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Silver 1994

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Contents

1. Introduction

This review is a representative, but not comprehensive, survey of the coordination chemistry of silver published in 1994. It is based on searches of *Chemical Abstracts* (volumes 120, 121 and 122) and the Cambridge Crystallographic Data Base, as well as individual searches of ten major journals of the field. While organometallic complexes were excluded, a few silver–carbonyl complexes of general interest to coordination chemistry are presented in Section 4.7. Also excluded were clusters containing $AgPR_3$-units, but a few examples of cubane structures involving such units are discussed in Section 4.6. Several figures in this review were redrawn from crystallographic coordinates available through the Cambridge Structural Data System.

Theoretical calculations of total energy and hardness values for Ag^+, several bases and their Ag complexes, show that the HSAB principle is valid in the majority

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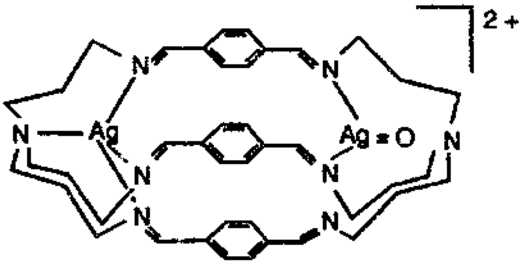
of cases, although a few exceptions do exist; e.g. ammonia is calculated to bind to silver in preference over phosphine, contrary to HSAB predictions [1].

2. Silver(III)

Theoretical calculations have been carried out in order to estimate the ligand field effects on the structural and thermodynamic parameters of 3d and 4d metal aqua di- and trications. For $[Ag(H_2O)_6]^{3+}$, a Ag–O bond length of 2.127 Å and a Raman band at $\nu = 460\ cm^{-1}$ for the symmetrical Ag–O stretching vibration are predicted. For $[Ag(H_2O)_6]^{2+}$, Ag–O(ax) = 2.486 and Ag–O(eq) = 2.223 Å (tetragonally elongated Jahn–Teller distorted cation) and $\nu = 317\ cm^{-1}$. The Jahn–Teller stabilization energy of 1203 cm^{-1} for Ag^{2+} is more than twice that for Cu^{2+}. Binding energies, ΔE_b, of 2459 (Ag^{3+}) and 1155 kJ mol^{-1} (Ag^{2+}), as well as a hydration enthalpy of -1931 kJ mol^{-1} (Ag^{2+}) are also calculated for the hexaaqua complexes. For square-planar $[Ag(H_2O)_4]^{3+}$, the corresponding calculated values are Ag–O = 1.976 Å and $\Delta E_b = 2195$ kJ mol^{-1}. A Mulliken population analysis estimates the metal atom charges to be +1.90 (Ag^{3+}) and +1.69 (Ag^{2+}), and the ionization potentials to be 34.83 (Ag^{3+}) and 21.49 eV (Ag^{2+}) for the $[Ag(H_2O)_6]^{n+}$ cations [2].

Condensation of $(H_2NCH_2CH_2)_3N$ and p-$(CHO)_2C_6H_4$ with $AgNO_3$ in MeOH yields, after addition of $NaClO_4$, a dinuclear silver cryptate $[Ag_2OL][ClO_4]_2$ (**1**), described as the second Ag(I,III) complex known, and characterized by elemental analysis, IR, ^1H NMR and UV–VIS spectroscopy and conductivity measurements, as well as crystallography. The four-coordinate Ag(I)-centre is located at the basis of a trigonal pyramid with bonds to three imino N-atoms (2.286(6), 2.301(5), 2.308(5) Å) and the bridgehead-N (2.455(5) Å). The Ag(III)-centre is three-coordinate, having distorted-T geometry, with Ag–N = 2.181(6), 2.198(6) Å and Ag–O = 1.586(4) Å. Distinction of the Ag(I) and Ag(III) sites is not possible by XPS spectroscopy as only one peak is recorded for each of the $3d_{3/2}$ (373.6 eV) and $3d_{5/2}$ (367.6 eV) orbitals [3]. The nature of (**1**) has been questioned by a subsequent reinvestigation of its crystal structure. According to this second interpretation of the X-ray diffraction data, the structure consists of a dinuclear Ag(I) cryptate $[Ag_2L][ClO_4]_2$ containing Ag-atoms in two different coordination environments: one in a four-coordinate trigonal pyramidal site (similar to the Ag(I)-centre of the disputed structure) and one disordered between a tetrahedral AgN_4 and a trigonal planar AgN_3 site (with a fourth long interaction to a perchlorate anion), having occupancy factors of 22% (**2**) and 78% (**3**) respectively. The latter interpretation is supported by the absence of an ESR signal. The ^1H NMR spectrum at 230 K indicates that the minor component of the disordered model is dominant in solution [4].

Silver(III) is capable of oxidizing N(III) to N(V). A kinetic study of the reaction of $[Ag(H_2L)]^{3+}$ (H_2L = ethylenebis(guanidine)) with NO_2^- reveals a first-order dependence on $[N^{III}]$ and a rate law containing the rate constants of four pH-dependent reactions: $[Ag(H_2L)]^{3+}/HNO_2$ (k_1), $[Ag(H_2L)]^{3+}/NO_2^-$ (k_2), $[Ag(HL)]^{2+}/NO_2^-$ (k_3), and $[Ag(L)]^{+}/NO_2^-$ (k_4). In the pH range 1–3 only the k_1



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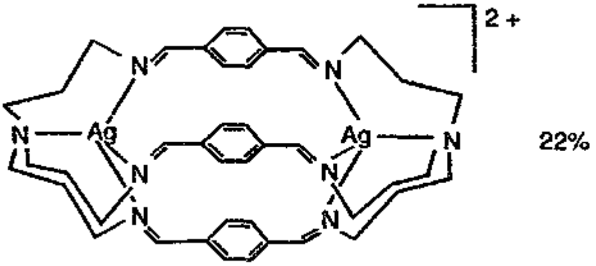

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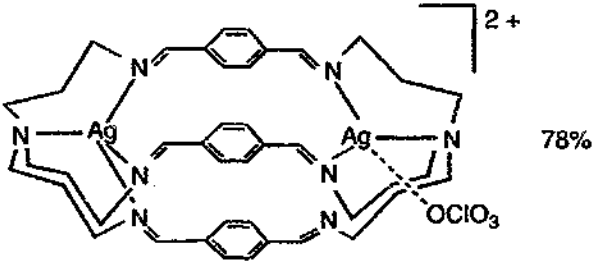
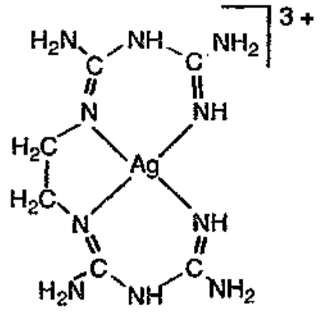


(3)

and k_2 terms are significant, while at pH = 5.5–7.5 the relevant terms are k_2 and k_4. Conversion to Ag^+ and NO_3^- is quantitative while >95% of H_2L is recovered [5]. The electron transfer from organic or metal complex reductants to the Ag(III) complex (**4**) has been studied by stopped-flow techniques in aqueous media. The Ag(III)→Ag(I) process takes place in two one-electron steps where the first electron is provided by the external reductant, while the second one results from either intermolecular or intramolecular electron transfer with oxidation of the ligand [6].



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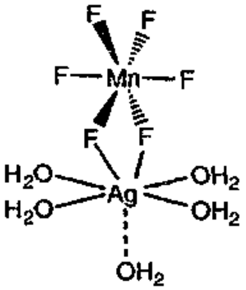
3. Silver(II)

Formation constants have been determined potentiometrically for the *N*-bound complexes $Ag(Hpic)^+$ and $Ag(Hpic)_2^+$ in acetonitrile, while the formal redox potentials of the corresponding Ag^+/Ag^{2+} couples have been determined by chronovoltamperometry. Bulk electrolysis of $Ag(Hpic)_2(ClO_4)$ in 0.1 M Et_4NClO_4/CH_3CN at 1.85 V (vs. NHE) gives a product consistent, by elemental analysis, with $Ag(Hpic)_2(ClO_4)_2$ [7]. The estimation of structural and thermodynamic parameters for $[Ag(H_2O)_6]^{2+}$ by theoretical calculations has been discussed in Section 2 [2].

4. Silver(I)

4.1. Complexes with halide and pseudo-halide ligands

An unusual seven-coordination has been observed in the structure of $AgMnF_4 \cdot 4H_2O$ (5); the Ag-atom occupies the top of a compressed AgO_4 square pyramid and its coordination is completed by a fifth, long $Ag \cdots OH_2$ interaction and two Ag–F contacts with MnF_4^- (Ag–F = 2.657(4) Å) [8].



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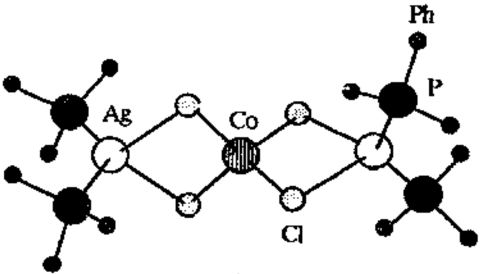
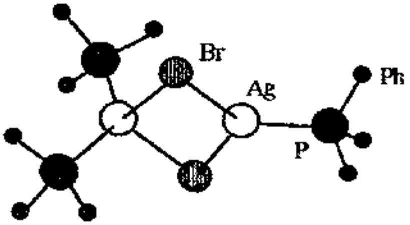


(6)

A trinuclear $Co[(\mu\text{-}Cl)_2Ag(PPh_3)_2]_2$ (**6**) complex has been prepared from $[CoCl_2(PPh_3)_2]$ by the addition of $AgBF_4$ and PPh_3. The long Ag–(μ-Cl) bonds of 2.687(6)–2.776(6) Å, which separate the metal atoms by distances of 3.503(3) and 3.514(3) Å, as well as the similarity of the UV–VIS spectrum of (**6**) to that of $[CoCl_4]^{2-}$, suggest an ionic formulation, $[(PPh_3)_2Ag]_2[CoCl_4]$, which is countered by the absence of solution conductivity and of an observable $^{31}P\{^1H\}$ NMR spectroscopic resonance [9]. In the asymmetric complex $Ag_2(\mu\text{-}Br)_2(PPh_3)_3$ (**7**), however, there is a shorter Ag···Ag separation of 3.317 Å [10].



(**7**)

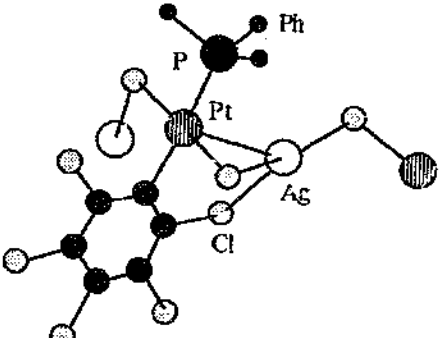
Ag–Br = 2.586–2.825 Å
Ag–P = 2.411–2.462 Å
Br–Ag–Br = 98.95–108.95°

The reaction of *trans*-$PtX_2(C_6F_5)L^-$ and Ag^+ affords polymeric $[PtAgX_2(C_6F_5)L]_x$ (X = Cl, L = PPh_3, tht, *p*-$MeC_6H_4NH_2$, py; and X = Br, L = PPh_3). Crystallographic characterization of the X = Cl, L = PPh_3 species (**8**) shows that the polymeric chain consists of *trans*-$[PtCl_2(C_6F_5)PPh_3]$ square-planar anions linked by Ag-cations, which occupy two-coordinate sites between the Cl-atoms of consecutive Pt-units. Of the alternating long/short Ag···Pt distances, the short one is bonding, as also indicated by the acute Ag–Cl–Pt angle (Table 1). Addition of PPh_3 breaks one of the Ag–Cl bonds of the chain and forms the dinuclear $(PPh_3)Ag(\mu\text{-}Cl)PtCl(C_6F_5)PPh_3$ (**9**) containing a weaker Pt···Ag bond, since the acidity of Ag^+ is partially satisfied by the PPh_3 ligand [11].

