2[Ti(OTeF_5)_6]$; the centrosymmetric anions bridge between symmetry related cations [19]. The compound $[Ag(1,2,3\text{-}C_3H_5Cl_3)(OTeF_5)]$ (**44**), can be crystallised from a solution of $[AgOTeF_5]$ in 1,2,3-$C_3H_5Cl_3$. The solid state structure consists of a chain-like array, in which centrosymmetric {$Ag_2(\mu\text{-}OTeF_5)_2$}-units are linked by the chlorinated solvent molecules [20].

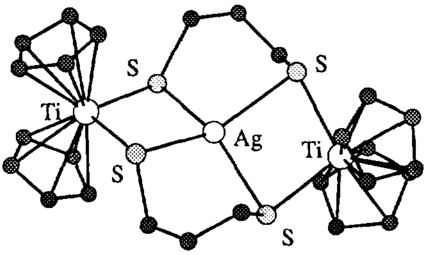


Only Cl atoms of the solvent molecules are shown.

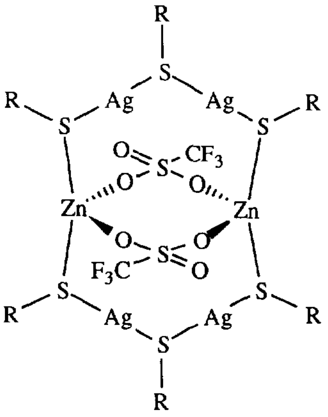
(4)

8.3.3 Complexes with sulfur donor ligands

The reactions of [Cp_2TiCl_2] with $HS(CH_2)_2SH$ and $HS(CH_2)_3SH$ in the presence of imidazole lead to dititanium complexes of type [$\{Cp_2Ti\}_2(\mu\text{-}L)_2$] (L = dithiol), the structural nature of which depends upon the length of the dithiol chain. Both complexes act as macrocyclic ligands and react with $AgBPh_4$. The complex cation [$Ag\{Cp_2Ti\}_2(\mu\text{-}HS(CH_2)_3SH)_2$]$^+$ (**5**) has been isolated as the tetraphenylborate salt and crystallographically characterised. The arrangement of the two titanium and silver centres is an approximately linear one. The silver(I) centre is coordinated within a distorted tetrahedral array of sulfur donor atoms with Ag-S distances lying in the range 2.518(8) to 2.70(1)Å for two independent molecules. Cation (**5**) is reduced (one electron reduction) on treatment with Cp_2Co. Electrochemical studies have also been carried out. The initial dititanium complexes show irreversible reductions but with the silver(I) present, a quasi-reversible one-electron reduction is observed. (A second irreversible wave is due to the Ti(IV)/Ti(III) couple) [21].



(**5**)



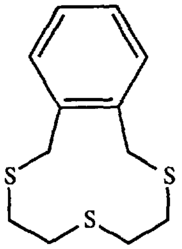
R = 2,4,6-$^iPr_3C_6H_2$

(**6**)

The silver(I) salt [AgO_3SCF_3] reacts with 2,4,6-$^iPr_3C_6H_2SH$ and $Zn\{N(SiMe_3)_2\}$ (4:6:4 ratio) to give a tetrasilver-dizinc product (**6**) which is remarkably stable in solution, but is moisture sensitive. The product has been characterised by ^1H NMR spectroscopy and X-ray crystallography. The $Ag_4Zn_2S_6$-ring adopts a chair conformation in the solid state [22]. The results of a study using circular dichroism of silver(I) bonding to rabbit liver zinc metallothionen have been reported [23].

The reactions of silver(I) nitrate with imidazolidine-2-thione, 1,3-diazinane-2-thione and their derivatives (L) lead to complexes of the general type $[AgL(NO_3)]$. From the results of NMR spectroscopic studies, it is concluded that the diazinane-based ligands bind more strongly than the imidazolidine ligands [24].

Macrocyclic chemistry involving silver(I) complexes of sulfur-containing ligands is well represented in the 1992 literature. The reactions of ligand L = (7) with AgX ($X^- = ClO_4^-$, BF_4^-, BPh_4^- or $CF_3SO_3^-$) in which the ligand is present in a two-fold excess lead to the formation of the complexes $[AgL_2]X$. The solid state structures of these species are dependent upon the anion. In the perchlorate and tetrafluoroborate salts, octahedrally coordinated Ag^+ centres are observed, with two facially coordinated ligands. In the tetraphenylborate salt, the silver(I) environment is a distorted tetrahedral one; two sulfur donor atoms are involved per ligand. In $[AgL_2][CF_3SO_3]$, the silver(I) centre is again tetrahedrally coordinated, but this time the coordination shell involves three *S*-donors from one ligand and one from the second macrocycle. Variable temperature ^1H NMR spectroscopic studies indicate that the cationic complex is fluxional in solution [25]. Ligand (7) has also been studied in conjunction with isomeric macrocycles (8) and (9), the aim of this work being to relate conformational properties of the ligands to their selectivity towards silver(I) ions. Structural and spectroscopic data have been analysed in detail [26].



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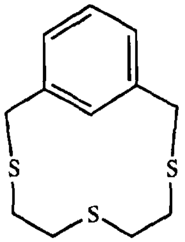

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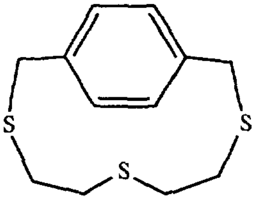

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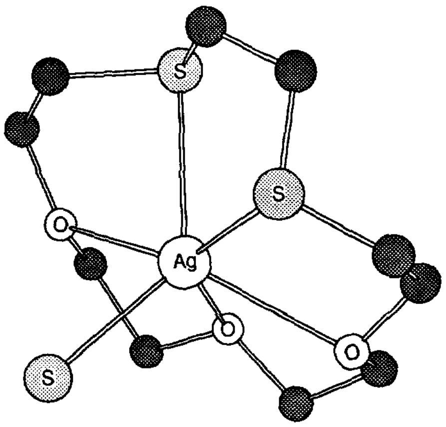
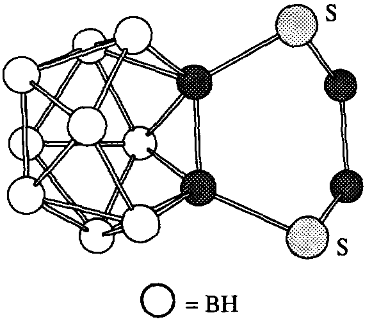


