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2. Silver 1993

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INTRODUCTION

This review surveys the coordination chemistry of silver reported during the year 1993 and follows a similar format to the corresponding review of the 1992 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; for most of the structures, the hydrogen atoms have been omitted for clarity.

Compounds with polynuclear cores or which possess polymeric structures in the solid state are generally described in section 2.4, although some cross-referencing between other sections has been inevitable. 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.

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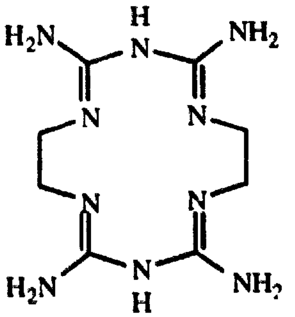
Sutton has reviewed the chemistry of diazo complexes and the discussion includes silver-containing species [3]. A thermochemical study has focused on determining the standard enthalpy of formation of the silver(I) salt of 3-nitro-1,2,4-triazol-5-one: $\Delta H_f^0(298.15) = -47.1 \pm 1.4$ kJ mol^{-1} [4].

2.1 SILVER(III)

The complex $[Ag(H_2L)]^{3+}$ where H_2L = (1) oxidizes ascorbic acid (H_2asc) in acidic aqueous solution and the products are dehydroascorbic acid, silver(I) and free H_2L. The kinetics of this reaction have been investigated — the mechanism is inner sphere. The equilibrium constant for the formation of the initial adduct $[Ag(H_2L)(H_2asc)]^{3+}$ is 4.08±0.45 mol^{-1}dm^3 [5].



(1)

2.2 SILVER(II)

The ligand 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_2L) and its silver(II) complex [AgL] have been studied using SERRS. The reaction conditions allow an investigation of the direct adsorption of the porphyrin onto the surface of a silver colloid as well as the attachment of the ligand to the surface by means of a non-ionic surfactant which functions as a molecular spacer [6]. The results of a crystallographic study of the silver(II) macrocyclic complex {*rac*-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)}silver diperchlorate dihydrate have been reported. The environment about the Ag(II) centre is approximately square planar [7].

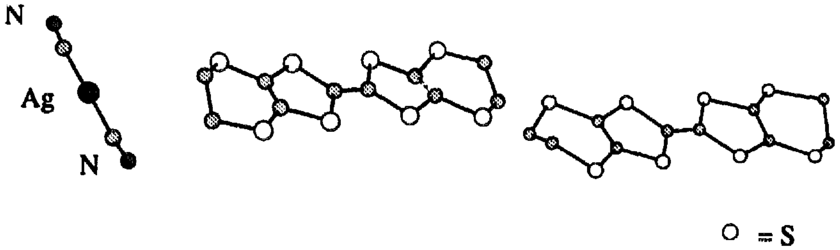
2.3 SILVER(I)

2.3.1 Complexes with halide and pseudo-halide ligands

The photoluminescence of mixed AgCl-AgBr crystals of stoichiometry $AgCl_{0.45}Br_{0.55}$ has been investigated; both absorption and emission spectra have been recorded in addition to the excitation spectra and a study of the influence of temperature on the main emission bands. The results have been compared with those for pure AgCl and AgBr. At 515 nm, the emission band of the mixed crystals matches that of pure AgCl. The results also suggest that nominally pure AgBr may contain iodide impurities [8].

The reactions of AgX (X = BF_4, PF_6, NO_3) with ethene in CH_2Cl_2 or MeOH followed by treatment with iodoalkanes lead to complexes of the type $(RI)_x(AgX)_y$ in which x and y are variable. For example, [$AgPF_6$] reacts with $CH_2ICH_2CH_2I$ to give bis(1,3-diiodopropane)silver(I) hexafluorophosphate for which crystallographic data reveal that the organo ligands bridge between silver(I) centres to give a polymeric chain structure. Each silver(I) centre is tetrahedrally coordinated. In solution, ^1H NMR spectroscopy indicates that the $[AgL_2]^+$ cations may contain chelating ligands. X-Ray crystal structures of the complexes *catena*-$AgNO_3.CH_2I_2$, *catena*-$[Ag(CH_2I_2)_2][PF_6]$ and *catena*-$[AgO_2PF_2]_2.4\text{-}MeC_6H_4I$ have also been reported. In the latter, 4-methyliodobenzene is coordinated to silver(I) through the iodo-substituent and is also bound in an η^2-fashion to an adjacent Ag(I) centre. The difluorophosphate groups are bridging ligands, coordinating through the oxygen atoms [9].

Spear-shaped crystals of the ethylenetetrathiafulvene salt $[C_{10}H_8S_8][Ag(CN)_2].C_{10}H_8S_8$, have been studied by single-crystal X-ray diffraction and the packing of the thiafulvenes is a dominant feature of the lattice [10].



(2)

2.3.2 Complexes with oxygen donor ligands

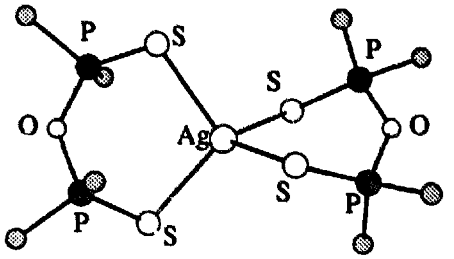
Ammonium silver(I) citrate may be prepared by adding NH_3 to an aqueous solution containing 2:1 quantities of $AgNO_3$ and citric acid. In the solid state, the results of a crystallographic study show that there are two independent carboxylato-bridged dimers which are linked into infinite chains. Each silver(I) centre is tetrahedrally coordinated [11].

β-Diketonate complexes of silver(I) have been prepared by the reactions of $AgNO_3$ with the diketone in dry methanol and acetonitrile. A range of complexes has been reported, and these have been characterized by elemental analysis and IR spectroscopy [12]. The preparations of $[AgL(PMe_3)]$ and $[AgL(PMe_3)_2]$ (HL = $CF_3C(O)CH_2C(O)CF_3$) from AgL and PMe_3 have been reported — the aim of this investigation was to pursue molecules which may be suitable precursors for silver thin-films. The compounds have been structurally characterized: $[AgL(PMe_3)]$ possesses a trigonal planar silver(I) centre, and in $[AgL(PMe_3)_2]$, the metal is tetrahedrally coordinated. Chemical vapour deposition studies have been carried out over the temperature range 200-450°C under vacuum and in the presence of H_2 [13].

Further complexes containing *O*-donor ligands are described in section 2.4.