Brominated carboranes bind to silver through the bromine atoms. The silver–carborane complex $Ag(Br_5CB_9H_5)$, prepared from $AgNO_3$ and $Cs(Br_5CB_9H_5)$ in H_2O, has been characterized by ^{11}B NMR and IR spectroscopy, and elemental analysis.

Table 1
Bond lengths (Å) and angles (deg) for (**8**) and (**9**)

	(8)	(9)
Ag–Pt	2.855(2)	2.945(1)
Ag–(μ-Cl)	2.556(6)	2.514(2)
Ag–Cl	2.458(5)	–
Ag–P	–	2.382(3)
Ag–Cl–Pt	71.6(2)	71.7(2)°



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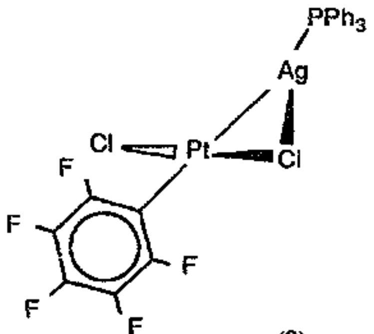
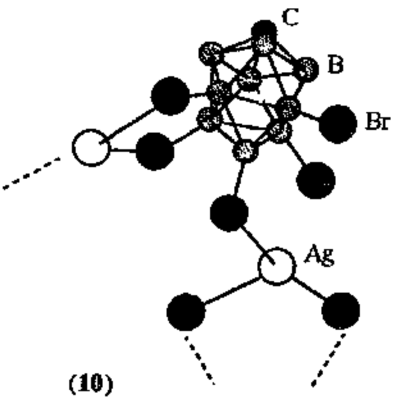


(9)

The crystal structure of its toluene solvate (**10**) is a zigzag chain of $Br_5CB_9H_5$-anions bridging Ag-cations by the formation of two shorter Ag–Br bonds of about 2.78 Å to one Ag-atom, and a longer Ag–Br bond of 2.84 Å to another Ag-atom. Reaction of (**10**) with trityl bromide yields a stable trityl carborane [12]. Treatment of Fe(tpp)Br with two equivalents of $Ag(Br_6CB_{11}H_6)$ in *p*-xylene gives crystallographically characterized $[Fe(tpp)][Ag(\eta^3\text{-}Br_6CB_{11}H_6)_2]$. Its anion, (**11**), consists of two carborane units octahedrally coordinated to the Ag^+-centre through three Br-atoms from each $(Br_6CB_{11}H_6)^-$; Ag–Br = 2.865(3), 2.882(3) and 2.891(3) Å. The inert bis-(carborane)silver anion, (**11**), is appropriate for the isolation of coordinatively unsaturated cations, such as the formerly elusive $[Fe(tpp)]^+$ [13].



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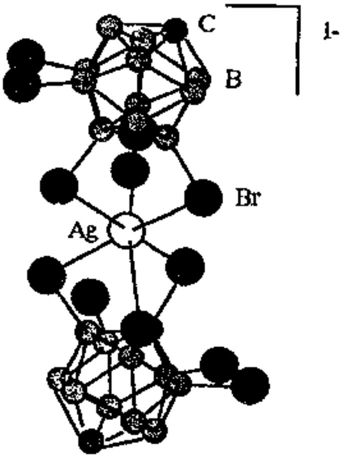
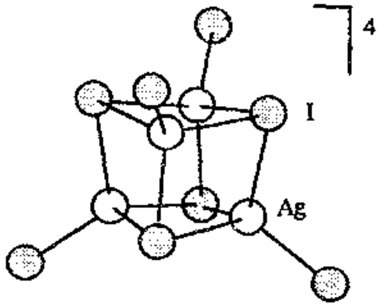


(11)

A novel cubane, the third known form of $[Ag_4I_8]^{4-}$, has been identified in the crystal structure of $[n\text{-}Pr_4N]_4[Ag_4I_8]$ (**12**): Ag–(μ_3-I) = 2.897(2)–2.932(3) Å, Ag–I = 2.748(2)–2.765(2) Å, Ag···Ag = 3.296(3)–3.850(3) Å [14]. The complex

$[Cu_3(O(CH_2)_3NH_2)_4][Ag_3I_5]$, characterized by elemental analysis and IR spectroscopy, is a poor ionic conductor, $\sigma = 1.13 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 323 K [15].



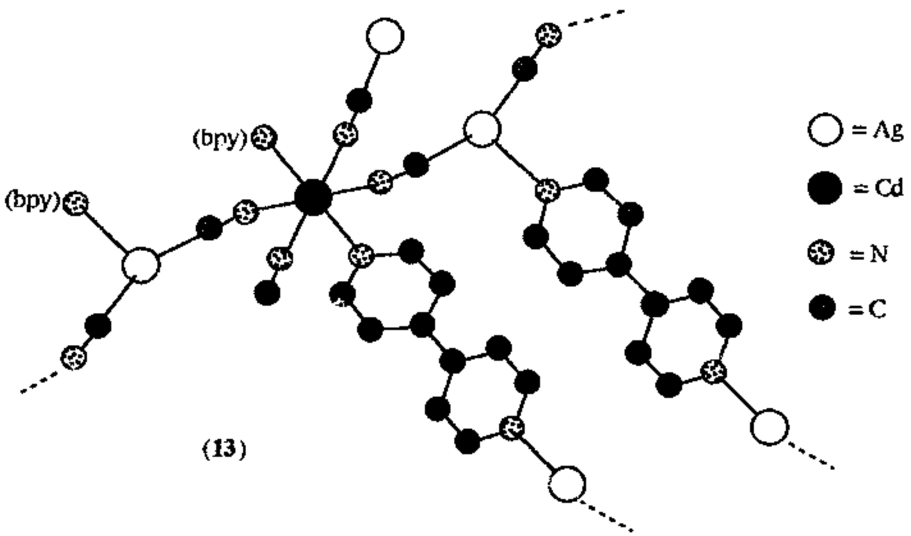
(12)

Three articles describe the use of silver–cyanide connectors in the construction of impressive interpenetrating networks. In the structure of $Cd(bpy)_2\{Ag(CN)_2\}_2$ **(13)**, Cd-atoms are linked in two dimensions by bent (153.6(2)°) NC–Ag–CN units forming $Cd\{Ag(CN)_2\}_2$ sheets. Penetrating adjacent sheets, bpy-ligands link Ag- and Cd-atoms of alternate sheets. For the three-coordinate Ag-atoms, Ag–N (bpy) = 2.463(3) Å [16]. Using 4-Mepy, instead of bpy, produces interwoven $Cd\{Ag(CN)_2\}_2$ networks where Cd(4-Mepy) units are connected by bent (166.2(7)°) NC–Ag–CN rods. This structure is the host to additional intercalated 4-Mepy molecules [17]. In the more complex structure of $[Cd(pyrz)\{Ag_2(CN)_3\{Ag(CN)_2\}]$ (pyrz = pyrazine), Cd-atoms are linked by NC–Ag–(CN)–Ag–CN units in one direction and pyrazines in the other, forming $Cd(pyrz)\{Ag_2(CN)_3\}$ sheets, interwoven by NC–Ag–CN rods which connect Cd-atoms of the first and fourth, second and fifth, etc., sheets [16]. Similarly, a triple interpenetrating framework is shown in the structure of $Rb[Cd\{Ag(CN)_2\}_3]$, which contains Cd-cations octahedrally coordinated by the N-atoms of linear NC–Ag–CN connectors [18]. $\{Ag_2(CN)_3\}^-$ connectors are also encountered in the linear chain structure of $[Cd(4\text{-}Mepy)_4\{Ag_2(CN)_3\}][Ag(CN)_2]$ **(14)** in which square-planar $Cd(4-Mepy)_4$ units are linked by $\{Ag_2(CN)_3\}^-$ rods, while $\{Ag(CN)_2\}$-anions are arranged between and perpendicularly to the chains with short Ag–Ag distances of 2.9879(9) Å [17]. Some related three-dimensional coordination polymers involving silver and N-donor ligands are discussed in Section 4.5.

In the crystal structure of $[Ni(bpy)_3][Ag(CN)_2]_2$, the anion contains linearly coordinated cyanides with Ag–C = 2.052(5) and C–N = 1.138(8) Å [19].

4.2. *Complexes with oxygen ligands*

Structural studies of silver carboxylates have been the focus of two research groups. The crystal structure of silver glycolate, $Ag_2(HOCH_2CO_2)_2$ **(15)**, consists of a centrosymmetric dimer with a short Ag–Ag contact of 2.8810(9) Å, Ag–O = 2.253(2), 2.234(2) Å, and O–Ag–O = 150.95(7)°. Longer Ag–O interactions with hydroxy and carboxy O-atoms of neighbouring dimers generate a polymeric structure



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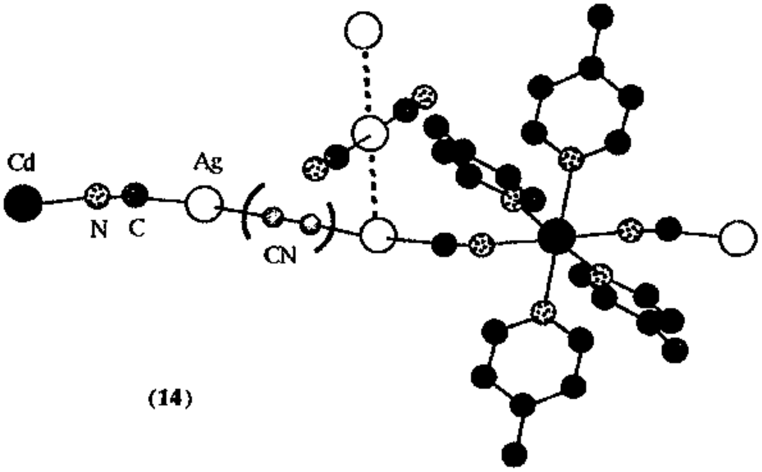

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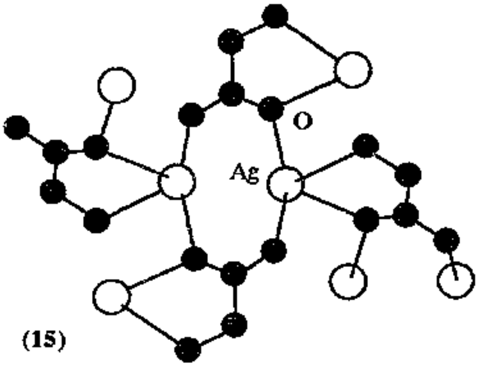
[20]. A shorter Ag–Ag distance of 2.831(2) Å is measured in the structure of dimeric aquasilver *N*-acetylanthranilate (**16**), containing three-coordinate Ag-atoms with Ag–O = 2.185(2), 2.207(2) Å and Ag–O(H_2O) = 2.518(4) Å [21]. In the structure of silver (+)–Htartrate (**17**), silver is found in an unusual five-coordinate environment, when Ag–O interactions of up to 2.684(4) Å are taken into account, while there is a sixth, long Ag···O interaction of 2.801(3) Å; one tartrate acts as didentate and two further tartrates as monodentate ligands, while the fifth coordination site is occupied by a water molecule [22]. Crystallographic and analytical data have been reported for a silver (+)–tartrate complex [23]. The crystal structure of silver

o-nitrobenzoate has been described. It consists of $[Ag(\mu\text{-}O_2CC_6H_4NO_2)]_2$ **(18)** units (Ag–Ag = 2.804(1), 2.892(1) Å) linked by secondary Ag···O(carboxylate) interactions forming a three-dimensional network [24]. Related structures of silver complexes with mixed N/O-donor carboxylate derivatives are discussed in Section 4.8.