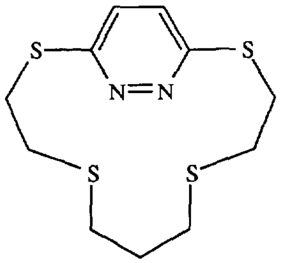
(10)

The reaction of silver(I) nitrate with the ligand [15]aneS_2O_3 (L) in the presence of the hexafluorophosphate ion leads to the formation of the two complexes $[Ag_nL_n][PF_6]_n$ and $[Ag_2L_3][PF_6]_2$. Both have been crystallographically characterised. In the latter, there is a distorted trigonal planar array of sulfur donor atoms about each Ag^+ centre and only long range Ag---O contacts are observed. In the former, the cationic units are bridged by sulfur atoms to generate a polymeric-chain. Each silver(I) centre is in a six-coordinate S_2O_3S-array as shown in (**10**); the unique sulfur donor atom belongs to the next macrocyclic ligand in the chain [27].

The reaction of $AgNO_3$ with the sulfur-containing macrocyclic ligand $[7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (**11**) leads to a novel product. However, the conditions of the reaction are critical; in methanol, ethanol or water-acetone, silver metal precipitates, but in the presence of cobalt(II) nitrate in water-acetone, the anion $[Ag\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}_2]^-$ is generated. The tetramethylammonium salt has been characterised in the solid state by X-ray diffraction and in solution by ^{11}B and ^1H NMR spectroscopies. The anion exhibits a chain-like structure with a sequence ····Ag-S-carb-S-(ScarbS)Ag-S-carb-S-Ag(ScarbS)-S-carb-S-Ag···· [28].



(**11**)



(**12**)

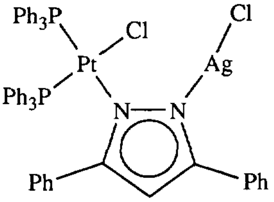
The preparation of ligand (**12**) and a study of its properties, including complex formation with silver(I) ions have been reported. The complexes [Ag(**12**)][ClO_4].MeCN, [Ag(**12**)][NO_3] and $[Ag(\mathbf{12})(ClO_4)]_x$ have been synthesised. In the solid state, the structure of $[Ag(\mathbf{12})(ClO_4)]_x$ consists of a polymeric, two-dimensional sheet. Each silver (I) centre is tetrahedrally coordinated by an S_2-donor set from ligand (**12**) and two *O*-donors from perchlorate ions. Infrared spectral data are also reported [29].

8.3.4 Complexes with nitrogen donor ligands

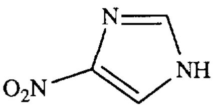
The formation of ammonia complexes is often part of undergraduate practical exercises. Such an experiment has been detailed for student use: the titration of silver(I) nitrate with ammonia and 1,2-diaminoethane. This experiment has two aims — to illustrate chelation and to initiate the student into simple analytical techniques [30].

The crystal structure of $[Ag(NH_3)_2]_2[SO_4]$ has been redetermined. Metal-over-metal stacks are observed in the lattice, with Ag-----Ag distances of 3.200Å. Hydrogen bonded interactions are an important feature in the structure. In the $[Ag(NH_3)_2]^+$ cation, the value of ∠N-Ag-N is 174.3° and the bending away from linearity is attributed to additional Ag---$O_{sulfate}$ interactions [31].

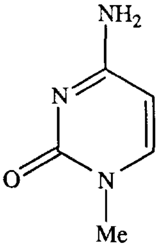
A series of heterometallic complexes involving the 3,5-diphenylpyrazolate ligand (L^-) has been described. The group includes complex (**13**) which is formed by reacting *cis*-$[PtCl(PPh_3)_2L]$ (the synthesis of which is detailed) with silver(I) chloride in dichloromethane. Colourless crystals of (**13**) have been analysed by X-ray diffraction methods. The two metal atoms are at a non-bonded separation of 3.317(2)Å. The Ag-N distance is 2.076(18)Å [32]. The reaction of $AgNO_3$ or $AgBF_4$ with the substituted imidazole (**14**), HL, in a neutral or weakly acidic solution leads to the formation of an insoluble complex [AgL]. Infrared and ^{13}C NMR spectroscopic data are consistent with the presence of a polymeric system with bridging ligands. If the reactions are carried out in strongly acidic solution, the products are $[Ag(\mathbf{14})_2]X$ ($X^- = NO_3^-$ or BF_4^-). Both salts have been crystallographically characterised. In each cation, the silver(I) centre is slightly bent (∠N-Ag-N = 169.9(1)° for $X^- = NO_3^-$, and 175.2(1)° for $X^- = BF_4^-$) with the two ligands being in a primarily *N*-donor mode. Secondary Ag----O interactions involving the NO_2-groups appear to be responsible for the deviations from linearity. In dmso solution, ^1H and ^{13}C NMR spectroscopic data illustrate that dissociation of the complex cations occurs. Infrared and CP-MAS ^{13}C NMR spectroscopic results are also reported [33].



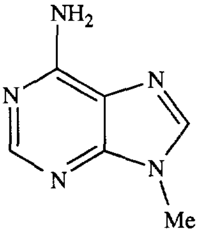
(**13**)



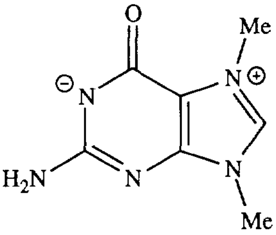
(**14**)



(**15**)



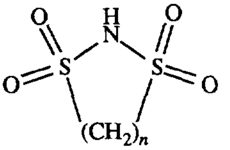
(**16**)



(**17**)

The model nucleobases (**15**)–(**17**) have been synthesised, and their participation in complex formation studied. Silver(I) complexes described are $[Ag(\mathbf{15})(\mathbf{17})(NO_3)]_2.[(\mathbf{15})(\mathbf{17})(PF_6)].10H_2O$ and $[Ag(\mathbf{15})(\mathbf{16})(H_2O)][NO_3]$. An X-ray diffraction study of the latter complex reveals that ligand (**15**) bonds through atom N^3 whilst ligand (**16**) is coordinated through atom N^7. The silver(I) centre is described as being in a severely distorted trigonal planar environment; distances are Ag-N = 2.128(2) and 2.120(2)Å and Ag-O_{water} = 2.664(2)Å. The Ag-O interaction is therefore weak, but the results are in accord with the water molecule being a part of the metal-modified base-pair. The information gained from the study permits Menzer *et al* to set out a discussion of a novel view of metal ion-nucleobase interactions [34].