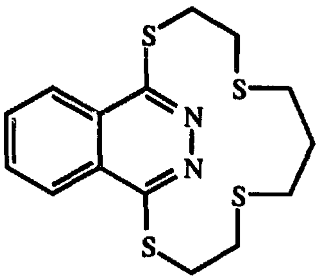
2.3.3 Complexes with sulfur donor ligands

The solid state structure of the sulfide $AgPbBi_3S_6$ has been reported [14]. Complex formation between silver(I) and $[R_2PS_2]^-$ (R = Et, ^{n}Pr or Ph) has been studied by potentiometric methods and the stabilities of the complexes determined [15]. The reaction of $AgAsF_6$ with $P\{P(=S)Me_2\}_3$ in CH_2Cl_2 in the presence of SO_2 yields a polymeric product, but when $AgAsF_6$ reacts with $\{Me_2P(S)\}_2O$, L, the product is $[AgL_2][AsF_6]$. In the solid state, the silver(I) centre in the cation (3) is tetrahedrally sited and Ag-S bond lengths range from 2.564(2) to 2.633(2) Å [16].



(3)

Macrocyclic complexes containing *S*-donor atoms have drawn significant attention this year, with the work of Schröder *et al* once again providing contributions. Silver nitrate reacts with 1,4,7,10,13-pentathiacyclopentadecane (L) in methanol/water at reflux to yield $[AgL]^+$, $[Ag_2L_2]^{2+}$ and $[Ag_nL_n]^{n+}$ depending upon the cation that is present — $[B(C_6F_5)_4]^-$, $[BPh_4]^-$ or $[PF_6]^-$ respectively. All three salts have been crystallographically characterized. In acetonitrile solution, $[AgL]^+$ shows a chemically reversible Ag^I/Ag^{II} couple (E = +0.76 V vs. Fc/Fc^+) and a quasi reversible Ag^I/Ag^0 couple (E = −0.37 V). The Ag^{II} oxidation product has been studied using X- and Q-band ESR spectroscopy [17]. Cyclic tetrathioethers (L) with ring sizes of 12, 13, 15 or 16-atoms extract silver(I) from $CHCl_3$ and 1,2-dichloroethane in the presence of picrate ions (pic^-). The salts formed were of the general type [AgL][pic] and this result contrasts with the previously reported formation of $[AgL_2][pic]$ in the case of L being a 14-membered cyclic tetrathioether [18]. Ligand (4) = L has been prepared as one of a series of related macrocycles and its structure has been determined. Complex formation with silver(I) leads to $[AgL]^+$, which has been isolated as the pale yellow perchlorate salt. Characterization by IR spectroscopy and a comparison with the analogous copper(I) complex indicate that ligand (4) binds to the metal centre only through the *S*-donor atoms [19]. The template reaction of $[Me_4N]_2[Mo(CO)_3(SCH_2CH_2SCH_2CH_2S)]$ with tetrabromodurene (2:1) leads to the formation of $[Mo_2(CO)_6(\mathbf{5a})]$ from which ligand (5a) can be isolated. Reaction of this ligand with $AgBF_4$ in the presence of phosphines leads to disilver complexes with one Ag(I) centre bound by each macrocycle. If the phosphine is monodentate (PPh_3 or PPh_2Me), the product possesses an *anti*-conformation as confirmed by the single crytsal structure of (5b) but a didentate phosphine, not surprisingly, restricts the complex to a *syn*-arrangement [20].



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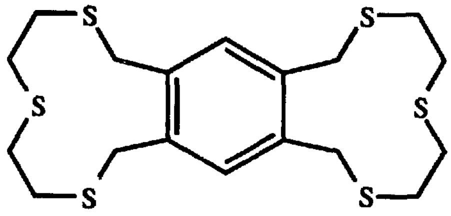
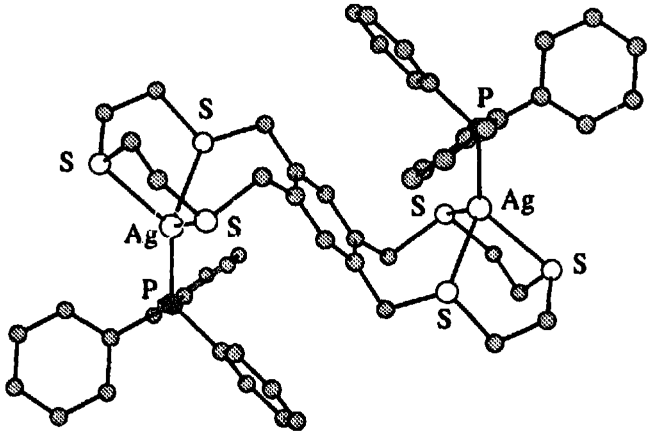
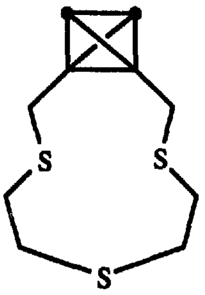


(5a)



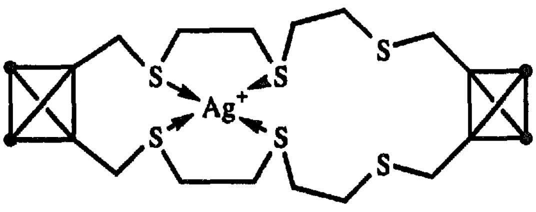
(5b)

The functionalization of carbaborane clusters with sulfur-containing macrocycles has been reported in previous reviews, for example reference 28 cited in [1]. The feature of the cluster that permits its incorporation into the macrocycle is the C–C bond, and Co_2C_2-clusters are therefore suitable candidates for similar functionalization. Ligand (6) reacts with $AgBF_4$ in the presence of PPh_3 to give $[Ag(6)(PPh_3)][BF_4]$. The cation contains a tetrahedrally coordinated silver(I) centre with the four coordination sites occupied by the three *S*-donor atoms of (6) and the phosphine ligand. With a related ligand with a larger macrocyclic cavity, complex (7) is formed and this has also been crystallographically characterized; the silver(I) centre is tetrahedrally sited [21].