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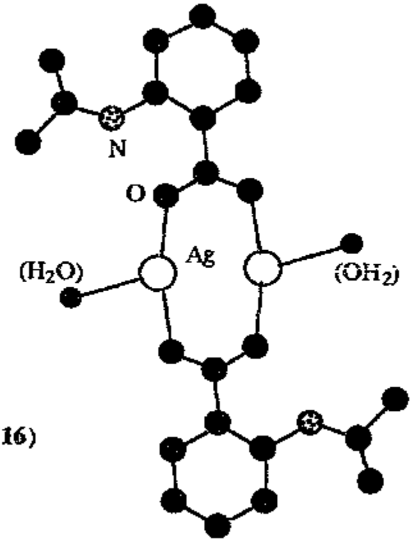

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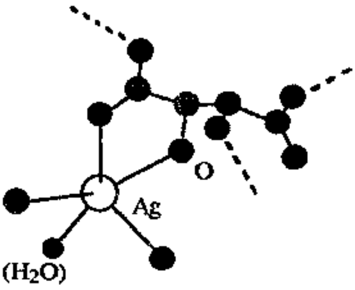

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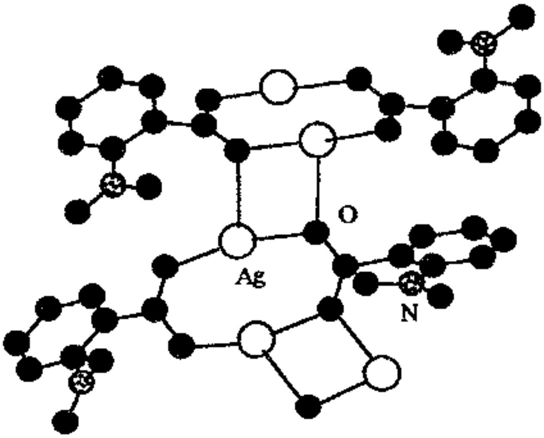
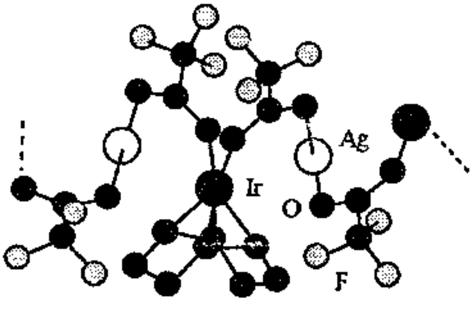


(18)

An infinite Ag–Ir zigzag chain, with alternating Ag···Ir distances of 2.9078(5) and 2.9097(5) Å, is contained in the structure of $[(cod)Ir(\mu\text{-}O_2CCF_3)_2Ag]_n$ **(19)**, prepared from $[Ir(cod)Cl]_2$ and $Ag(O_2CCF_3)$ in toluene. The Ag-atoms are linearly coordinated by two bridging CF_3CO_2 with Ag–O = 2.194(7), 2.225(6) Å. The ^1H, ^{13}C, ^{19}F and ^{109}Ag NMR spectra indicate that the solid state structure is maintained in solution [25]. The reaction of Ag_2O with Hhfacac yields the asymmetric dimer (**20**) with the chelating hfacac in both the endo- and exodentate modes. For the four-coordinate silver atom, Ag–O = 2.346(4)–2.419(5) Å, and for the three-coordinate one, Ag–O(hfacac) = 2.415(4), 2.441(3) Å, Ag–O(H_2O) = 2.263(6) Å. Both Ag-atoms of (**20**) have long interactions with C-atoms of adjacent molecules, so that their overall geometries approximate to square pyramidal and tetrahedral, respectively. The water molecule of (**20**) is readily displaced by a variety of ligands to yield mononuclear (hfacac)AgL complexes (see Section 4.8) [26].



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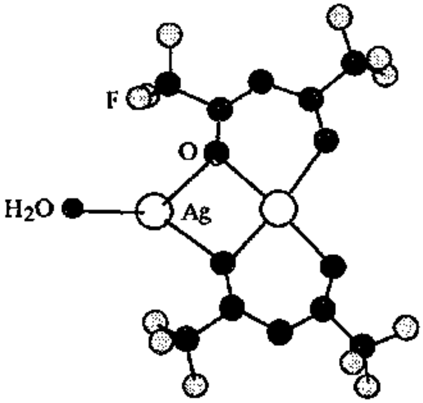
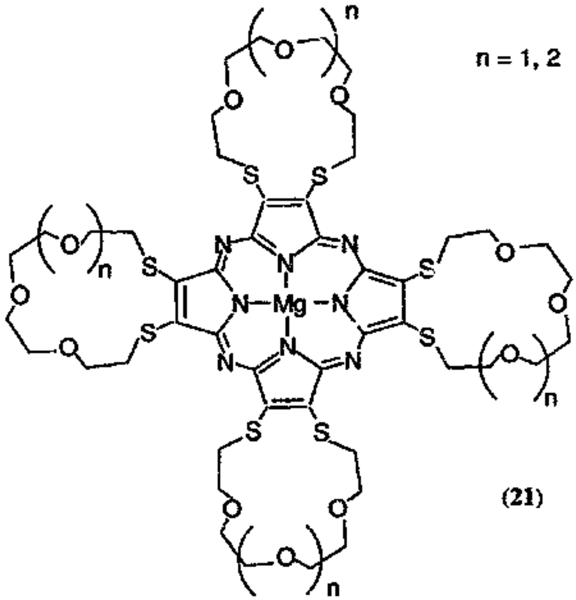


(**20**)

Measurements of the standard Gibbs transfer energies, ΔG_t°, of the [Ag(18-crown-6)]ClO_4 complex at 303 K show the transfer from MeOH to MeOH/CH_3CN solutions to be thermodynamically unfavourable. Analysis of ΔG_t° to the ionic components, $\Delta G_t^\circ(Ag^+)$ and $\Delta G_t^\circ(ClO_4^-)$, reveals that this salt is heteroselectively solvated in MeOH/CH_3CN; $[Ag(18\text{-crown-}6)]^+$ is preferentially solvated by CH_3CN, while for ClO_4^- MeOH is preferred [27]. Two magnesium porphyrazines substituted at ,-position with a dithio-18-crown-5 or dithio-18-crown-6 (**21**) have been examined with respect to their complexing ability towards Ag^+. Based on spectroscopic data, it is suggested that a dimeric complex is formed, containing four Ag-atoms sandwiched between the two porphyrazines and four Ag-atoms on either side of the dimer. Proton NMR chemical shifts indicate that the 12 Ag-atoms are located in the crown ether rings [28]. A new "crownophane" containing two pendant pyridine groups (**22**) is shown to extract Ag^+ from an aqueous to an organic phase with an efficiency superior to that of commercially available agents. This is achieved by formation of a 1:1 complex between Ag^+ and (**22**) in which both polyether and pyridine moieties participate, as indicated by ^{13}C NMR spectroscopic study [29].

Kinetically stable silver complexes of two calixspherands with O-donor atoms and a highly shielded cavity were prepared in an effort to identify compounds which can be used in cancer radioimmunotherapy. Silver exchange between a non-deuterated and a partially deuterated calixspherand can be followed by ^1H NMR spectroscopy. Even though the decomplexation rates are the lowest reported for silver to date



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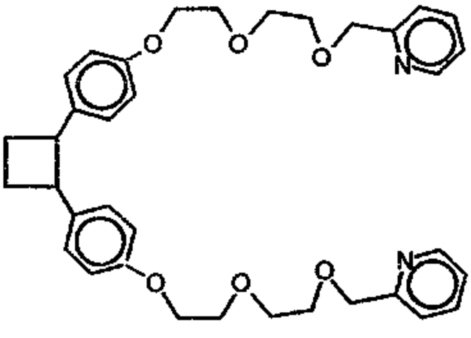
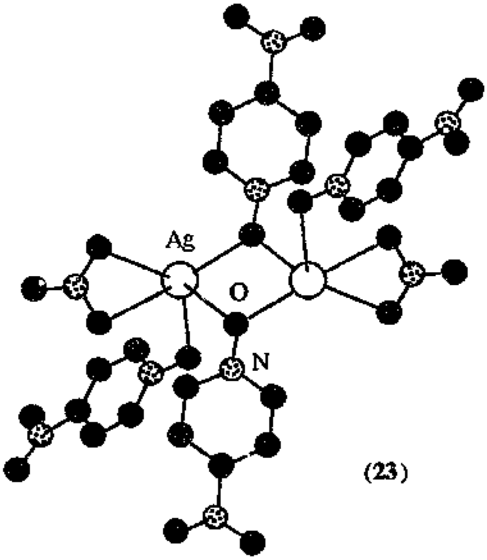


(22)

(50.9 and 131 h), these complexes are not sufficiently stable for in vivo use [30]. One-electron reduction of quinone-functionalized calix [4] arenes results in cyclic voltammetric observation of enhanced Ag^+ binding, which cannot be attributed to π-quinone interactions with the metal [31].

The crystal structure of a 4-nitropyridine N-oxide adduct with silver nitrate (**23**) has been reported. The Ag-centres are five-coordinated by two nitrate-O and three N-oxide O-atoms, with Ag–O distances ranging from 2.320(4) to 2.612(4) Å, while there is a sixth, long interaction of 2.919(7) Å with a nitrate-O [32]. In the structure of the dimeric complex (**24**) tetrahedral Ag-cations bridge enantiomeric $[(\text{trien})Co(\text{gly})]^{2+}$ units [33].



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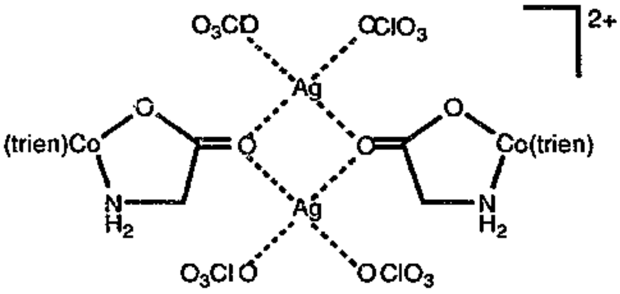

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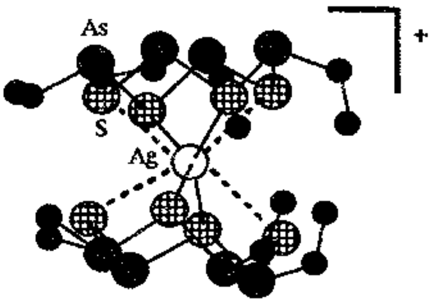
4.3. *Complexes with sulfur ligands*

The arsathiane ligand *cyclo*-(EtAsS)$_n$ reacts with silver triflate to form [{*cyclo*-(EtAsS)$_4$}$_2$Ag][O_3SCF_3] containing cation (**25**), in which the Ag-atom is sandwiched between two crown-shaped ligands having their S-atoms directed towards the metal. The eight S-atoms define a quadratic antiprismatic coordination geometry which is unusual for a d^{10}-metal; it shows alternating short (2.767(5) and 2.716(7) Å) and long (3.328(9) and 3.218(6) Å) Ag–S distances [34].

Silver(I) forms a 1:2 complex with 2-methylindole-3-carboxyaldehyde thiosemicarbazone, for which stability constants of 298–313 K have been determined spectrophotometrically; the negative ΔG values are intermediate between those of the corresponding Cu and Hg complexes [35]. Stability constants and thermal stability



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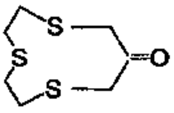
of metal (including silver) semithiocarbazide complexes have been reported [36]. The formation of Ag^+ complexes with thiourea and *N*-substituted thioureas has been studied in EtOH, and the determined thermodynamic parameters for AgL^+, AgL_2^+ and AgL_3^+, were compared to those of earlier studies in MeOH and H_2O [37]. An *N,N'*-disubstituted thiourea has been proposed as a spectrophotometric reagent for Ag^+ determination [38].