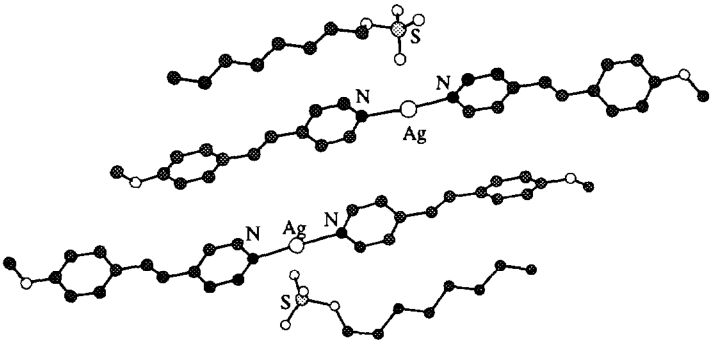
The results of structural investigations of some silver(I) salts containing cyclic sulfonamides, HL, (**18**) have been reported. The two complexes [AgL].H_2O possess lamellar structures with stacked two-dimensional polymeric layers of ions. The layers exhibit a hydrophobic inner region which contains the silver(I) ions; the latter bind strongly to the sulfonyl and imide groups [35].



$n = 3$ or 4

(**18**)

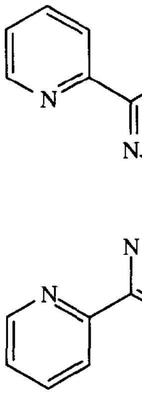
Reports of silver(I) complexes incorporating pyridine-based ligands are varied. The following discussion is organised according to the increasing complexity of the ligands involved. The reactions of $[AgL_2][CF_3SO_3]$ (L = 4-(4-alkoxystyryl)pyridine in which the alkoxy group ranges from methoxy to dodecyloxy) with $NaO_3SO(CH_2)_7Me$ lead to the complexes $[AgL_2][O_3SO(CH_2)_7Me]$ in good yields. These are mesomorphic systems which exhibit a nematic phase for short alkoxy chains, and S_C and S_A phases for longer chain lengths. The crystal structure of $[AgL_2][O_3SO(CH_2)_7Me]$ (**19**) where L = 4-(4-methoxystyryl)pyridine has been elucidated. Centrosymmetric pairs of molecules are linked via hydrogen bonding interactions which involve water molecules present in the crystal lattice. These interactions are not shown in the structure drawn in (**19**) [36].



(**19**)

The crystal structure of $[AgL][NO_3]$ in which L is 6,6'-dimethyl-2,2'-bipyridine, has been determined. In the solid state, dimers are present due to interactions between symmetry related cations. Weak Ag---Ag interactions as well as π-stacking between slipped heterocyclic rings are features that are discussed. The coordination environment about each silver(I) centre approximates to being planar, but there is a 15° distortion in the direction of it being a tetrahedral coordination sphere. The nitrate ions are coordinated in an asymmetrical fashion [37].

Double-helical self-assembly has been demonstrated for the ligand 2,2':6',2":6",2"'-quaterpyridine (**20**) in the formation of $[Ag_2(\mathbf{20})_2][BF_4]_2$. This ligand is not sterically constrained and from the structural data available, it is possible for Constable *et al* to suggest that double-helical complexes can form in the *absence* of steric constraint. However, substituents do control the pitch of the helix. In $[Ag_2(\mathbf{20})_2]^{2+}$, each silver(I) centre is four-coordinate and the Ag-Ag separation is 3.107(2)Å which is considered to be consistent with an interaction [38]. Silver(I) binding by the ligands (**21**) has been investigated by using spectroscopic and potentiometric methods. The double stranded helicate $[Ag_3L_2]^{3+}$ assembles in a process that illustrates binding-cooperativity [39]. Amongst new bpy-derived ligands used by Beer *et al* are (**22**) and (**23**). Silver(I) complexes that have been prepared are $[Ag_2(\mathbf{22})]^{2+}$ and $[Ag(\mathbf{23})]^{+}$. The spectroscopic (including solution ^{1}H NMR) characterisation of these cations has been detailed. In the disilver species, it is proposed that each silver(I) ion is bound in an *N,N'*-mode by a bpy-moiety in addition to interactions with either two *O*- or *S*-donor atoms [40].



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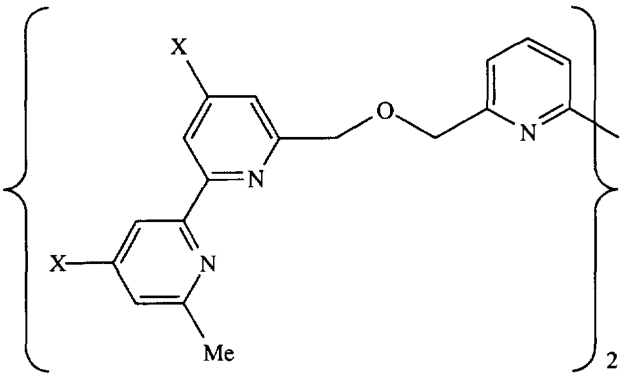
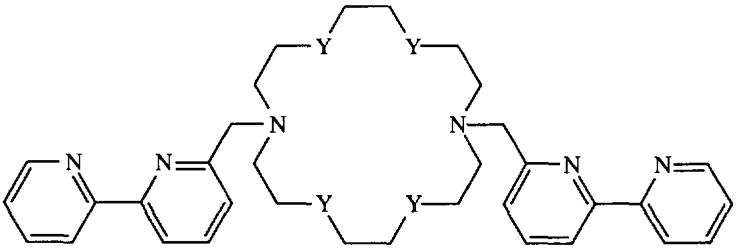


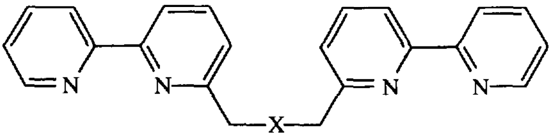
X = H or $CH_2CH_2CO_2{}^tBu$

(21)