● = $Co(CO)_3$

(6)

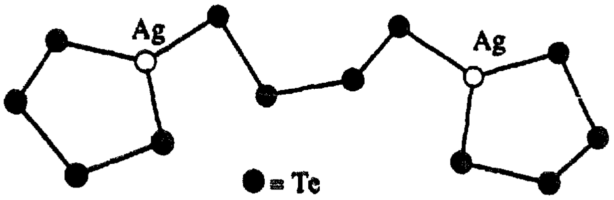


● = $Co(CO)_3$

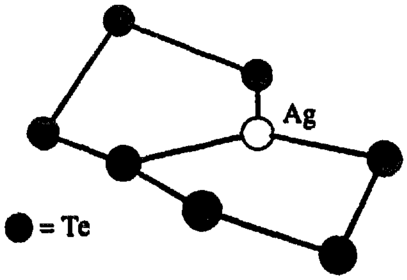
(7)

2.3.4 Complexes with telluride ligands

Several reports of silver(I) complexes containing polytelluride ligands were reported in 1993. The reaction between $AgBF_4$ and K_2Te in dmf in the presence of $[Me_4N]Cl$ leads to the formation of $[Me_4N][AgTe_4]$. An X-ray diffraction study reveals that the $[AgTe_4]^-$ anions form layers in the solid state with 5-membered $AgTe_4$-rings connected by bridging tellurium atoms; the end result is that each silver(I) centre is coordinated by three $[Te_4]^{2-}$ ligands [22]. When Na_2Te_3 reacts with $AgNO_3$ in dmf in the presence of $[PPh_4]Br$, black needles of $[PPh_4]_4[Ag_2Te_{12}]$ may be isolated. The anion has the structure shown in (8), and a copper(I) analogue has also been reported [23]. Independently, the tetraethylammonium salt of (8) has been prepared and structurally characterized [24]. This salt is formed in the reaction of polytelluride with $[AgI(PMe_3)]_4$ in the presence of PEt_3 in dmf, but if sodium is present in the reaction mixture as well as $[PPh_4]Cl$, then the product is $[PPh_4]_2[NEt_4][AgTe_7]$. The crystallographically determined structure of the anion (9) confirms the presence of a trigonal planar Ag(I) centre and one tellurium atom in a T-shaped environment [25].



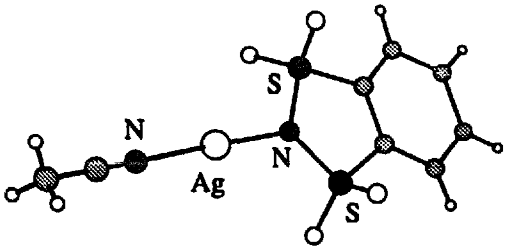
(8)



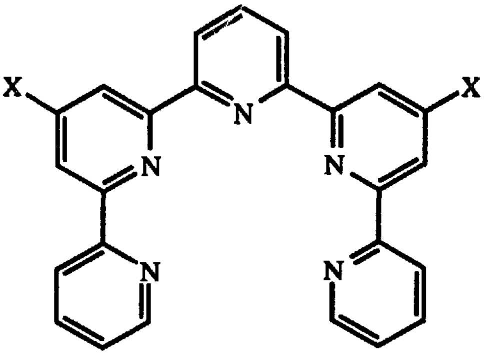
(9)

2.3.5 Complexes with nitrogen donor ligands

The silver(I) disulfonylamides $[Ag\{N(SO_2Me)_2\}]$, $[Ag\{N(SO_2C_6H_4\text{-}4\text{-}X)_2\}]$ (X = F, Cl, Br, I) and $[Ag\{N(1,2\text{-}(SO_2)_2C_6H_4)\}]$ have been prepared. Structural data for the complexes, crystallized from MeCN, reveal significantly different features between them. In the solid state, $[Ag\{N(SO_2Me)_2\}]$ forms an ionic salt: $[Ag(MeCN)_4]^+[Ag\{N(SO_2Me)_2\}_2]^-$. In the cation, the silver(I) centre is tetrahedrally coordinated, and in the anion, it is linear. Thermochemical studies show that the complex desolvates in two steps over the temperature ranges −15 to 60°C, and 60 to 95°C, and it has been proposed that this observation corresponds to the formation of $[Ag\{N(SO_2Me)_2\}.MeCN]$ as an intermediate. The solid state structure of the compound $[Ag\{N(1,2\text{-}(SO_2)_2C_6H_4)\}].MeCN$ (10) confirms the presence of a linear silver(I) centre ($\angle$N-Ag-N = 174.3°). On heating, this complex desolvates between 60 and 200°C but the process is not a simple one [26]. The structure of the $[Ag(MeCN)_4]^+$ cation has also been determined for the perchlorate salt [27].



(10)

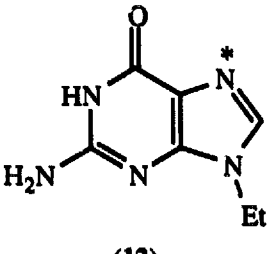


X = H, MeS, Ph, 4-ClC_6H_4

(11)

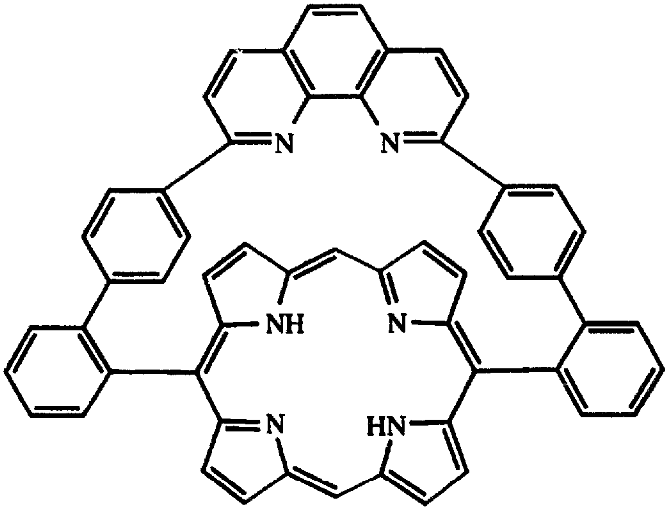
The conductivity behaviour of $AgClO_4$ and $AgBrO_4$ in water-pyridine solutions of varying compositions has been investigated. The results are interpreted in terms of the selective solvation of Ag(I) by pyridine [28]. The silver(I) complex $[AgL]^+$ of the oligopyridine ligand (**11**) with X = H reacts with $[CoL(MeOH)_2]^{2+}$ (L = (**11**) with X = H) to give the double-helical heterodimetallic complex $[CoAgL_2]^{3+}$. Similar reactions occur with the substituted ligands (**11**) (X = MeS, Ph or 4-ClC_6H_4). The coding for this assembly of a double helix is contained in the preferred coordination numbers and geometries of the cobalt(II) and silver(I) centres, six-coordinate octahedral and four-coordinate tetrahedral respectively [29]. Related ligands have also been used to assemble a heterometallic silver-ruthenium complex: $[\{(terpy)RuL\}_2Ag]$ in which L is 2,4,6-tripyridyltriazine [30].

A crystalline nucleobase complex of silver(I) has been prepared by a gel-growth method. Ligand L, (**12**), reacts with silver nitrate to yield $[AgL_2][NO_3]$ which has been characterized by IR spectroscopy and X-ray diffraction studies. Coordination is through the N(7) atom [labelled N* in (**12**)] and the silver(I) centre is in a linear environment and located at an inversion centre (Ag-N = 2.11(1) Å). The two guanine rings are coplanar and in the lattice, the cations form stacks. Water molecules present in the lattice are hydrogen bonded to the O(6) atom of ligand L and the nitrate oxygens. The results of solution ^{13}C and ^{109}Ag NMR spectroscopic studies have been reported [31].