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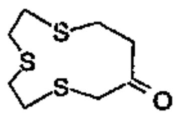

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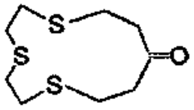
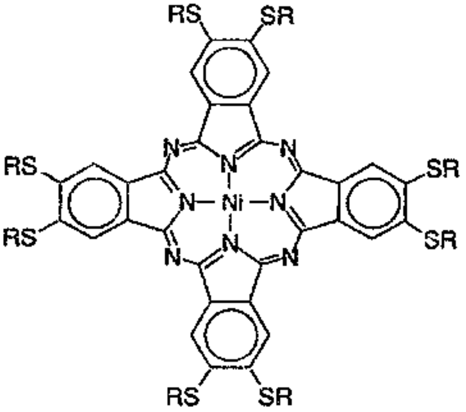


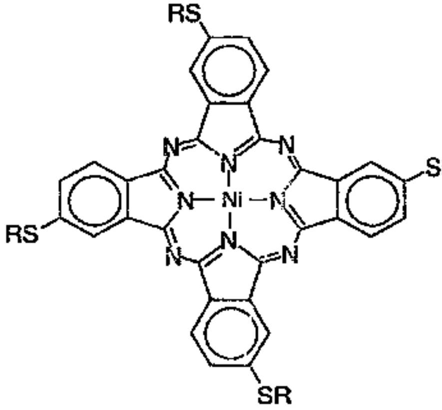
(28)

The synthesis of three novel thiacrown ethers (**26**–**28**) has been reported along with a conductiometric titration study of their Ag-coordination in MeCN and thf. The importance of the solvent becomes evident as complexes of various, well or incompletely defined, compositions are formed in the two solvents studied [39]. Three papers from the same group describe the syntheses of metal–phthalocyanines with extended peripheral groups, as well as the complexation of heterometal cations to those groups. The Ni–phthalocyanines (**29**), with eight alkylthio, and (**30**), with four alkylthio functional groups, form the $[NiL][AgNO_3]_2$ and $[NiL][AgNO_3]_4$ complexes, respectively, which have been characterized by elemental analyses and IR. Monitoring the Ag-complexation by UV in the Q-band region verifies the Ni–phthalocyanine:Ag ratios, suggesting a polymeric structure for these materials [40,41]. In contrast, the zinc phthalocyanine complex (**31**) with four fused $[13aneS_4]$ functional groups, forms the monomeric pentanuclear $ZnAg_4$ complex, where each Ag-atom is presumably coordinated by a $[13aneS_4]$-ring [42].

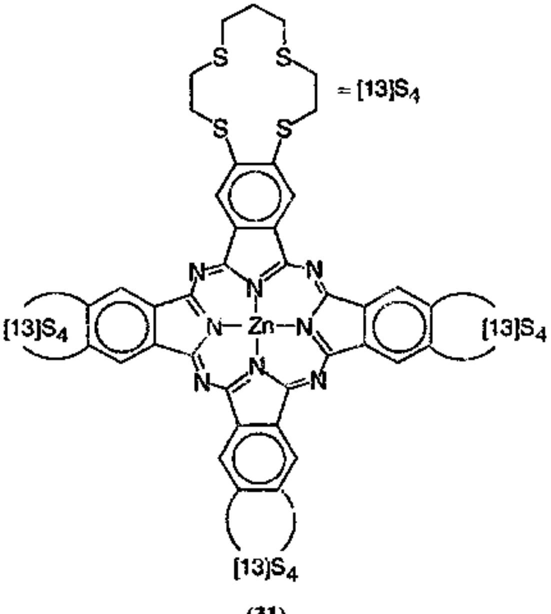
A novel macrocyclic hexadentate S_6-ligand, ligand L, forms a dinuclear complex $[Ag_2(NCMe)_2L][BF_4]$ (**32**) with the two silver centres in a distorted tetrahedral AgS_3N environment, each one utilizing two S-atoms from one side chain and one from the other; Ag–S = 2.487(4), 2.595(4), 2.603(4) Å, Ag–N = 2.27(1) Å, angles



(29) R = C_6H_{13}



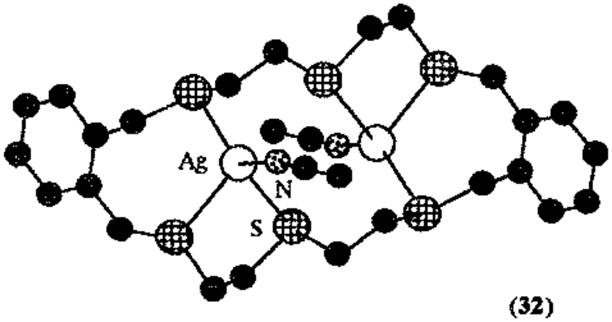
(30) R = $C_{12}H_{25}$



(31)

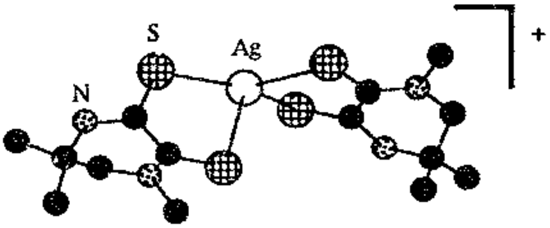
S–Ag–S and S–Ag–N = 85.7(1)–127.2(3)°. The corresponding Cu(I) dinuclear complex has also been reported [43].

The crystal structure of the $[AgL_2]Br$ (**33**) complex with a heterocyclic dithione ligand has been reported. The two dithiones chelate in an asymmetric fashion, placing the Ag-atom in a four-coordinate, distorted trigonal-pyramidal environment with average Ag–Br = 2.58(10) Å [44]. Besides the general tendency of the potentially



(32)

tetradentate dithiooxalates to form multinuclear complexes, a couple of isostructural mononuclear $(Ph_3P)_2ML$ complexes, M = Cu, Ag (**34**), have been reported. In complex (**34**), each metal is tetrahedrally coordinated by two S-atoms and two PPh_3-ligands [45]. Thiodipropionic acid forms an S-bound, insoluble silver complex, with an unspecified degree of polymerization [46].



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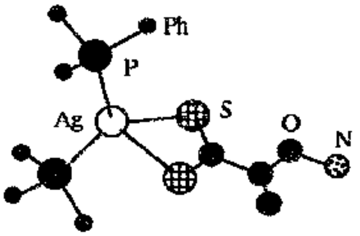
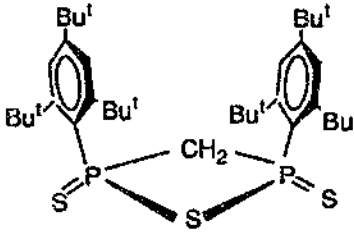


(34)

Ag–S = 2.698(1), 2.738(1) Å
S–Ag–S = 66.2°

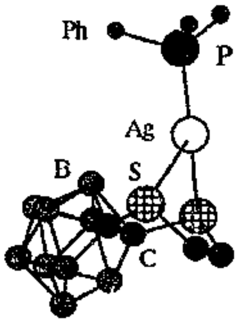
The S-donor ligand (**35**) forms 1:1 complexes with Ag^+, extracting it from aqueous solutions selectively over Pd^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, and UO_2^{2+}. It is proposed that (**35**) binds to silver using the S(=P)-atoms but not the $S(P_2C)$-atoms [47].

Two papers by the same group dealt with the coordination chemistry of thio- and



(35)

dithiocarboranes. Several [AgL] and [AgLX] complexes ($X = PPh_3$, bpy; $L = nido\text{-}C_2B_9H_{12}^-$ dithio derivatives) have been prepared from the corresponding NaL or Me_4NL salts, and characterized by IR, ^1H and ^{11}B NMR spectroscopy. In all cases, silver is coordinated to the S-atoms of the side-chains in a non-symmetrical fashion, as proved by the crystal structures of monomeric $[AgL(PPh_3)]$ **(36)** and polymeric [AgL] **(37)** complexes [48]. Reaction of a dithio-substituted *closo*-carborane ligand $B_{10}C_2H_{10}\text{–}(SC_2H_4)_2O$ with $MCl(PPh_3)$, M = Cu, Ag, affords



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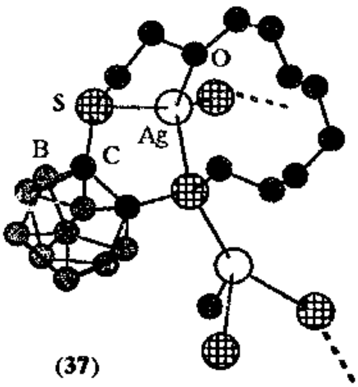

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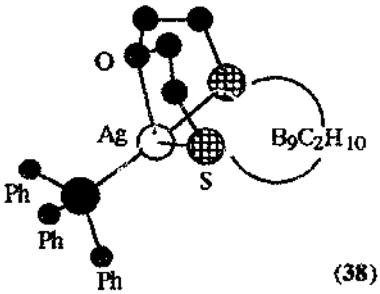
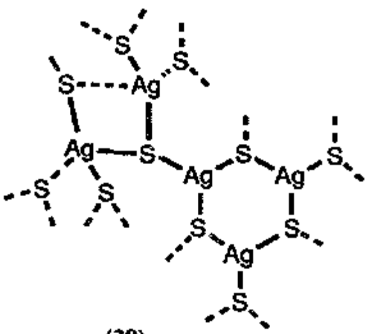


(38)

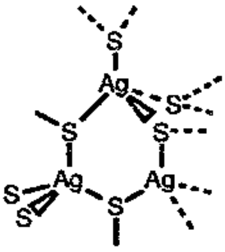
Ag–S = 2.505(5) Å
Ag–O = 2.627(9) Å
Ag–P = 2.337(5) Å

mononuclear $[(Ph_3P)ML]$ complexes of the corresponding *nido*-carborane, $B_9C_2H_{10}$–$(SC_2H_4)_2O$ by formal elimination of {BCl}. In the Ag complex, (**38**), the metal is in a roughly tetrahedral AgS_2OP environment [49].

Hydrothermal conditions in alkaline solutions were employed for the preparation of the three-dimensional materials $[NH_4][Ag_2(AsS_2)_3]$ (**39**) and $[NH_4]_5[Ag_{16}(AsS_4)_7]$ (**40**). In (**39**), one of the four-coordinate Ag-atoms is coordinated by two short and two long Ag–S bonds, and the other by three short and one long Ag–S interaction; Ag–S = 2.453(2)–3.160(2) Å and Ag⋯Ag = 2.931(1), 3.052(1) Å. Two of the 16 Ag-atoms of (**40**) are disordered between two positions separated by 2.07(3) Å and 1.98(3) Å, respectively. The Ag-atoms are four- or five-coordinate with Ag–S = 2.47(2)–3.30(2) Å and Ag⋯Ag = 3.16(2)–3.47(2) Å [50].



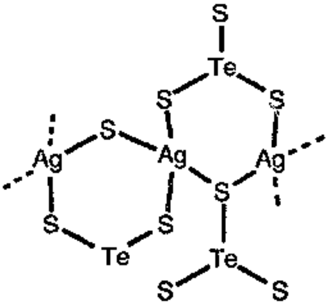
(**39**)



(**40**)

Four novel two-dimensional silver polychalcogenide materials, $AAgTeS_3$, A = K, Rb, Cs, were prepared by heating silver powder in an $A_2S/S/Te$ flux, and their thermal stabilities were probed by differential scanning calorimetry. Their structures consist of $[AgTeS_3]_n^{n-}$ networks (**41**) in which the Ag-atoms are coordinated by two monodentate and two didentate S-atoms. Two structural types were recognized: type I, isostructural with $KAgTeS_3$, $RbAgTeS_3$ and $CsAgTeS_3$, containing roughly tetrahedral Ag-atoms (Ag–S = 2.543(3)–2.667(4) Å, angle S–Ag–S = 106.1(1)–115.8(1)°); and type II isostructural with $KAgTeS_3$, containing flattened Ag-tetrahedra (Ag–S = 2.543(3)–2.667(4) Å, angle S–Ag–S = 89.9(1)–155.8(1)°). All four materials exhibit wide band gap semiconductor properties, with gaps of 2.4 and 2.2 eV [51].