Y = O or S

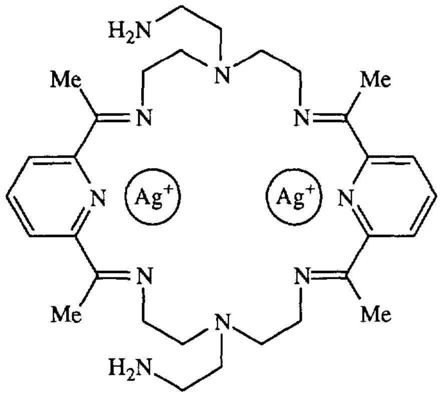
(22)



X = N(tosyl) or $N(tosyl)CH_2CH_2N(tosyl)CH_2CH_2N(tosyl)$

(23)

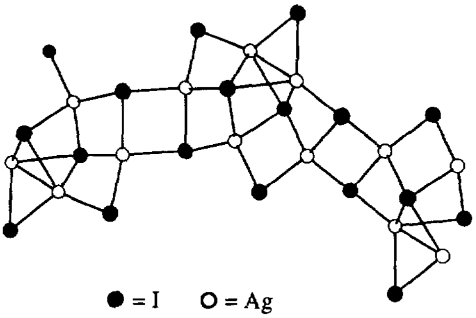
The silver(I)-templated cyclocondensation of tris(2-aminoethyl)amine and 2,6-diacetylpyridine has been previously reported to yield (**24**). In the present investigation of the system, it has been found that this disilver(I) complex reacts with acetone in a methanol solution to give a new yellow product in which the pendant amine groups of (**24**) have undergone a condensation reaction with acetone. An X-ray diffraction study of the new product illustrates that each silver ion in five-coordinate, bound by four *N*-donor atoms of the ring in addition to one of the pendant *N*-donor atoms. The ligand retains a relatively open conformation and the two silver(I) centres are considered to be remote from one another [41]. Further, related chemistry involving complexes of Schiff base ligands derived from *N,N*-bis(2-aminoalkyl)-2-phenylethylamines, has also been described [42].



(24)

8.3.5 Complexes with phosphorus donor ligands

The complex $[(Ph_3P)_2AgL]$ where HL is 2,4,6-trichlorophenol was described in section 8.3.2 [15]. A sterically hindered and very basic phosphine ligand has been incorporated into the silver(I) complexes $[\{(2,4,6\text{-}(MeO)_3C_3H_2)_3P\}AgX]$ (X = Cl or Br). Both products are mononuclear and exhibit an almost linear silver(I) centre; in the chloride complex, the angle P-Ag-Cl is 175.0° whilst in the bromide, the angle P-Ag-Br is 174.4°. In the far infrared spectrum, strong absorptions at 282 and 215 cm^{-1} are observed and these are assigned to the modes ν(Ag-Cl) and ν(Ag-Br) respectively. A ^{31}P NMR spectroscopic study of the complexes in solution shows that reaction with another equivalent of ligand takes place to generate the species $[\{(2,4,6\text{-}(MeO)_3C_3H_2)_3P\}_2Ag]^+X^-$ [43]. In related work by the same authors, the reaction of $P(C_3H_2(MeO)_3\text{-}2,4,6)_3$ with silver(I) iodide gives the unexpected product *catena*-$[\{(2,4,6\text{-}(MeO)_3C_3H_2)_3P\}_2Ag]_2[Ag_5I_7]$. The nature of this salt has been confirmed by use of X-ray crystallography. The lattice contains two crystallographically inequivalent cations. In one, the ∠P-Ag-P is 179(1)°, and in the other this angle is 175.9(9)°. The $[Ag_5I_7]^{2-}$ anion is indeed novel. It possesses a one-dimensional polymeric structure which is described as being a 'double stranded ladder' of AgI units. Part of this ladder is shown in structure (25) [44].



(25)

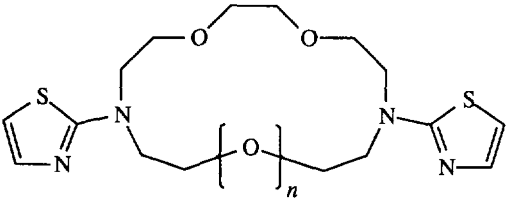
When silver(I) nitrate reacts with 1,1'-bis(diphenylphosphino)ferrocene, the product is a dimeric complex characterised as $[\{Ag(NO_3)(dppf)\}_2]$. In the presence of the sodium carboxylates NaO_2CMe, NaO_2CH or NaO_2CPh, the reaction yields $[\{Ag_2(MeCO_2)_2(dppf)\}_2]$, $[Ag_2(PhCO_2)_2(dppf)]$ or $[Ag_2(HCO_2)_2(dppf)_3]$, respectively. Crystallographic data have evidenced the varying nature of these complexes and the structural differences have been discussed; a variable ligation mode for the carboxylate ligands has been observed [45].

8.3.6 Complexes with mixed donor atom ligands

In this section, silver(I) complexes which involve ligands with mixed donor atom sets are described. These are grouped according to the donor atoms, in the sequence *N,O*-, *N,S*- and *O,S*-donors.

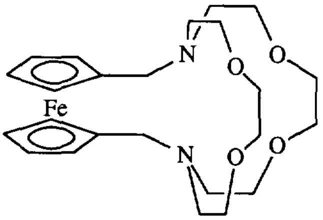
The doubly-substituted diaza-crown ether ligands (**26**) complex with silver(I) ions to yield dinuclear species. For $n = 2$ in (**26**), the compound $[Ag_2(\mathbf{26})(OSO_2CF_3)_2]$ has been isolated and crystallographically characterised. Each metal centre is bound to a nitrogen and an oxygen donor atom within the ring, and to an *N*-donor atom of the heterocyclic side-arm. An *O*-bound $[OSO_2CF_3]^-$ anion completes the silver(I) coordination shell. The Ag–Ag separation in the complex is 2.790Å, and this relatively short distance indicates the presence of a metal-metal bonding interaction. For $n = 1$ in (**26**), two silver(I) ions are again complexed. However, in this instance, one metal ion only is bound within the macrocyclic cavity; the crown ether functions as an *O,O',O''*-donor, and the silver(I) centre is in a four-coordinate environment with the fourth site occupied by an

O-bound $[OSO_2CF_3]^-$ ion. The second silver(I) ion interacts with *N*-donor atoms of the exo-heterocyclic substituents in addition to a $[OSO_2CF_3]^-$ anion. This mode of coordination for ligand (**26**) ($n = 1$) forces the two metal atoms further apart with respect to the mode adopted by (**26**) ($n = 2$); the Ag--Ag separation becomes 2.969Å [46].