(12)

Complex formation between the porphyrin ligand H_2L (**13**) and silver nitrate in dmf has been followed by UV-VIS spectroscopy and cyclic voltammetry. The first site of coordination occurs at the phen group and a 1:1 complex forms. With silver(I) ions present in excess, UV-VIS spectroscopic data indicate that the metal ions are bound by the porphyrin nitrogen donors with concomitant oxidation to silver(II) [32].

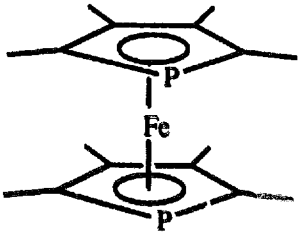


(13)

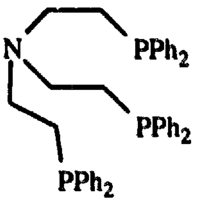
2.3.6 Complexes with phosphorus donor ligands

Structural data for the related complexes $[AgX(PPh_3)_2].nCHCl_3$ (X = Br, n = 0; X = Cl or Br, n = 2) have been reported. In the solid state, the unsolvated bromide is monomeric with the silver(I) centre in a trigonal planar environment (Ag-Br = 2.568(1)Å, Ag-P = 2.458(2)Å). The solvated chloride and bromide complexes are dimeric and the two silver atoms are bridged by halide ions. Far IR spectroscopic studies have been carried out and absorptions due to ν(Ag-X) stretches have been assigned. In the Raman spectrum of the bromide complex, an absorption has been assigned to the mode ν(Ag-P). In the solid state (CP MAS) ^{31}P NMR spectra for the compounds, ^{31}P-^{109}Ag spin-spin coupling is observed [33].

In experiments involving the reactions between the diphosphaferrocene derivative (14) and tcne or tcnq, a solution of (14) in thf was placed in the anode compartment of an electrochemical cell. The cathode compartment contained (for example) tcnq in thf. The metal electrodes were silver (anode) and platinum (cathode) and during the experiment, dark blue crystals, identified as $[Ag(14)_2][tcnq]$, formed at the anode. This product has been characterized by X-ray diffraction methods and the cation consists of a distorted-tetrahedral silver(I) centre with two P,P'-chelating ligands [34].



(14)



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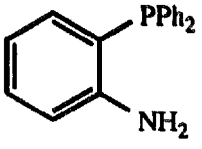
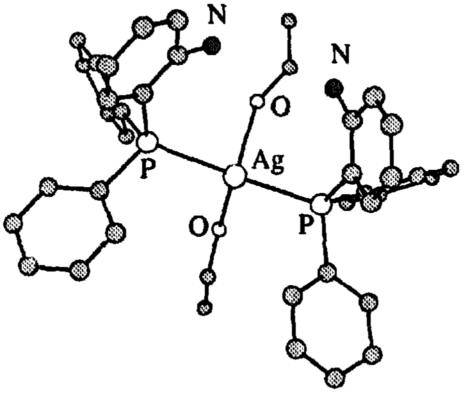


(16)

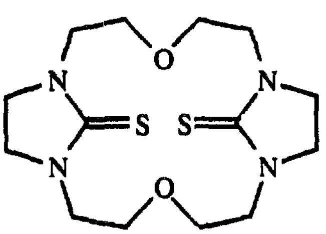
Silver(I) and gold(I) complexes of ligand (**15**) have been prepared and characterized by ^{31}P NMR spectroscopy and crystallographic methods. The reaction of $AgNO_3$ with (**15**) leads to the formation of [Ag(**15**)][NO_3], and an analogous reaction occurs with the hexafluorophosphate salt. The ligand is tridentate, adopting a *P,P',P''*-mode. In the nitrate salt, there is also a weak Ag–$O_{(nitrate)}$ interaction. Important distances in [Ag(**15**)][NO_3] are Ag–P = 2.477-2.524 Å, Ag–O = 2.55(1)Å, and Ag----N = 2.924(4)Å, and in [Ag(**15**)][PF_6], Ag–P = 2.464(2)Å and Ag---N = 2.662(3)Å [35]. The syntheses and crystal structures of the complexes [Ag(EtOH)$_2$L$_2$][NO_3] and [AgL$_3$][NO_3].H_2O where L = (**16**) have been described. The cation in [Ag(EtOH)$_2$L$_2$][NO_3] is shown in structure (**17**) and contains a highly distorted tetrahedral silver(I) centre: ∠P-Ag-P = 160.1°. The two Ag–O interactions are weak. In the cation in [AgL$_3$][NO_3].H_2O, the silver(I) centre is in a trigonal planar arrangement. There is no evidence in either compound for coordination by the amine group of the ligands [36].



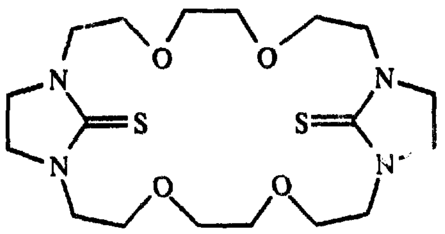
(**17**)

2.3.7 Complexes with mixed donor atom ligands

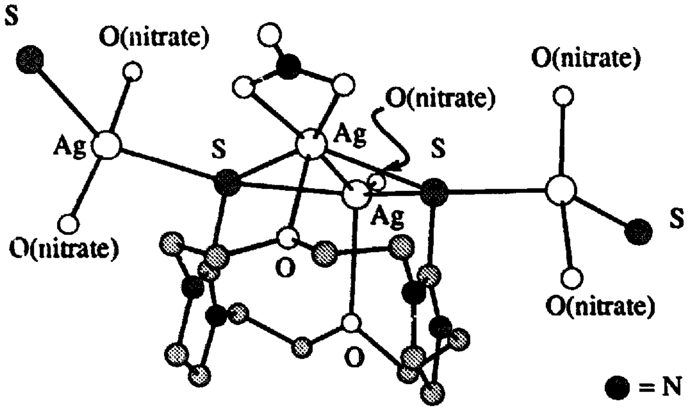
The tricyclic ligands (**18**) and (**19**) which contain bis(thiourea) subunits have been prepared. Reactions of (**18**) with an excess of $AgNO_3$ in MeOH yield a 1:3 (L:Ag$^+$) complex. For ligand (**19**), a corresponding reaction leads to a 1:1 complex as evidenced by FAB mass spectrometry. The structure of [Ag_3(**18**)][NO_3]$_3$ is drawn in (**20**) and consists of silver(I) centres bridged by sulfur donor atoms, whilst the ring *O*-donor atoms are involved in coordination to two silver atoms. nitrate ions are also coordinated, although some anions are disordered [37].