Solution electrospray–MS studies of $AgClO_4/M(S_2CNR_2)_n$ mixtures, R = Et, Pr, Bu, show that the metal–dithiocarbamate complexes act as S-donor ligands towards silver. Both heterodimetallic $[AgM_2(S_2CNR_2)_{2n}]^+$ and heterotrimetallic $[AgMM'S_2CNR_2)_m]^+$ cations have been observed for M = Hg, Co, Rh, Ir, Pt. In systems with mixed dithiocarbamates, scrambling of the $M(S_2CNR_2)_2$ units over silver, or global scrambling of $(S_2CNR_2)^-$ over M, is recognized by the presence of all possible MS peaks [52]. One more example of a metal complex acting as a S-donor ligand is the μ-sulfido $[CpMo(\mu\text{-}S)(NBu^t)]_2$, which forms a polymeric chain complex (**42**) comprising Mo_2S_2 and asymmetric Ag_2S_2 rings with alternating long/short Ag–S bonds averaging 2.72 and 2.54 Å [53].



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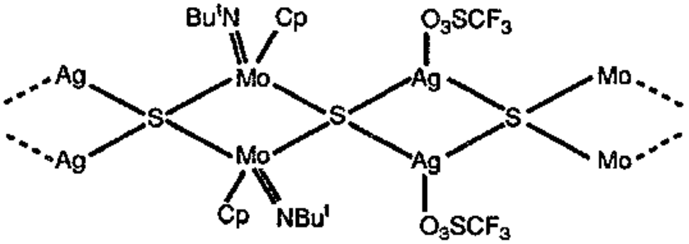


(42)

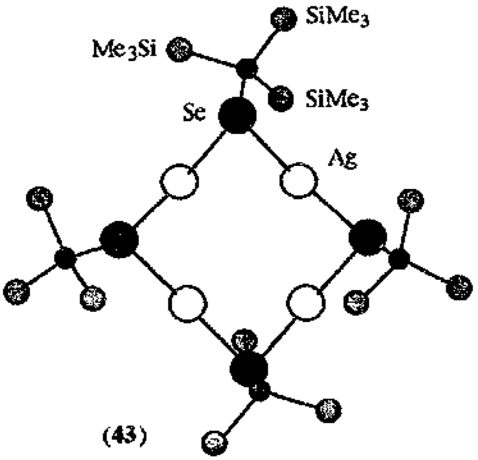
4.4. Complexes with selenium and tellurium ligands

The reactions of $AgNO_3$ with [(dme)LiSeC$(SiMe_3)_3$] in benzene or dme yield different silver selenolate products. From benzene, the monomeric [Li$(dme)_2$]{Ag[SeC$(SiMe_3)_3]_2$} was isolated, while from dme, Ag[SeC$(SiMe_3)_3$] (**43**), shown to be tetrameric in the solid state, was obtained. The planar Ag_4Se_4 core of (**43**) consists of linearly coordinated Ag-atoms with Ag–Se = 2.473(2)–2.488(2) Å, angle Se–Ag–Se = 172.45(6)–177.22(6)°, with the C$(SiMe_3)_3$ groups alternating on either side of the Ag_4Se_4 plane. A related Cu(I) material is also reported [54].

The synthesis and characterization of a silver selenourea complex [{μ-SeC$(NH_2)_2$}Ag{SeC$(NH_2)_2$}$_2]_2Cl_2$ (**44**) have been reported. Each Ag-atom is four-coordinate, with two terminal and two bridging selenourea ligands; Ag–(μ-Se) = 2.706(1), 2.750(1) Å and Ag–Se = 2.639(2), 2.645(1) Å. The acute Ag–Se–Ag angle of 65.7(1)° is a consequence of the short Ag···Ag contact of 2.983 Å [55].

4.5. Complexes with nitrogen ligands

In the structure of ethylenediamino silver icosadiborate hydrate, the dinuclear cation [(enH)Ag(en)Ag$(enH)_2]^{4+}$ was found to consist of almost linear, two-coordinate Ag-atoms, angle N–Ag–N = 171(2)°, between a bridging en and a terminal enH, with Ag–N distances of 2.15(4) and 2.10(3) Å, respectively [56]. The square-



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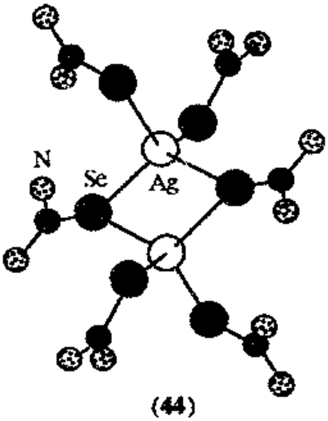
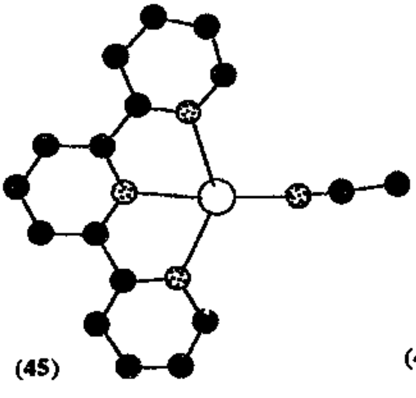


(44)

planar metal site M(en)$_2$ in the structure of ethylenediamino CuM–bis(tetraborate) hydrate has been determined crystallographically to be occupied by 40% Cu^{2+} and 60% Ag$^+$, with Cu/Ag–N distances between 2.00(1) and 2.05(2) Å; a hydrated Na$^+$ with 60% site occupancy balances the charges [57].

Mononuclear and trinuclear, four- and five-coordinate complexes have been prepared with tpy-ligands. Recrystallization of AgClO$_4$ and tpy from acetonitrile gives 4AgClO$_4$·5tpy·MeCN, which is shown by X-ray structure analysis to contain two independent complex cations—[(tpy)Ag(NCMe)]$^+$ (45) and [Ag$_3$(μ-tpy)$_2$(tpy)$_2$]$^{3+}$ (46). In the mononuclear cation, the Ag-atom is encountered in a distorted square-planar environment, with shorter Ag–N bonds to the acetonitrile and central tpy-*N* than to the two outer tpy-*N* atoms (2.174(7), 2.331(5), 2.399(7), and 2.433(7) Å).



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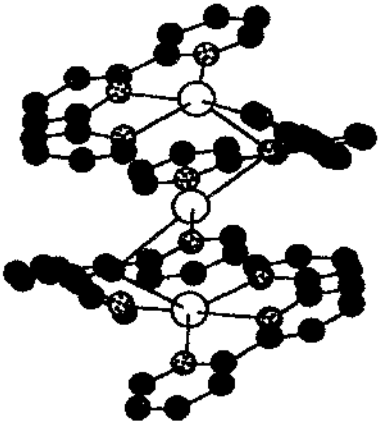
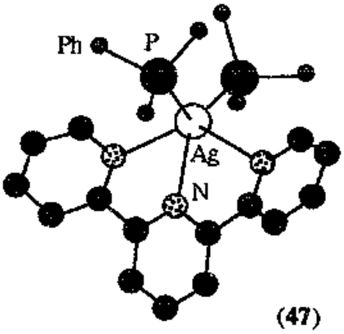


(46)

○ = Ag ⊛ = N ● = C

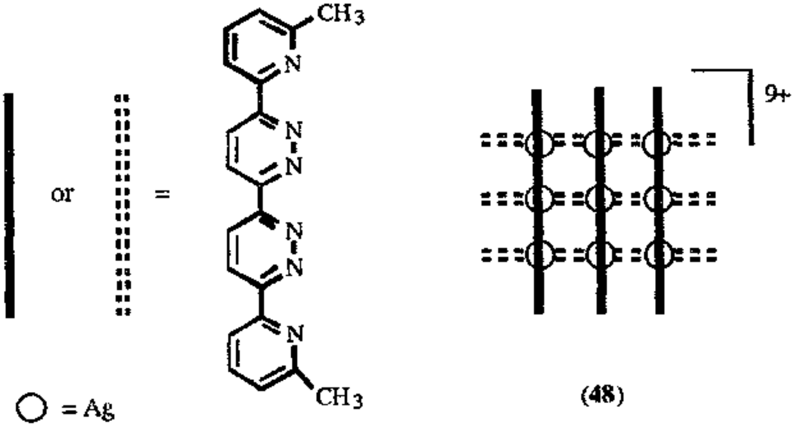
The trinuclear trication **(46)** contains a linear Ag_3 arrangement (Ag–Ag–Ag = 175.48(2)°, Ag···Ag = 3.066(1) Å) where each outer Ag is five-coordinate, with a planar tridentate tpy and two nitrogens from a μ-tpy in its coordination sphere, while the central Ag is four-coordinate planar with two N-atoms from each of the two μ-tpy ligands. The Ag–N bond lengths range from 2.188(5) to 2.818(5) Å for the central Ag, and from 2.266(5) to 2.704(4) Å for the outer ones [58]. Another five-coordinate silver complex, $[(Ph_3P)_2Ag(tpy)][ClO_4]$ **(47)**, has been reported along with its isostructural Cu analogue. Two phosphines and the central pyridine occupy the equatorial sites (Ag–P = 2.492(1), 2.525(1) Å, Ag–N = 2.457(2) Å), while the two distal pyridines occupy the axial sites (Ag–N = 2.561(2), 2.614(2) Å) of the distorted trigonal bipyramidal silver complex [59].



(47)

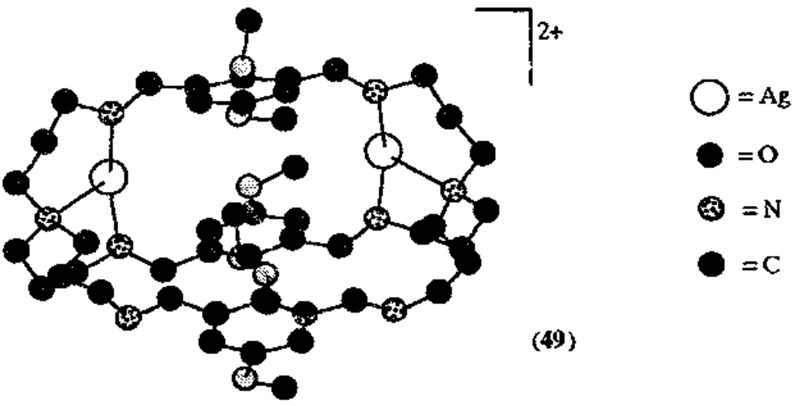
An impressive spontaneous assembly of 15 components is reported in the synthesis of $[Ag_9L_6](CF_3SO_3)_9$ **(48)**, where L is the hexadentate, tris-chelating 6,6′-bis[2-(6-methylpyridine]-3,3′-bipyrazine. The structure of this nonanuclear complex consists of a 3 × 3 grid of Ag-atoms (average Ag···Ag = 3.72(3) Å), sandwiched between two almost perpendicular (dihedral angle ≈ 72°) sets of three parallel L-ligands. The Ag-atoms occupy approximately tetrahedral sites with Ag–N bonds in the range of 2.323–2.437 Å. Solution ^1H and ^{109}Ag NMR spectroscopic results are consistent with the solid state structure [60].

Dinuclear cryptate complexes $[Ag_2L](ClO_4)_2$ **(49)** were prepared by template synthesis of the cryptands—condensation of $\{H_2N(CH_2)_3\}_3N$ with 2-OMe-5-R-1,3-$C_6H_2(C(O)H)_2$ in the presence of $AgNO_3$—and were characterized by conductivity measurements, ^1H NMR and IR spectroscopy. The crystal structure of the water solvate of the R = OMe species shows the Ag-centres to be three-coordinate with a flattened trigonal pyramidal geometry, having longer bonds (2.48(1), 2.47(1) Å) to the bridgehead N-atoms and shorter ones (2.16(2)–2.21(2) Å) to the N-atoms of two of the bridging chains. The third bridging chain does not participate in the metal coordination. The Ag···Ag separation is 7.468(12) Å. Solution NMR spectra are consistent with the solid state structure [61]. The structure of the same complex without the interstitial water molecule is by and large the same, but the Ag···Ag distance is 8.266 Å in this case [62]. A disilver cryptate similar to **(49)**, containing three- and four-coordinate *N*-bound



(48)

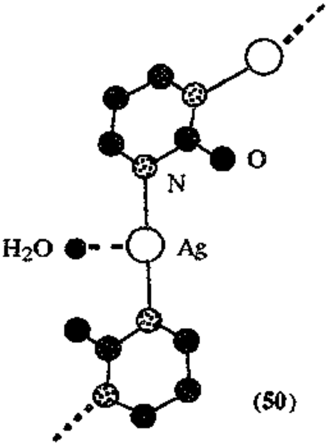
Ag-atoms (**2**, **3**), has been described in Section 2 [4]. The three-coordinate Ag-centre of the latter species has Ag–N bond lengths of 2.500(8), 2.192(6), 2.196(4) Å, which approximate to those of (**49**).