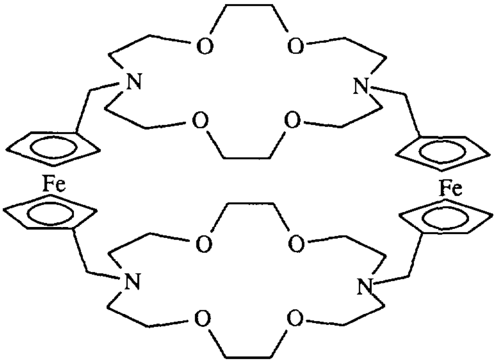


$n = 1$ or 2

(**26**)



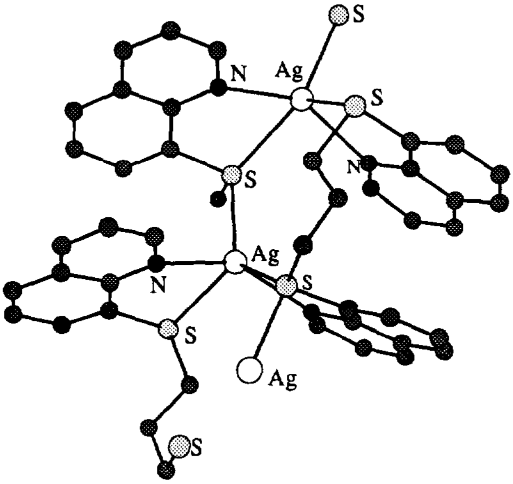
(**27**)



(**28**)

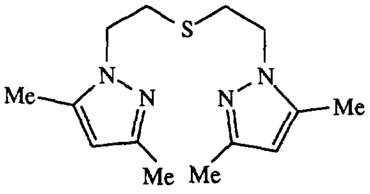
The ferrocene-cryptand ligands (**27**) and (**28**) are two in a series of three new such macrocycles prepared by Medina *et al.* The solid state structure of (**27**).H_2O has been elucidated. Complex formation between ligand (**27**) and *s* block metal or silver(I) ions has been studied; stability constants have been determined. The incorporation of Ag^+ by this cryptand involves an Ag–Fe interaction; this is supported by a large silver(I) binding constant, and ^1H NMR and UV-VIS spectroscopic data. The first observation of redox switching involving silver(I) ions in aqueous solution has been recorded with this system. Ligand (**28**) also complexes with silver(I) ions and the product contains the cation $[Ag_2(\mathbf{28})]^{2+}$. It is proposed that this possesses a structure in which each silver(I) ion coordinates to an *N,O,O'*-donor set of each half of the ligand with an additional Ag-Fe interaction stabilising the system [47].

Ligands with sulfur and nitrogen donor atoms span both acyclic and cyclic species. The single crystal structure of $[AgL][NO_3]$ in which L is 1,3-bis(8-quinolylthio)propane has been determined. The conformational preference of the ligand allows the formation of a polymeric species; part of this structure is shown in (**29**). Each silver(I) centre is five-coordinate. 1,3-Bis(8-quinolylthio)propane functions in a bis(didentate) manner, coordinating to two, symmetry related silver(I) ions. One sulfur atom per ligand takes part in a bridging interaction between adjacent silver centres [48].

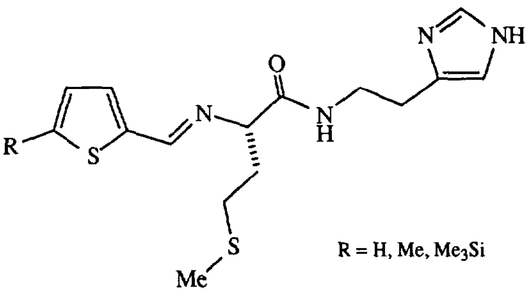


(29)

The complex [Ag(**30**)(NO_3)] is amongst a series of related species that have been prepared and studied. Crystallographic data for this complex show that the silver(I) ion is in a distorted tetrahedral environment. Ligand (**30**) utilises the sulfur and two nitrogen donor atoms, and each silver(I) ion is further coordinated to one *O*-donor atom of a nitrate ion. The Ag-N distances are 2.483(5) and 2.216(4)Å and the Ag-S bond length is 2.571(2)Å. The ligands are associated with the metal ions so as to generate a polymeric array in the crystal lattice; this arises because the two nitrogen donor atoms per silver(I) centre are from two different ligand molecules [49].



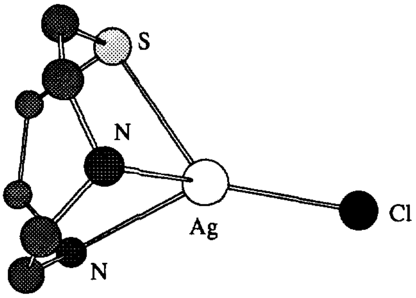
(30)



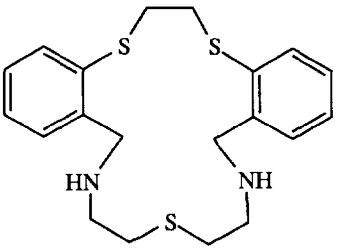
(31)

The reactions of [AgO_3SCF_3] with each of the ligands in the family shown in structure (**31**) produce stable silver(I) complexes. Complex characterisation has been by use of ^{19}F, ^{1}H and ^{109}Ag NMR, UV-VIS and CD spectroscopies. In addition, the crystal structure of [Ag(**31**)][O_3SCF_3] for R = Me has been determined. A polymeric array is observed, in which each ligand interacts with three silver(I) centres. The local environment at each metal ion is trigonal planar, and consists of an *N,N',S*-donor set. In addition, there is a weak Ag-O interaction (2.568Å) involving the amido-*O* atom. The solution spectroscopic results support the presence of an oligomeric structure [50].