(**18**)

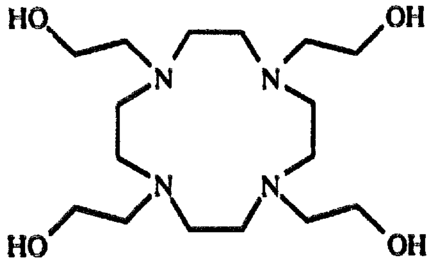


(**19**)

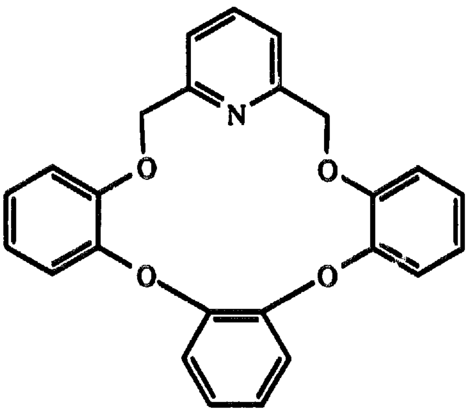


Part of the polymeric structure of **(20)**

Alkali metal and silver(I) ions in dmf and methanol solutions are complexed by the pendant arm macrocyclic ligand (**21**). A study of this system has included the determination of stability constant data; for Ag^+, $\log K = 12.57 \pm 0.04$ (MeOH) or 11.16 ± 0.05 (dmf) [38]. A 2:1 complex forms between the crown ligand (**22**) and silver(I) ions in the reaction of $AgNO_3$ and (**22**). The product is described as a charge-separated sandwich of formula $[Ag(\mathbf{22})_2]^+$ and crystallographic data confirm that each silver(I) centre is in a six-coordinate N_2O_6-donor atom sphere. The structure can be rationalized after a consideration of ion radius:ligand cavity ratios [39].



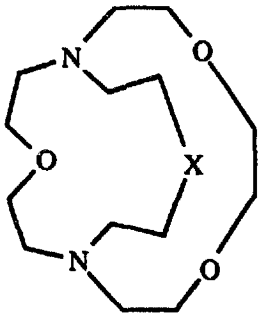
(21)



(22)

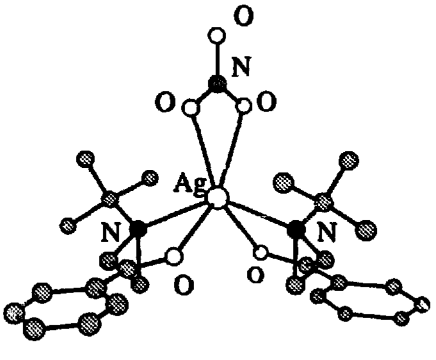
The complexation of silver(I) ions in tri-*n*-butyl phosphate by ligands (**23**) results in the formation of 1:1 complexes; complexation involving Li^+, Na^+ and Tl^+ ions has also been studied. Stability constants for these complexes in trialkylphosphates and a range of other solvents have been determined [40].

The ligand 1-^{t}butyl-2-benzoylaziridine, L, reacts with silver nitrate to yield $[AgL_2][NO_3]$. This has been characterized by X-ray diffraction studies, and in the cation (**24**), the silver(I) centre has been found to be six-coordinate, the donors being the two aziridine-*N* (Ag-N = 2.39(1)Å), the two benzoyl-*O* (Ag-O = 2.60(1)Å), and two nitrato-*O* (Ag-O = 2.60(1)Å) atoms [41].



X = O or CH_2

(23)

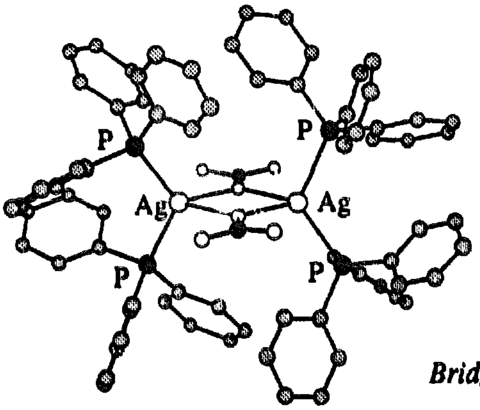


(24)

2.4 POLYNUCLEAR SILVER COMPLEXES

2.4.1 Disilver complexes

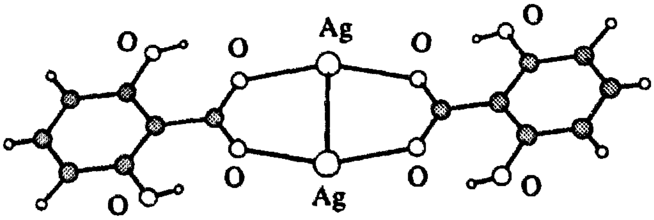
Two disilver [17] and heterodinuclear [29] complexes have already been mentioned. The crystal structure of $Ag(PPh_3)_2(NO_3)$ has been determined at 178 K and the compound shown to be dimeric. Structure (24) illustrates that the nitrate ions adopt bridging positions and each silver(I) centre is in a distorted tetrahedral environment [42].



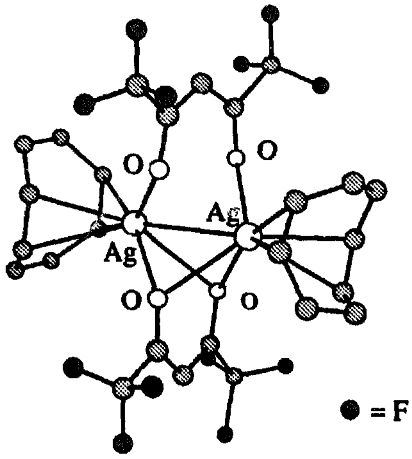
Bridging groups = NO_3

(25)

A second crystalline polymorph of silver(I) 2,6-dihydroxybenzoate (26) has been structurally characterized. It is dimeric and each molecule is approximately planar with the two silver atoms bridged by the carboxylate functionality [43]. An unusual β-ketonate complex of silver(I) has been prepared and characterized — Ag_2O, $CF_3C(O)CH_2C(O)CF_3$ (HL) and cod react to give the complex [Ag(cod)L] (27) which is dimeric in the solid state. This contrasts with the monomeric structure of the copper(I) analogue. The results of solid state FTIR spectroscopic studies allow a comparison of the stretching frequencies for the ν(C–O) and ν(C–C) modes in copper(I) and silver(I) complexes; in the former, the L^- ligands are in chelating modes [44].