(49)

The structure of polymeric silver 2-pyrimidinolate (**50**) is shown to consist of linearly coordinated Ag–pyrimidone chains with Ag–N = 2.114(3) and 2.117(3) Å [63]. Di-2-pyridyl ketone forms a *catena*-$[AgL(NO_3)]_n$ complex (**51**) where Ag–N = 2.249(4), 2.256(4) Å, angle N–Ag–N = 150.2(1)°, and the four-coordination of silver is completed by two long Ag–O(nitrate) interactions of 2.458(4) and 2.596(4) Å [64]. The 1:1 complex formed by silver and 2,1,3-benzothiadiazole, $\{[Ag(btd)][ClO_4]\}_n$ (**52**), consists of a polymeric chain of two-coordinate Ag-atoms and μ-btd groups; Ag–N = 2.236(6), 2.254(7) Å and angle N–Ag–N = 143.3(4), 166.6(4)°. Relevant Cu(I) two-dimensional materials are also reported [65]. The crystal structure of infinite chain {PhCOC(CN)NO}Ag has been determined. The silver atom is linear and two-coordinate, with Ag–N(NC) = 2.182(9) and

Ag–N(NO) = 2.254(8) Å, in contrast with the related thallium complex in which Tl is coordinated to the nitrosyl and carbonyl O-atoms [66].



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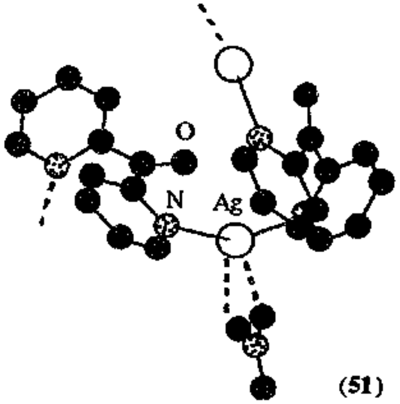

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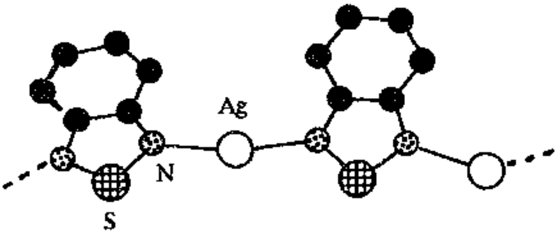
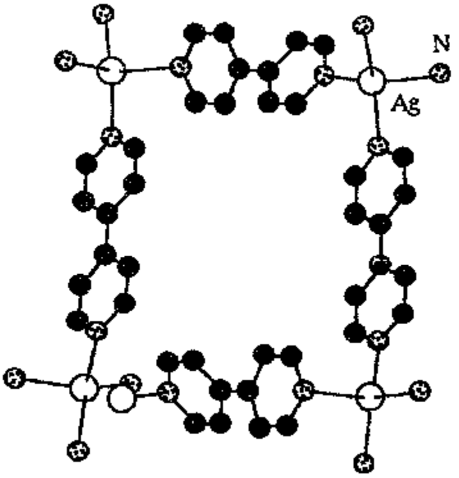


(52)

Two diamondoid structures of four interpenetrating frameworks, made up of four-coordinate Ag^+-centres and 4,4′-bpy or 4-CNpy rods, have been described. Of these, $[Ag(4,4'\text{-bpy})_2]CF_3SO_3$ (**53**) contains distorted tetrahedral Ag-cations with N–Ag–N = 98.8(2)–128.2(2)°, mean Ag–N = 2.270 and 2.380 Å, Ag···Ag = 11.6 Å (intraframe) and 6.69 Å (interframe), while in $[Ag(4\text{-CNpy})_2][BF_4]$ (**54**) the flattened Ag^+-tetrahedra have angles N_{py}–Ag–N_{py} = 127.7(5)°, N_{CN}–Ag–N_{CN} = 126.5(5)°, and distances Ag–N_{py} = 2.270(6), Ag–N_{CN} = 2.350(10), Ag···Ag = 9.93 (intraframe) and 4.822 Å (interframe). A second polymorph of $[Ag(4\text{-CNpy})_2][BF_4]$ was crystallized in smaller amounts from the same mother liquor. It contains Ag-centres linearly coordinated by pyridine N-atoms, (Ag–N_{py} = 2.175 Å, N_{py}–Ag–N_{py} = 173.4(3)°), and long interactions with two cyano N-atoms (Ag–N_{CN} = 2.71(1), 3.06(1) Å) forming distorted square nets, which are superimposed in the crystal. The Ag-atoms form distorted tetragonal meshes in both polymorphic structures, their difference being the coordination of the 4-cyanopyridine ligands, which in one polymorph act as a bridge between layers and in the other interact within the same layer [67].

The synthesis of a $[AgL_2]^+$ complex with *N*-bound 1-(*p*-$MeOC_6H_4$)-



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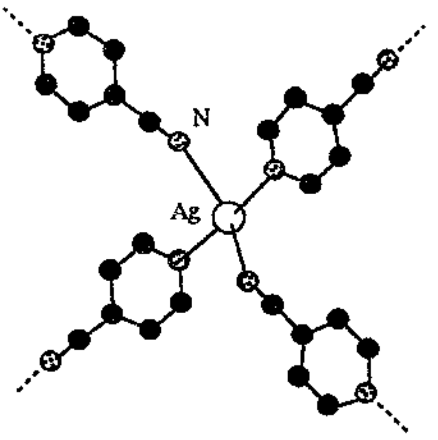
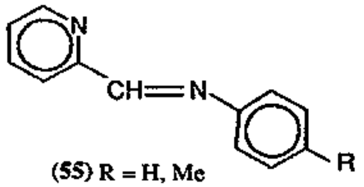


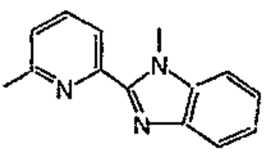
(54)

4-(CHNOH)-imidazole has been reported, along with the study of its anti-parasitic activity. Compared to the analogous Co(II), Ni(II), and Cd(II) species, the Ag(I) complex is shown to be the most active in vitro against the growth of epimastigotic forms of *Trypanosoma cruzi* [68]. The formation of an $AgN(SO_2CF_3)_2$ complex from Ag_2CO_3 and $HN(SO_2CF_3)_2$ and its use as an effective $[N(SO_2CF_3)_2]^-$ transfer agent have been reported [69]. The synthesis of $[AgL_2][ClO_4]$ complexes, where L = (**55**), was reported. Based on the observation that there is a difference between the ^{1}H NMR chemical shifts of free and coordinated (**55**) for all its hydrogen atoms, it is suggested that (**55**) acts as a chelating ligand with respect to a four-coordinate Ag-centre [70].



(55) R = H, Me

The didentate and tridentate moieties (**56**) and (**57**), when linked by CH_2 spacers, form the multidentate ligands L^1 = (**56**)–CH_2–(**57**) and L^2 = (**56**)–CH_2–(**57**)–CH_2–(**56**) containing distinct didentate and tridentate segments with different coordination preferences. Heterodinuclear $[FeAg(L^1)_2]^{3+}$ and heterotrinuclear $[FeAg_2(L^2)_2]^{4+}$ helical complexes, with two tridentate segments octahedrally coordinated to Fe^{2+} and two didentate segments tetrahedrally coordinated to Ag^+, were prepared and studied by spectrophotometric, electrospray–MS, and ^{1}H NMR spectroscopic titrations, as well as by cyclic voltammetry. A molecular mechanics energy minimization for the self-assembled, helical $[FeAg(L^1)_2]^{3+}$, points to a C_2 structure with a severely distorted tetrahedral geometry around the silver atom [71].



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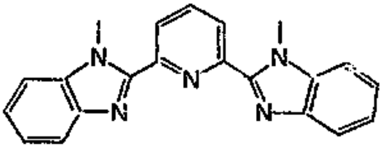
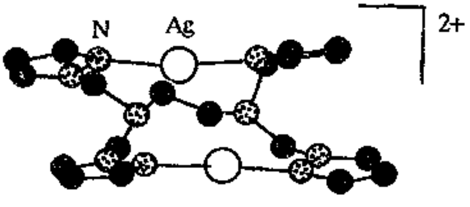


(57)

Silver nitrate forms the dinuclear complex **(58)** with a potentially hexadentate tetrapyrazolyl ligand. The silver atoms are two-coordinate and linear, with Ag–N = 2.136(4)–2.165(5) Å and angle N–Ag–N = 169.2(2), 174.3(2)°. The Ag–Ag separation of 3.1599(9) Å was considered too long for a bonding interaction, as were the long interactions (>2.70 Å) of silver with the nitrate anions and the tertiary amine N-atoms [72].



(58)

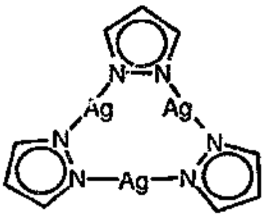
The synthetic pathway determines the nuclearity of silver pyrazolato (pz) complexes; a trimeric and a polymeric species were prepared by reactions (i) and (ii), respectively:

$$3[Ph_3PAg(pz)]_2 + H_2O_2 \rightarrow 2[Agpz]_3 + Ph_3PO \quad \text{(i)}$$

$$AgNO_3 + Hpz + NH_3(aq) \rightarrow \tfrac{1}{n}[Agpz]_n + NH_4NO_3 \quad \text{(ii)}$$

The structures of both the trimeric **(59)** and polymeric **(60)** compounds are determined by powder diffraction techniques. They contain approximately linear silver atoms, angle N–Ag–N = 172.1(7), 177(1)° for **(59)** and 165.5(1)° for **(60)**, with intramolecular Ag···Ag distances between consecutive silver atoms in the range of 3.40–3.449(6) Å, but shorter intermolecular contacts of 3.273 Å in the polymer case. A comparison is also made with the structures of two copper pyrazolato forms [73].

In the structure of $[Ag(NH_3)_2]_2[Ni(biu)_2]$ the cation consists of two-coordinate Ag-atoms with Ag–N = 2.119(5), 2.125(5) Å and angle N–Ag–N = 170.0(2)° [74]. The activation parameters of the oxidation reactions of ascorbic acid or hydrazine with a Ag–gelatin complex were studied kinetically. For ascorbic acid, $\Delta H^{\ddagger} = 20.67 \pm 2.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -24.1 \pm 4.5$ J K^{-1} mol^{-1}; for hydrazine,



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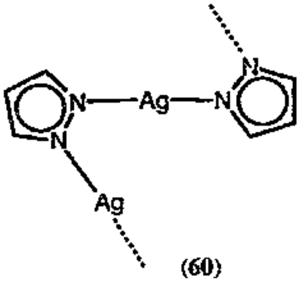


(60)

$\Delta H^{\ddagger} = 23.72 \pm 2.05$ kJ mol^{-1} and $\Delta S^{\ddagger} = -12.3 \pm 2.5$ J K^{-1} mol^{-1} [75]. A spectrophotometric method for the determination of silver in photographic paper and fixer waste has been developed; in the presence of cetyltrimethylammonium bromide, silver forms a 1:1 complex with *meso*-tetra(4-pyridyl)porphyrin where $\epsilon = 1.78 \times 10^5$ dm^3 mol^{-1} cm^{-1}, at 425.5 nm [76]. Stability constants for the AgL, AgLH, AgL_2, $Ag_2L_2H_2$, AgL_2H, Ag_2L_2, Ag_2L_2H and Ag_2L_3 species were determined potentiometrically in aqueous solutions for L = en, or one of seven other *N*- or *C*-methylated ethylenediamines. It is demonstrated that while *N*-methylation decreases the number of species in equilibrium as well as their stability constants, *C*-methylation does not have such an effect [77].