The nine-membered macrocyclic ligand [9]aneN_2S binds silver(I) ions. The complex [Ag{[9]aneN_2S}Cl] (**32**) has been isolated, and spectroscopically and structurally characterised. Tetrahedral coordination about the silver(I) centre is observed with bond distances of Ag-S = 2.629(2), Ag-N ≈ 2.414(5) and Ag-Cl = 2.399(2)Å [51]. The macrocyclic complex [Ag(**33**)][ClO_4] has been prepared and the crystal structure determined. All five donor atoms bind to the silver(I) ion [52].



(**32**)



(**33**)

Sulfur-oxygen mixed donor ligands are represented by a series of crown ethers which contain pendant thioether groups. A high selectivity is observed for silver(I) ions from a range of alkali and heavy metal ions. This is attributed to the synergistic ligation of the crown ether and the exo-cyclic *S*-donor atom-containing group [53].

8.4 SILVER(0)

At 77 K and in an adamantane matrix on a rotating cryostat, ^{107}Ag atoms react with PF_3 to yield $^{107}AgPF_3$. The magnetic parameters of this silver(0) complex have been measured. The compound is a silver-centred radical species with a $^2A_1$ ground state [54].

8.5 POLYNUCLEAR SILVER COMPLEXES

A number of complexes containing a discrete number of non- or weakly bonded silver atoms [11-13, 17, 20, 27, 37–42, 44, 46], heterometallic complexes [16, 22, 32, 45, 47] and polymeric systems [14, 27, 28, 29, 33, 35, 48–50] have already been mentioned in previous sections in this review. The discussion in this section focuses on some solid state species, complexes which contain two or more silver atoms which are within bonding distance, and on heterometallic multinuclear species.

8.5.1 Selected solid state systems and materials

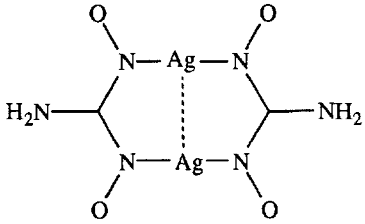
The compounds $Ag_2H_2P_2O_7$ [11], $Ag_4K_6P_{10}O_{30}.10H_2O$ [12], and $Ag_{20}O_{33}H_{22}(ClO_4)_4$ [13] were described in section 8.3.2.

The synthesis of Ag_5GeO_4 from Ag_2O, Ag and GeO_2, or Ag and GeO_2 both under oxidising conditions (high pressure of dioxygen) has been described [55, 56]. The product is formed as air stable, yellowish crystals. Jansen and Linke comment that the formula given for the new superconducting oxide is not a typing error! The solid state structure of Ag_5GeO_4 reveals the presence of Ag_6^{4+} octahedra, and the electrical and magnetic properties are consistent with the localisation of two paired electrons in each Ag_6-octahedron. The oxide decomposes in two steps (432.7 and 524.5°C); decomposition above 520°C occurs with loss of O_2.

The results of a crystallographic study have shown that the two salts $Cs_3Ba[Ag_2(SCN)_7]$ and $Cs_3Sr[Ag_2(SCN)_7]$ are isotypic. Each silver centre is tetrahedrally coordinated by *S*-SCN^- ions. Their electro-optical properties have been investigated, and the effect of exchanging silver for copper has been detailed [57].

8.5.2 Di- and polynuclear complexes excluding clusters

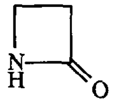
Nitrosolato complexes of silver(I) have been reported by Olbrich *et al.* An X-ray crystallographic study of silver(I) aminomethylnitrosolate has revealed the presence of dimeric units (34). These nearly planar units form stacks in the solid state lattice to generate a layered structure. Reactions of the new compounds include that of the ethylnitrosolate complex with bpy [58].



(34)

Silver(I) bromide reacts with bis(diphenylphosphino)methane (dmpm) to give $[Ag_2(dmpm)_2Br_2]$; this possesses a polymeric structure in the solid state. The bromide ligands function as bridging units. The intramolecular Ag----Ag separation is 3.605(2)Å and the intermolecular distance is 3.916(2)Å. Infrared, Raman and ^{31}P NMR spectroscopic data for $[Ag_2(dmpm)_2Br_2]$ have been reported. Vibrational spectroscopic data have also been recorded for related complexes, and correlations have been made between the force constants and the metal-metal separations [59]. The same P-C-P ('A-frame'-like) unit is found in the product of the reaction of AgO_3SCF_3 with $HC(PPh_2)_3$. The crystal structure of the perchlorate salt of $[Ag_3\{HC(PPh_2)_3\}_2]^{3+}$ reveals that the three silver atoms form a triangular array with one ligand acting as a 'clamp' on each side of the Ag_3-unit. Two molecules of acetonitrile solvent are associated with each cation. An analogous trigold species has also been prepared and structurally characterised; UV-VIS spectroscopic data for the products have been recorded [60].

The tetranuclear complex $[\{Ph_3PPt(\mu\text{-}OAc)_2(\mu_3\text{-}OAc)Ag\}_2]$ has been prepared from silver(I) acetate, and crystallographically characterised [61]. Two other disilver-platinum complexes are $[Pt_3(S_2CN^iPr_2)_6Ag_2]^{2+}$ and $[Pt_3(S_2CN^nBu_2)_6Ag_2]^{2+}$ isolated as the tetrafluoroborate and perchlorate salts respectively. Both have been characterised by X-ray diffraction methods. In the NMR spectrum, values of $^{195}Pt\text{-}^{107,109}Ag$ spin-spin coupling constants (≈ 200 Hz) indicate the presence of direct Pt-Ag bonding [62]. Mixed silver-mercury complexes are formed in the reactions of $AgNO_3$ and $Hg(O_2CMe)_2$ with the ligands (**35**) or (**36**) in methanol. The products are the polymeric species $[AgHg(\mathbf{35})_2(NO_3)]_n$ or $[AgHg(\mathbf{36})_2(NO_3)]_n$ and the crystal structures of these two complexes confirm different three-dimensional assemblies. The structure of $[AgHg(\mathbf{35})_2(NO_3)]_n$ consists of dimeric units, each containing a folded cyclic-Ag_2O_2 core. In $[AgHg(\mathbf{36})_2(NO_3)]_n$, the silver(I) centres are linked by $\{Hg(\mathbf{36})_2\}$-units to generate a helical chain in which each silver(I) centre is tetrahedrally coordinated [63].