(26)

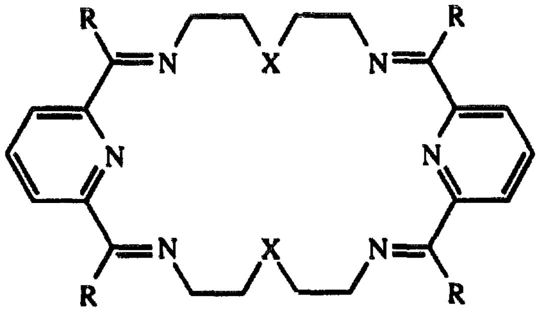


(27)

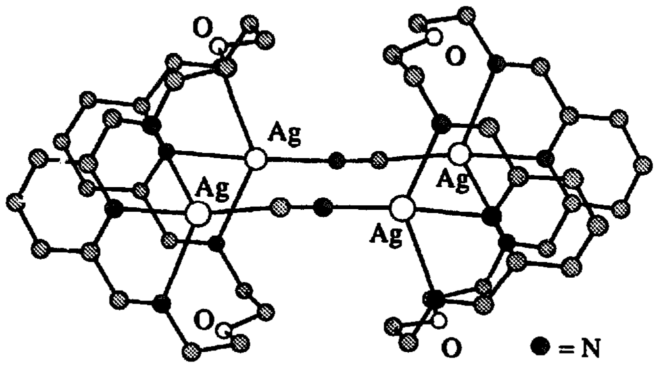
Two papers [45, 46] from Fenton and coworkers report related Schiff base macrocyclic complexes. Ligand (**28**) binds two Ag(I) ions and recrystallization of the perchlorate salt from MeCN leads to crystals of $[Ag_2(\mathbf{28})(CN)][ClO_4]$; the origins of the cyano ligands are uncertain. In the crystal structure of the complex, the ligand in cation (**30**) folds, forming a cleft which accommodates the metal ions. Cyano ligands bridge between pairs of silver(I) centres in the crystal lattice, and further association occurs to generate a polymeric structure. The template synthesis of ligand (**29**) in the presence of silver(I) ions in MeOH solution leads to the formation of the complex cation $[Ag_2(\mathbf{29})]^{2+}$. The tetrafluoroborate salt has been structurally characterized and the ligand is folded as in the previous complex cation. The pendant arms reach into the cavity such that each Ag(I) centre is ligated by an amino-group; the two ring tertiary amino-N atoms are in bridging sites rendering each silver atom six-coordinate. The complex $[Ag_2(\mathbf{29})]^{2+}$ is a precursor to a trinuclear copper-containing complex which is a model for the Cu_3-site in ascorbate oxidase.

(**28**) $R = H, X = O$

(**29**) $R = Me, X = NCH_2CH_2NH_2$



The reaction between 1,3,5-trithiane, L, and [AgOTf] in MeCN/thf leads to the formation of the complex $[L(OTf)Ag(\mu\text{-}L)_2AgL(OTf)]$ for which the results of an X-ray diffraction study have been reported. The structure of 1,3,5-trithiane has also been redetermined; a chair conformation is confirmed in the solid state. In $[L(OTf)Ag(\mu\text{-}L)_2AgL(OTf)]$, the two terminally bound ligands are monodentate, whilst the two bridging ligands coordinate through different *S*-atoms to different silver(I) centres; the distances $Ag\text{-}S_{term} < Ag\text{-}S_{bridge}$. The reaction of 1,4-dithiane with silver(I) ions produces an infinite polymer [47].

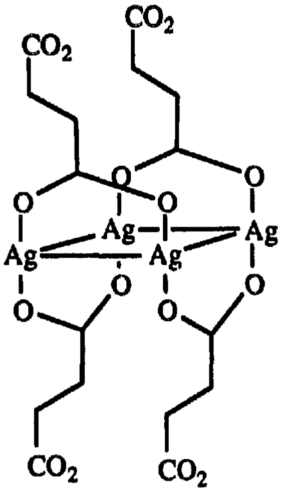


(30)

2.4.2 *Trinuclear and higher complexes*

Several complexes which are polymeric in the solid state have already been discussed [9, 12, 17, 22, 36], and we have already mentioned the heterometallic compound $[\{(terpy)RuL\}_2Ag]$ in which L is 2,4,6-tripyridyltriazine [30]. Two further heterotrinuclear complexes have been reported — $[L(H)Rh(\mu\text{-}H)_2Ag(\mu\text{-}H)_2Rh(H)L]^+$ in which $L = MeC(CH_2PPh_2)_3$ (formed by treating $AgCF_3SO_3$ with $[LRhH_3]$) [48] and $[Pt_2Ag(\mu\text{-}tht)(C_6F_5)_6]^+$ (formed from $AgClO_4$ and $[Pt(C_6F_5)_3(tht)]^+$) [49]. Solution NMR spectroscopic studies of both complexes have been carried out as well as X-ray diffraction studies. The bonding in $[Pt_2Ag(\mu\text{-}tht)(C_6F_5)_6]^+$ has been described in terms of Pt→Ag and S→Ag donor-acceptor bonds. The remaining part of this section in organized according to the nuclearity of the complex, beginning with trisilver species, and moving through to polymers and selected silver clusters.

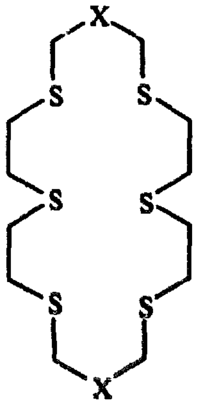
The preparation and structural characterization of $[Ag_3WS_3\{S_2P(OEt)_2\}(S)(PPh_3)_3]$ have been reported. A novel structural feature is the presence of a neutral and incomplete cubane-like core [50]. Related to this is the complex $[Ag_3W(\mu_3\text{-}S)_3(S)Br(PPh_3)_3].H_2O$, the structure of which has been determined [51].



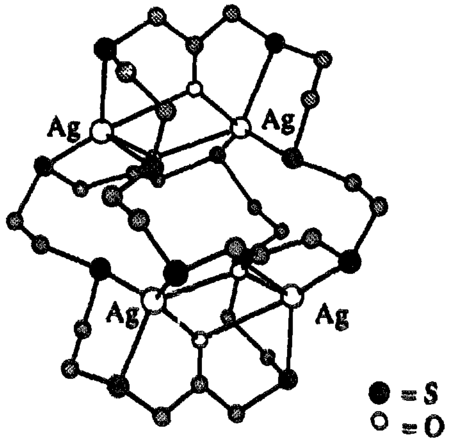
(31)

The reaction of silver nitrate, sodium silicate and aqueous succinic acid (pH 5.6) produces a pale yellow complex of formula $[Ag_2\{O_2C(CH_2)_2CO_2\}]$. In the solid state, tetrasilver moieties (31) are present; the Ag_4 units are planar and run parallel to the *ac* plane. Perpendicular to this plane, the Ag_4-units form helicoidal sequences which follow quasi-4_1 axes. Ultimately, a polymeric structure is produced [52]. The ligand $1,2\text{-}(^t\text{BuHNMe}_2\text{SiO})_2\text{C}_6\text{H}_4$ (H_2L) reacts with ^{n}BuLi in diethyl ether to give $Li_2L.(OEt_2)_2$. Treatment of this compound with silver bromide leads to the formation of $[Ag_4L_2]$ in which the silver atoms form a planar array with Ag-Ag distances in the range 2.917(1) to 3.018(2) Å [53].