4.6. *Complexes with phosphorus ligands*

The solid state structures of $(Ph_2BuP)AgX$ (X = Cl, Br, I) have been determined crystallographically and shown to consist of Ag_4X_4-cubanes (**61**). A single doublet resonance was recorded in the CP/MAS ^{31}P NMR spectra for compounds with X = Cl or Br with $^1J_{Ag,P}$ 640 Hz (X = Cl) or 595 Hz (X = Br), while only a broad resonance was observed for the compound with X = I owing to lattice disorder [78]. The cubane structures of $[Ag_3WSe_4I(PMe_2Ph)_3]$ [79] and $[Ag_3MSe_4I(PPh_3)_3]$ (M = Mo, W) [80], all three containing tetrahedrally coordinated Ag-atoms, have been described.

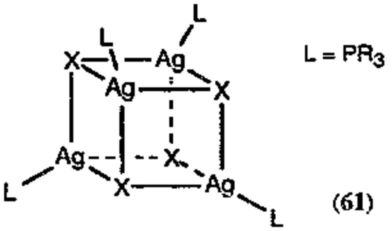
Table 2 shows the silver–ligand bond lengths for $Ag_3MSe_4I(PR_3)_3$ cubanes.

Replacement of a halide by a dithiophosphate group, as in $[Ag_3MoS_3(S_2P(OEt)_2)(PPh_3)_3]$ (**62**), distorts the cubane structure and, while two of the silver atoms remain four-coordinate, the third one becomes distorted trigonal planar; Ag–S = 2.525(4)–2.698(4) Å, Ag–P = 2.420(4)–2.454(4) Å [81].

A ^{31}P NMR spectroscopic study of $(Me_3P)AgI$ in d_3-acetonitrile shows two

Table 2
Silver–ligand bond lengths for $Ag_3MSe_4I(PR_3)_3$ cubanes

	Ag-I (Å)	Ag–Se (Å)	Ag–P (Å)
$Ag_3WSe_4I(PMe_2Ph)_3$	3.109(1)	2.593(1), 2.622(1)	2.391(2)
$Ag_3WSe_4I(PPh_3)$	3.040(4)–3.107(4)	2.611(4)–2.700(5)	2.398(9)–2.414(8)
$Ag_3MoSe_4I(PPh_3)_3$	3.039(6)–3.113(6)	2.583(6)–2.703(7)	2.40(1)–2.43(1)



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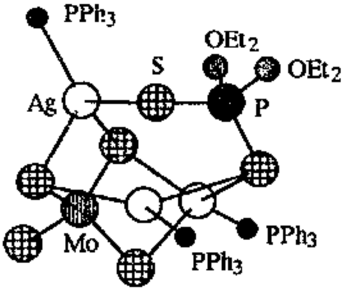
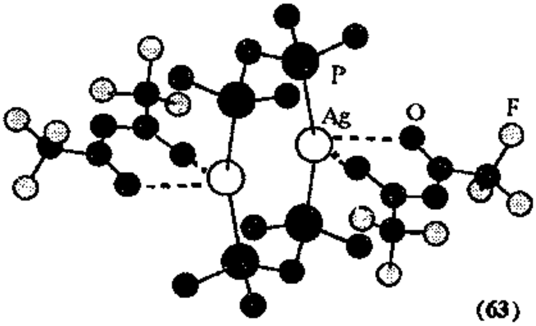


(62)

resonances, at δ −45.6 and −34.1, which are assigned to tetranuclear and mononuclear forms of the complex, respectively. It is proposed that the tetrameric $Ag_4I_4(PMe_3)_4$-cubane form partially dissociates (≈3%) in CH_3CN to monomeric $AgI(PMe_3)$ with an equilibrium constant $K_c = 1.3 \times 10^{-14}$ mol^3 dm^{-9} [82].

The synthesis of [(μ-dmpm)Ag(hfac)]$_2$ (63)—from Ag_2O, hfacH, and dmpm—

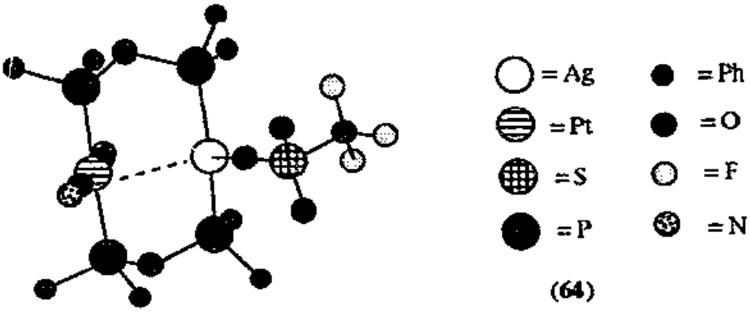


(63)

Ag–P = 2.408(2), 2.411(2) Å
Ag–O = 2.528(5), 2.632(5) Å
Ag–Ag = 3.153(1) Å
P–Ag–P = 160.02(7)°

and its characterization by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, and crystal structure determination have been reported. The complex consists of a dimeric $Ag_2(\mu\text{-dmpm})_2$ metallocycle with approximately linear two-coordination around silver and the hfac-anions only weakly chelated to Ag. Consistent with linear coordination is the solution measurement of $^1J(^{31}P^{107}Ag)$ of 500 Hz [83].

The Ag/Pt heterodimetallic complex $[AgPt(dppm)_2(CN)_2(O_3SCF_3)]$ **(64)**, prepared from AgO_3SCF_3 and $[Pt(dppm)_2(CN)_2]$, contains Ag-atoms in a distorted trigonal geometry arrangement (Ag–P = 2.433(4), 2.446(4) Å, Ag–O = 2.46(1) Å, angle P–Ag–P = 139.2(1)°) with a close Ag–Pt contact of 3.002(1) Å. Absorption at 317 nm and 77 K, attributed to a $^1(d\sigma^* \rightarrow p\sigma)$ excitation with significant $PtP_2(CN)_2$-MLCT contribution, generates an emission at 435 nm. These results are compared to the luminescence properties of the Au-analogue [84].



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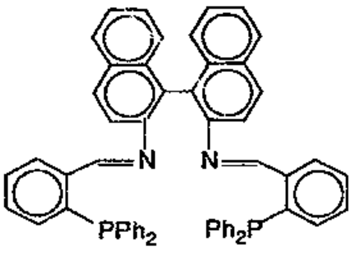
The potentially tetradentate ligand binap-P_2N_2 **(65)** forms 1:1 complexes with silver. The structurally characterized $[Ag(binap\text{-}P_2N_2)][BF_4]$ has Ag coordinated to the two P-atoms (Ag–P = 2.379(3), 2.415(4) Å, angle P–Ag–P = 151.0(1)°) with an exceptionally long interaction to one of the N-atoms of 2.56(1) Å which, however, persists in solution, as indicated by the ^{1}H NMR spectroscopic non-equivalence of the imino-H. Binap-P_2N_2 acts as a tetradentate ligand in the corresponding Cu(I) complex [85].



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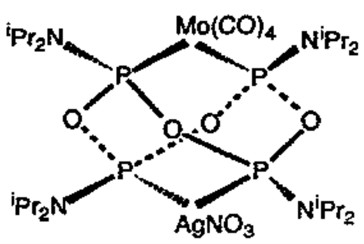


(66)

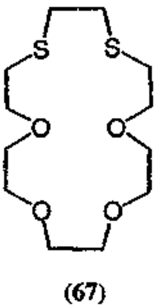
In the complex $[(CO)_4Mo\{(^iPr_2N)_4P_4O_4\}]$, the Mo-atom binds with two of the four P-atoms of the P_4O_4 heterocycle, leaving two more P-atoms available for further coordination. A variety of metals, including silver, form 1:1 complexes **(66)** with this metallaligand. The heterodimetallic $[(CO)_4Mo\{(^iPr_2N)_4P_4O_4\}AgNO_3]$ is characterized by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy [86].

4.7. Complexes with carbon ligands

The use of weakly coordinating anions has allowed the formation of "non-classical" Ag-carbonyls—unusually bonded carbonyls with little or no π-backbonding. Two such carbonyl cations, one-coordinate $[Ag(CO)]^+$ and linear two-coordinate $[Ag(CO)_2]^+$, have been isolated under CO pressure at low temperatures with the anions $B(OTeF_5)_4^-$, $OTeF_5^-$, $Zn(OTeF_5)_4^-$, $Ti(OTeF_5)_6^{2-}$, and $Nb(OTeF_5)_6^{2-}$. Consistent with σ-only Ag–CO bonding are the IR ($\nu_{CO}=2204$, 2198 cm^{-1}) and Raman ($\nu_{CO}=2206$, 2220, cm^{-1}) spectra, as well as structural data (Ag–C = 2.10(1), 2.14(5)–2.20(4) Å, C–O = 1.077(16), 1.07(5)–1.09(5) Å) [87]. A silver tricarbonyl complex, $[Ag(CO)_3][Nb(OTeF_5)_6]$, has been prepared from $Ag[Nb(OTeF_5)_6]$ under 13 atm of CO for 4 h at 298 K. It is stable at 196 K and 10^{-5} Torr, but readily loses all CO in toluene solution at 298 K. An IR spectroscopic study of $Ag[Nb(OTeF_5)_6]$ in solution as well as in the solid state under variable CO pressure reveals the stepwise formation of $[Ag(CO)]^+$, $[Ag(CO)_2]^+$, and $[Ag(CO)_3]^+$, with increasing pressure favouring the higher carbonyl. A 2192 cm^{-1} IR spectroscopic band is assigned to the tricarbonyl E′ ν(CO) mode [88].

4.8. Complexes with mixed donor atom ligands

The potentially hexadentate macrocyclic ligand $[18]aneS_2O_4$ (**67**) forms a 1:1 silver complex consisting of dimeric units (**68**), two of which are held together by a S–S interaction to form a tetrameric aggregate. Peaks assigned to both dimeric and tetrameric species were observed in the FAB–MS. Within the dimeric $\{Ag_2([18]aneS_2O_4)_2\}^{2+}$ (**68**) cations with Ag···Ag = 4.214(1) Å, one silver atom is four-coordinate ($AgOS_3$) while the other is five-coordinate (AgO_3S_2) using O- and S-atoms from both macrocycles; Ag–O = 2.458(7)–2.661(6) Å and Ag–S = 2.521(2)–2.706(2) Å. The uncoordinated O- and S-atoms of the hypodentate (**67**)



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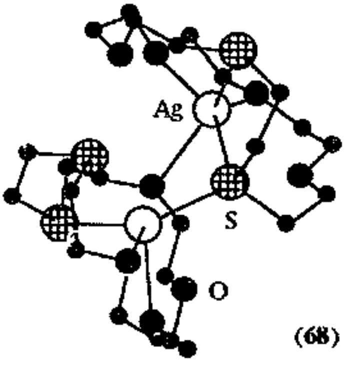
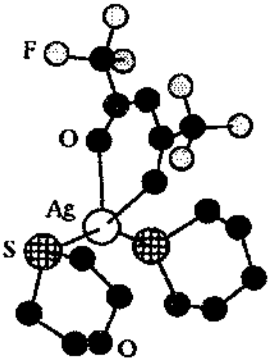


(68)

undergo long interactions with the metals [89]. Mononuclear (hfacac)AgL complexes were prepared by addition of L = SMe_2, SEt_2, SPr_2, SBu_2, 1,4-oxathiane, to $Ag_2(hfacac)_2(H_2O)$ (**20**) in an effort to identify materials with good Ag-CVD properties. The structural characterization of (hfacac)$Ag(SOC_4H_8)_2$ (**69**) shows that the oxathiane ligand binds to silver through its S-atom [26].