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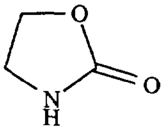


(36)

In studies of complex formation involving the ligands 3-mercapto-1,2-propanediol and its 1-methoxy and 1-ethoxy derivatives [$HSCH_2CH(OH)CH_2OR$ where R = H, Me or Et], silver(I) dimers of the type $[(Ph_3P)_2Ag(\mu\text{-}SCH_2CH(OH)CH_2OR)_2Ag(PPh_3)_2]$ have been formed. These grey or grey-white complexes are diamagnetic and have been characterised by elemental analysis, molar conductivity measurements and IR spectroscopy [64].

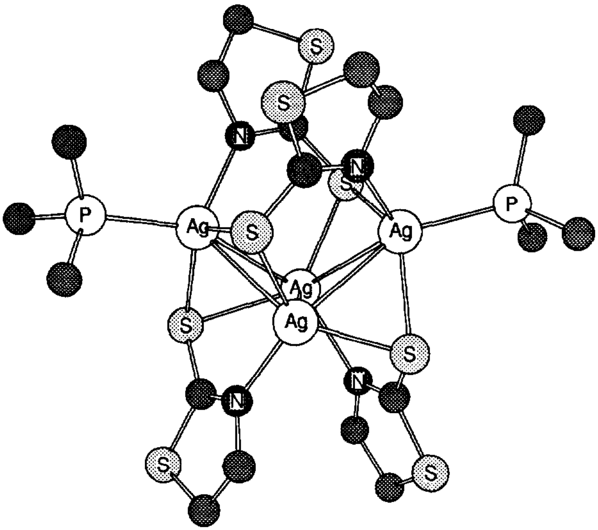
The preparation and characterisation of the silver(I) complex $[\{AgL_2\}Y]_n$ where L = 1,8-diisocyano-*p*-menthane and Y = PF_6, NO_3 or BF_4 have been reported. The new compounds are air stable, insulating materials. For Y = PF_6, crystallographic data show that the ligands L are in a *syn*-configuration; the Ag---Ag separation is ≈ 5 Å. At 77 K, a ethanol solution of $[\{AgL_2\}PF_6]_n$ exhibits a blue emission (λ_{max} = 385 nm) when it is irradiated with UV light (λ < 240 nm). The emission lifetime is 1.10 ± 0.02 µs [65].

8.5.3 Selected clusters

Clusters that have been included in this review meet the criterion that they contain an aggregate of silver atoms as a central core, or that they are heterometallic clusters with silver atoms as an integral part of the cluster-core. Thus, organometallic (low oxidation state metal) clusters in which the silver centres feature only in peripheral units, have not been included.

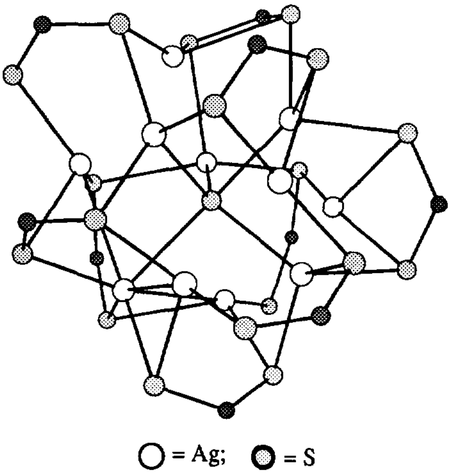
The tetranuclear clusters $[(Ph_3P)_2Ag_2Cu_2(C_3H_4NS_2)_4]$ and $[(Ph_3P)_2Ag_4(C_3H_4NS_2)_4]$ (**37**) have been prepared from silver(I) and copper(I) acetates, for example as given in equation (i) where $[C_3H_4NS_2]^-$ is the 2-mercaptothiazolinato ligand. The cluster possesses a butterfly skeleton, which has been confirmed by X-ray crystallography in both cases. In the heterometallic cluster, the two silver atoms reside in the wing-tip sites and in both clusters each of these atoms carries a terminal PPh_3 group. The framework is supported by a bridging 2-mercaptothiazolinato group [66].

$$4\,Ag(OAc) + 4\,C_3H_4NS_2H + 2\,PPh_3 \rightarrow [(Ph_3P)_2Ag_4(C_3H_4NS_2)_4] + 4\,HOAc \qquad (i)$$



Only the *ipso*-C atoms are shown for phenyl rings.

(37)



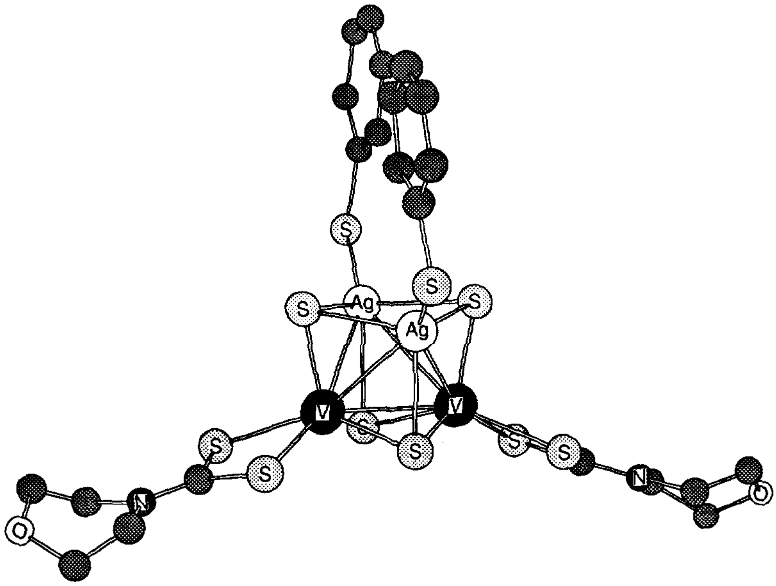
NEt$_2$ groups have been omitted

(38)

The compound $[Ag_{11}S(Et_2dtc)_9]$ (**38**) has been synthesised electrochemically, and chemically by reacting of $AgNO_3$ with $Na[Et_2dtc].3H_2O$ and $[NH_4][MoS_4]$ in dmf. This is a paramagnetic cluster, which has been characterised by ^1H NMR spectroscopy and an X-ray diffraction study. It exhibits as unusual bridging sulfide ligand at the heart of the array [67].