The reaction between $HSCH_2CH_2SCH_2CH_2SH$ and 1,3-dibromopropane in thf/alcohol solvent in the presence of boron and aluminium alkoxides yields the macrocyclic ligand (32); the related ligand (33) has also been prepared. Complexation studies with silver(I) ions are exemplified by the reaction of $Ag(CF_3SO_3)$ with (33) which leads to the formation of $[Ag_4(33)_2][CF_3SO_3]_4$. In the solid state, each silver(I) ion is coordinated by both *S*- and *O*-donor atoms and the cation (34) is centrosymmetric with the two ligands lying above and below the plane containing the four metal centres [54].



(32) X = CH_2
(33) X = C=O

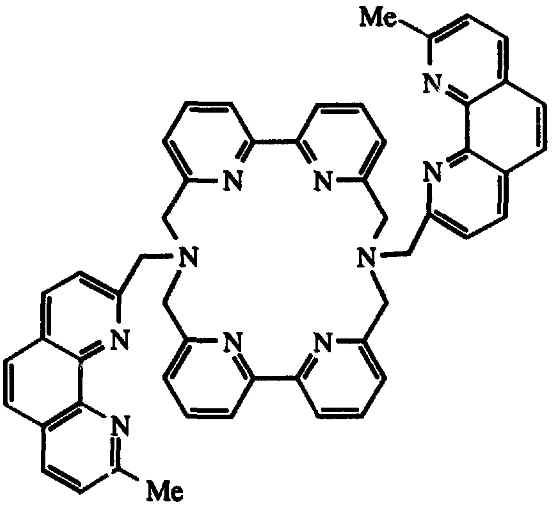


(34)

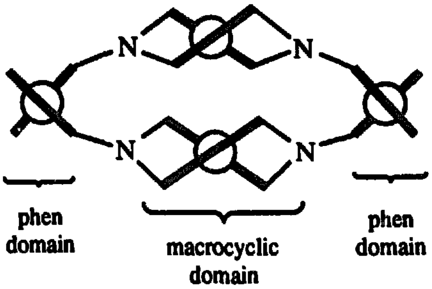
Ligand (35) contains two distinct domains — the macrocyclic cavity and the phenanthroline groups. The preparation of this ligand and its complex-forming reaction with silver(I) ions have been described. Light-sensitive crystals of $[Ag_4(35)_2]$ have been characterized by electronic and NMR spectroscopies and mass spectrometry. The crystal structure of the corresponding copper(I) complex confirms that metal ions are taken up, two by two macrocyclic cavities and two by four phen domains as represented in structure (36) [55].

Recrystallization of $[Ag\{N(SO_2Me)_2\}]$ from water at room temperature leads to the formation of crystals of the hydrate $[Ag_4\{N(SO_2Me)_2\}_4(H_2O)]$ (37). In the lattice, there are four independent silver(I) centres and the molecules form zig-zag chains [56]. In related work, the complex $[AgL].H_2O$, in which HL = (38), has been prepared and structurally characterized. In the solid state, the compound is polymeric with the silver atoms being present within $Ag(\mu\text{-}H_2O)_2Ag$ units containing planar Ag_2O_2-rings as shown in (39). The thermochemical properties of solid $[AgL].H_2O$ have been investigated — water is lost above 220°C and a value of +13.9(5) kJ mol^{-1}

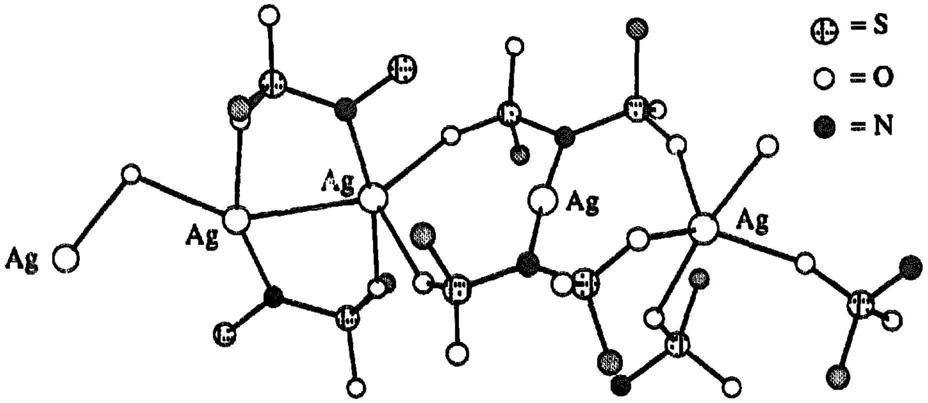
has been determined for $\Delta H^{\circ}_{\mathrm{dehydration}}(298)$ [57]. A crystallographic study of a silver(I) saccharin salt [HL = (**40**)] has been carried out. In the solid state, the complex is polymeric, with disilver units bridged by two deprotonated ligands which function as *N*,*O*-donors (carbonyl oxygen atom). These dimeric units are linked together by $O_{(S=O)}$→Ag coordinate bonds [58].



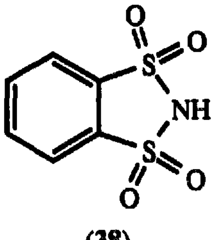
(**35**)



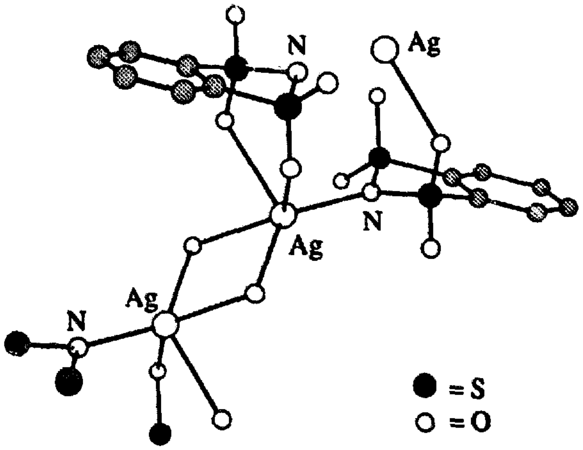
(**36**)



(**37**)

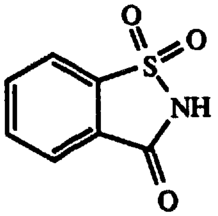


(**38**)