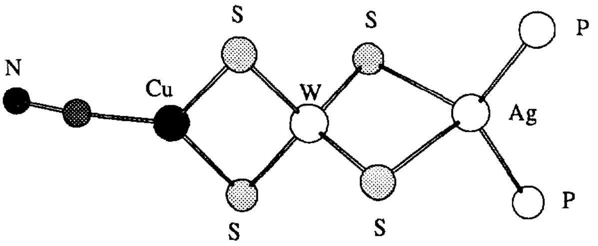
The reaction of silver(I) tetrafluoroborate (in thf) or silver(I) nitrate (in acetonitrile) with $Na_2[Fe(CO)_4].x$thf leads to the formation of the paramagnetic cluster anion $[Ag_{13}Fe_8(CO)_{32}]^{4-}$. This has been isolated as the $[Me_3NCH_2Ph]^+$ and $[PPN]^+$ salts and structurally characterised. Electron spin resonance spectroscopic data have been recorded. The unpaired electron is strongly coupled with the unique interstitial silver centre and is weakly coupled to the remaining twelve silver centres. The bonding in $[Ag_{13}Fe_8(CO)_{32}]^{4-}$ has been explored using extended Hückel MO calculations [68]. The cationic cluster $[Au_{13}Ag_{12}\{P(4\text{-}MeC_6H_4)_3\}_{10}Cl_8]^+$ has been prepared and crystallographically characterised. It possesses a bi-icosahedral metal core [69]. A gold-centred icosahedral core is present in $[Au_9Ag_4Cl_4(PMePh_2)_8]^+$, which has been prepared from the reaction of $[Au_{11}(PMePh_2)_{10}]^{3+}$ and $[(Ph_2MeP)AuCl]$, and isolated as the solvated species $[Au_9Ag_4Cl_4(PMePh_2)_8][C_2B_9H_{12}].H_2O.{}^1/_2CH_2Cl_2$. In the cationic cluster, each silver atom bears a terminal chloride ligand [70].

The reaction of $[Ag(PPh_3)_2][NO_3]$ with $[VS_4]^{3-}$, $[OC_4H_8dtc]^-$ and $[PhS]^-$ in dmf solution, leads to the formation in low yield of the cubane-like cluster (**39**). The results of an X-ray diffraction study show that the silver environment is distorted tetrahedral; additional Ag···V interactions are indicated in structure (**39**). The analogous copper(I) species has also been reported [71].



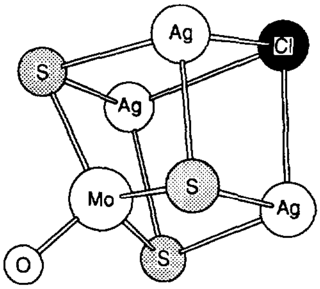
(**39**)

A series of heterometallic clusters containing silver (I) centres in conjunction with group 6 metal atoms has been reported [72-77]. The salt $[Ag(PPh_3)_2][NO_3]$ reacts with $[Et_4N]_2[OWS_3Cu(CN)]$ to give $[Et_4N][(Ph_3P)_2(AgS_3WOCu)CN]$. This has a butterfly core, confirmed by X-ray crystallography. During the reaction, the $\{OWS_3Cu(CN)\}$-unit remains as an entity. The chirality of the product has been discussed [72]. Related to this compound are the salts $[Et_4N][(Ph_3P)_2(AgS_3MoOCu)CN]$ and $[Et_4N][(Ph_3P)_2(AgS_2MoS_2Cu)CN]$ [72,73]. In both anions, the silver centre is tetrahedrally sited. A report of the synthesis and characterisation of the tungsten analogue of the latter compound has also appeared. The compound $[Et_4N][(Ph_3P)_2(AgS_2WS_2Cu)CN]$ is formed when $[Et_4N]_2[WS_4Cu(CN)]$ is treated with the silver(I) salt $[Ag(PPh_3)_2][NO_3]$. An X-ray crystal structural analysis shows that the three metal centres in the $[(Ph_3P)_2(AgS_2WS_2Cu)CN]^-$ anion (**40**) are approximately co-linear [74]. A novel cubane-like complex in this series of compounds is produced by treating silver(I) chloride with triphenylphosphine and the $[MoS_4]^{2-}$ anion. The nature of the cubane $[\{MoAg_3S_3Cl\}(PPh_3)_3S]$ has been confirmed crystallographically. Each silver atom in the cubic cluster carries a terminal PPh_3 ligand, and one sulfur atom is terminally attached to the molybdenum centre. Four of the eight vertices of the cube are composed of triply bridging sulfur (three) and chlorine (one) atoms. The average Ag-Cl distance is 2.815(3)Å [75]. A similar structure is observed for the compound $[\{MoAg_3S_3Cl\}(PPh_3)_3O]$ [the core of which is shown in structure (**41**)] which assembles when AgCl and PPh_3 react with $[Mo_2O_2S(S_2)_4]^{2-}$. The average Mo-Ag distance in cubane (**41**) is 2.980(2)Å which is too long to be considered to be bonding; this appears then to confirm the structural role of four μ_3-ligands [76].



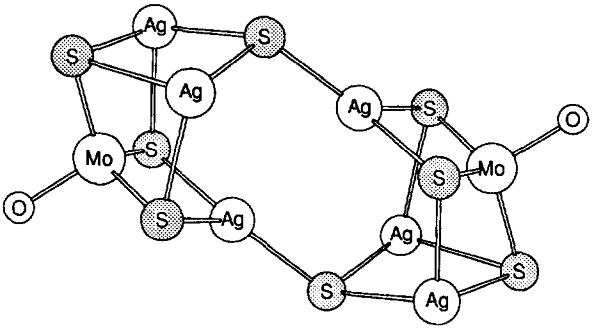
Phenyl groups are omitted for clarity.

(**40**)



(**41**)

The double cubane $[\{Mo_2Ag_6S_6(S^tBu)_2\}(O)_2(Ph_3)_4]$ (**42**) has also been prepared. A structural investigation of $[\{Mo_2Ag_6S_6(S^tBu)_2\}(O)_2(Ph_3)_4]$ reveals the presence of two opened-cubane units linked by two Ag-S^tBu bonds; the core of $[\{Mo_2Ag_6S_6(S^tBu)_2\}(O)_2(Ph_3)_4]$ is drawn in structure (**42**). Each of the Ag and S atoms which compose these bridges are integral parts of the cubane cores. The Ag-S bond distances lie in the range 2.389 to 2.644(3)Å [77].



(**42**)

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