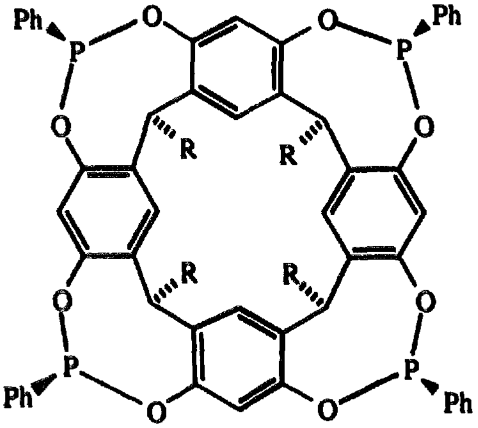
Part of the polymeric structure

(39)



(40)

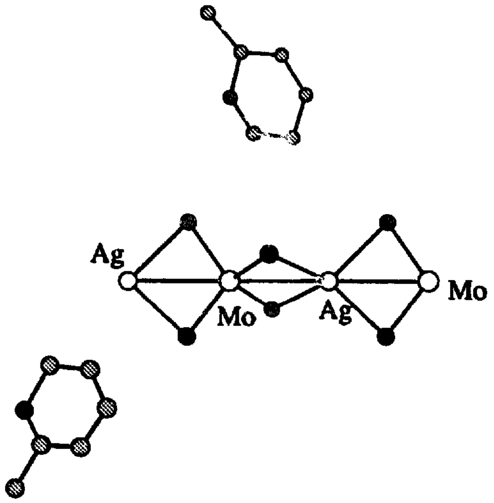
Treatment of silver nitrate or $[Ag(CCPh)]_n$ with the calixarene (**41**) in the presence of pyridinium chloride leads to the formation of the complex $[pyH][(\mathbf{41})Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)]$. Each chloride ligand can be replaced by bromide or iodide, and the chloro-complex has a high affinity for group 1 metal ions (including Li^+), extracting them from aqueous solution into organic solvents. The crystal structure of $[pyH][(\mathbf{41})Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)]$ has been determined [59].



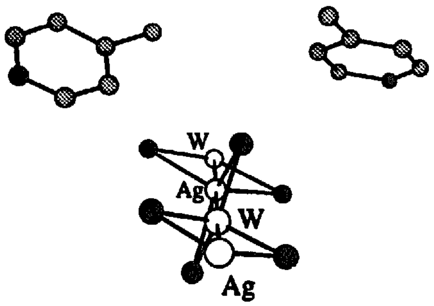
(41)

The syntheses of the complexes $[Ag_5As_4L_4(H_2O)_5X]_n$ ($X = NO_3$, ClO_4) in which H_4L = (+)-tartaric acid have been reported. Both complexes have been structurally characterized and possess polymeric structures; $\{As_2L_2\}^{2-}$ dimers are linked by chains of silver atoms, bonded through hydroxy- and carboxylate-oxygen donor atoms. The water molecules are also associated with the metal centres [60].

The reactions of $[NH_4]_2[MS_4]$ (M = Mo, W) with AgI and 2-methylpyridine or 4-methylpyridine (L) yield the polymers $[AgMS_4.L]$. In the solid state, extended structures are observed in which there are continuous --M-Ag-M-Ag---chains. Two of the systems are represented in structures (**42**) and (**43**) [61].

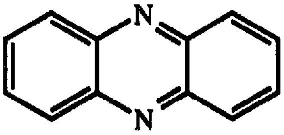


(42)



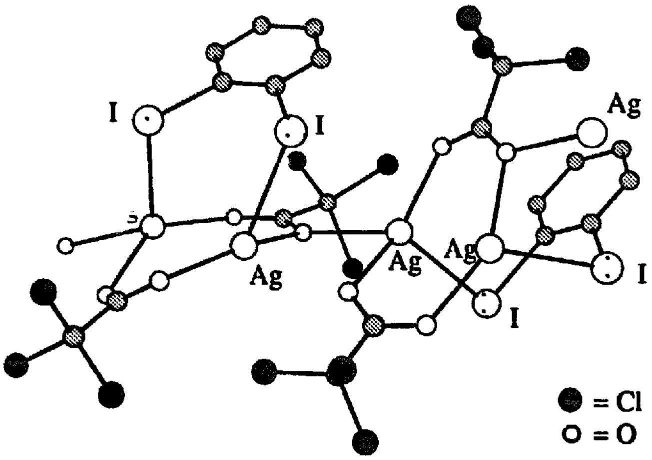
(43)

One-dimensional cationic chains are present in the solid state of the complex $[Ag_4(Me_3NCH_2CO_2)_6]_n[ClO_4]_{4n}$. The structural motif consists of a centrosymmetric tetrasilver unit which contains two independent silver(I) centres. Pairs of silver atoms are bridged by three carboxylate groups and adjacent Ag_2-units are connected by bridging carboxylate-oxygen atoms [62]. Phenazine (44) links silver(I) centres together to produce polymeric structures in the solid state of the complexes $[Ag(44)][ClO_4]$ and $[Ag_2(44)][NO_3]_2$ — the preparations of these compounds have been reported as well as single crystal X-ray diffraction studies. In the perchlorate salt, infinite --Ag-N-Ag-N-Ag-N--- chains run along the *a* axes and π-π interactions are present along the *c* axes. The nitrate salt possesses a 2-dimensional framework of Ag_6-rings with weak Ag-O interactions giving a sheet structure; once again, π-π interactions are present between the phenazine ligands [63]. Novel examples of complexes containing a μ-iodo-organic ligand have been described — Ag_2O reacts with an excess of CCl_3CO_2H and aryl iodide (aryl iodide = PhI or 1,2-$I_2C_6H_4$) to give $[Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(PhI)]$ or $[Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(1,2\text{-}I_2C_6H_4)]$. The solid state structure of $[Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(PhI)]$ shows it to be polymeric with the iodo-functionalities involved in bridging interactions ($\angle$Ag-I-Ag = 61.4(1)°). Part of the polymeric structure of $[Ag_2(O_2CCCl_3)_2(HO_2CCCl_3)(1,2\text{-}I_2C_6H_4)]$ is shown in (45) and again illustrates the bridging role of the halogen atoms [64].



(44)

Finally, three related inorganic clusters involving silver and gold atoms in their cores have been reported, two by Teo *et al.* The clusters have common $Ag_{12}Au_{13}$ core-stoichiometries which are present in the cations $[Ag_{12}Au_{13}(PMe_3)_{10}Cl_2(\mu\text{-}Cl)_6]^+$ [65], $[Ag_{12}Au_{13}(PPh_3)_{10}Cl_2(\mu\text{-}Cl)_5]^+$ [66] and $[Ag_{12}Au_{13}(PPh_3)_{10}Br_2(\mu\text{-}Br)_4(\mu_3\text{-}Br)_2]^+$ [67].



(45)

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