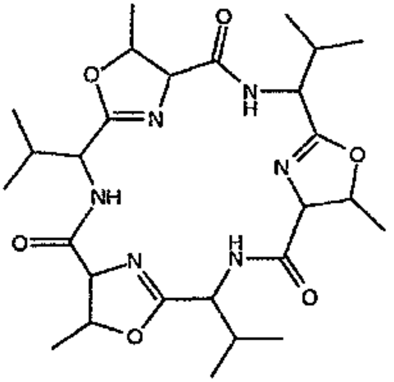


(69)

Ag–S = 2.468(2), 2.473(2) Å
Ag–O = 2.400(7), 2.477(7) Å
S–Ag–S = 149.6(1)°
O–Ag–O = 74.4(2)°

Westiellamide (**70**), a marine cytotoxin, forms the $[Ag_4L_2][ClO_4]_4$ complex (**71**) with an association constant $K_a = 2.8 \times 10^{13}$ M^{-5} in 90% d_4-MeOH/D_2O. The ^1H NMR spectroscopic determination of K_a between 304 and 325 K gives $\Delta H^\circ = -123$ kJ mol^{-1} and $\Delta S^\circ = -191$ J K^{-1} mol^{-1}. The crystal structure determination of $[Ag_4L_2][ClO_4]_4$ shows that the distorted trigonal-planar Ag_4 unit (**72**) is sandwiched between two molecules of **70**, while there are no close contacts with the perchlorate anions. The central Ag-atom is coordinated by six carbonyl-O atoms, three from each westiellamide, in a trigonal prismatic arrangement with long Ag–O distances ranging between 2.41 and 2.55 Å. The three peripheral Ag-atoms are linearly coordinated by two oxazole-N atoms with short Ag-N bonds, 2.10–2.15 Å [90]. In the symmetric dimer (**73**), the silver atoms are in a distorted tetrahedral-S_2O_2 environment [91].

Stability constants have been determined potentiometrically for the $[AgL]^+$ complexes of the bibracchial lariat ethers (**74**) and (**75**) in six different solvents. Lower stability is measured in N-donor solvents which are known to solvate silver strongly [92]. In propylene carbonate, methanol, dimethylformamide or water, silver is complexed by (**75**) with higher stability (12.2(1)–7.57(5) dm^3 mol^{-1}) than alkali metal cations. However, in acetonitrile and pyridine, the $[AgL]^+$ stability constants, 7.08(5) and 1.8(1) dm^3 mol^{-1}, are lower than those of alkali metals [93]. Potentiometric methods have been employed to study the complexation of alkali metal cations and



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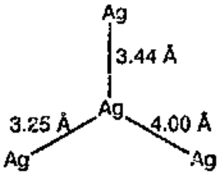

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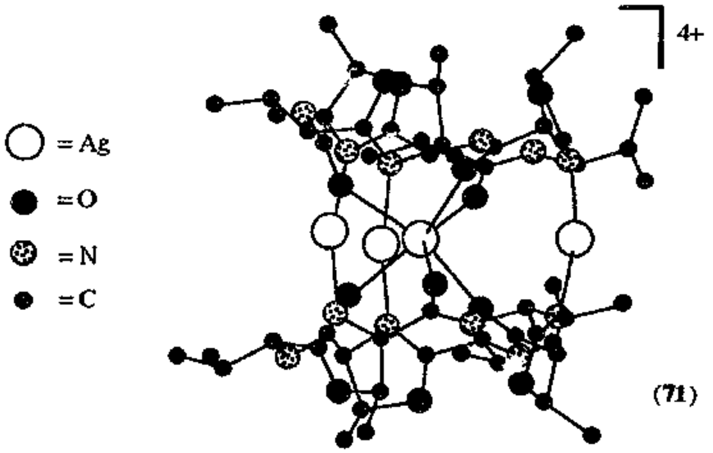
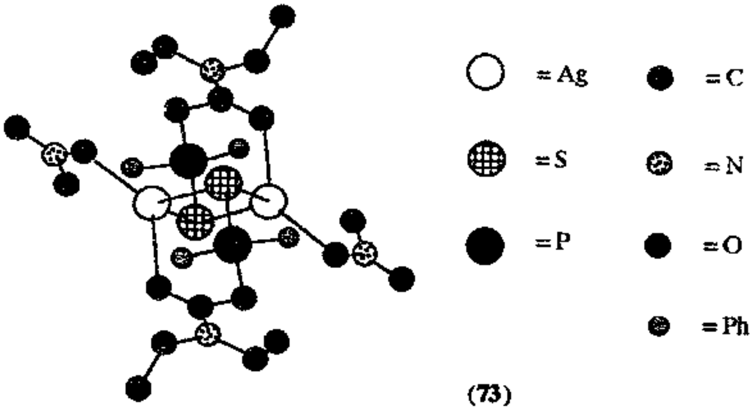


(71)

Ag^+ by the bicyclic cryptand **(76)** in various solvents. The results have been discussed in comparison with similar cryptands with regard to solvation, ring size, and donor atom effects [94]. Pseudo-crowns, pseudo-thiacrowns, and pseudo-thiolariat ethers (linear polyethers which become cyclic by chelation of their outer donor atoms to a Cu(I)-centre) were used to evaluate the donor atom role in the selective extraction of Ag^+ [95].

Carboxylate ligands based on pyridine or pyrazine form polymeric silver complexes. Six such materials have been structurally characterized. Two structures of polymeric silver complexes with nicotinic acid, **(77)** and **(78)**, as well as one with dipicolinic acid, **(79)**, have been presented. The polymeric structure of $[Ag(C_5H_4NCO_2)]_n$ **(77)** consists of Ag–OC(R)O chains, with Ag–O = 2.280(8), 2.258(8) Å, while a third nicotinate is *N*-bound to the three-coordinate Ag, Ag–N =



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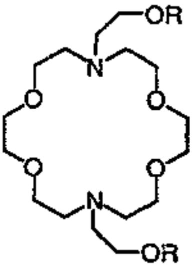

R = H, Me

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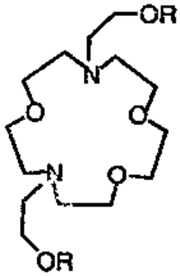

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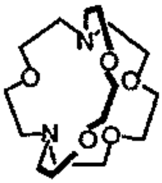
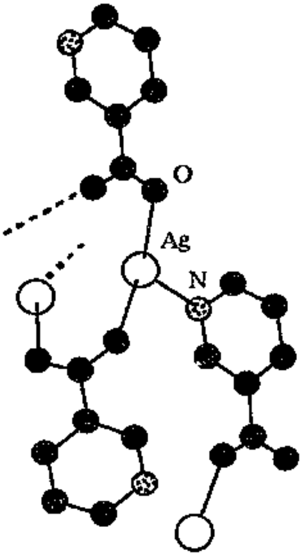
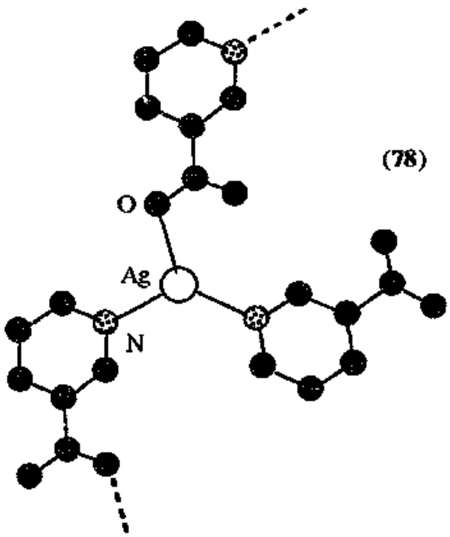


(76)

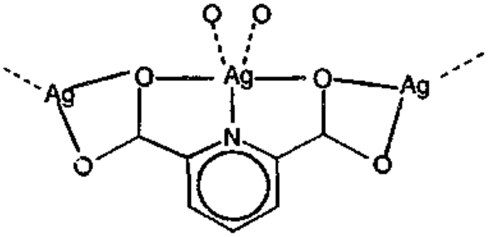
2.362(10) Å [21]. The structure of (**77**) has also been independently reported by another group [96]. In the structure of $\{NH_4[Ag(C_5H_4NCO_2)]\cdot H_2O\}_n$ (**78**), the polymeric chain is formed by alternating Ag–O (2.342(3) Å) and Ag–N (2.269(3) Å) bonds to two nicotinate ligands, while a third nicotinate binds to the trigonal planar silver through its N-atom (AgN = 2.248(3) Å) and a NH_4^+-cation balances the charge [21]. Each carboxylic group of the dipicolinate ligand of $[Ag_2(C_9H_8NO_3)_2(H_2O)_2]\cdot 2H_2O$ (**79**) chelates asymmetrically to a silver atom, which is also coordinated by one nitrogen and two oxygen atoms of a neighbouring dipicolinate. The five-coordinate Ag-centres are approximately planar pentagonal with Ag–O = 2.20(3)–2.90(3) Å and Ag—N = 2.24(2) Å [21]. In contrast with nicotinates, silver forms a two-coordinate, *N*-bound (Ag–N = 2.166(3) Å), isonicotinate complex (**80**) with a chain structure composed of [LAgLH] units connected by H-bonds [96]. Similarly to pyridine carboxylates, the pyrazine carboxylate and dicarboxylate complexes of silver are three-dimensional in the solid state with four- and three-coordinate Ag-atoms, respectively. In the structure of $[Ag(2\text{-}CO_2\text{-pyrz})]_n$ (**81**) (pyrz = pyrazine) three ligands, one chelating and two monodentate, are bound to each Ag-atom in a roughly tetrahedral AgN_2O_2 environment, while in the structure of $[Ag(2,3\text{-}(CO_2)_2\text{-pyrz})]_n$ (**82**) each Ag-atom is coordinated by three monodentate ligands (long Ag–O interactions ignored), one N- and two O-bound [97].



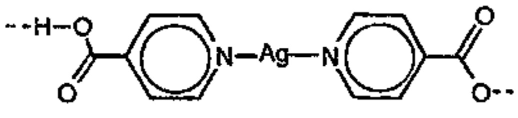
(**77**)



(**78**)

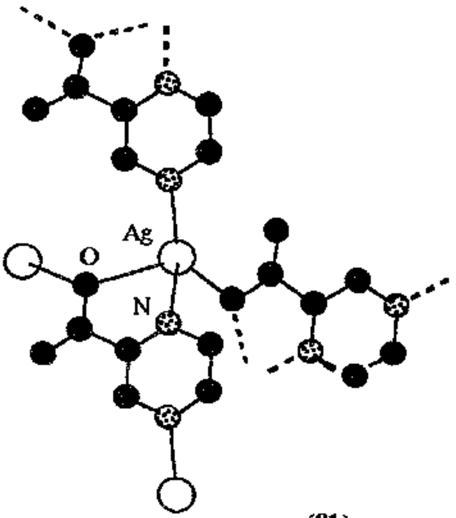


(**79**)



(**80**)

The crystal structure of $\{[(4\text{-Me-}C_6H_5SO_2)_2NAg]_2\}_n$ (**83**) has been reported. The polymeric structure is made up of dimeric $\{[(4\text{-Me-}C_6H_5SO_2)_2NAg]_2\}_2$ units linked by long interactions between Ag and two O-atoms of neighbouring molecules (Ag–O = 2.432(3), 2.533(3) Å). A close Ag···Ag interaction of 2.954(2) Å is found within the eight-membered $(Ag\text{–}NSO\text{–})_2$ rings with Ag–N = 2.260(3) Å, Ag–O =



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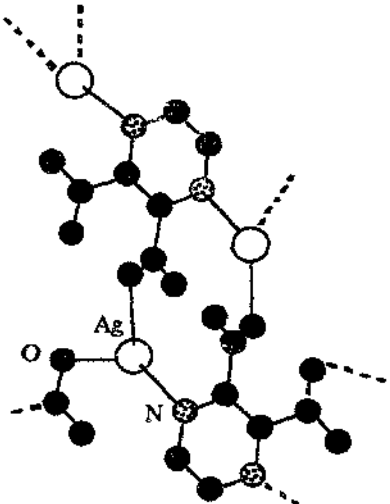
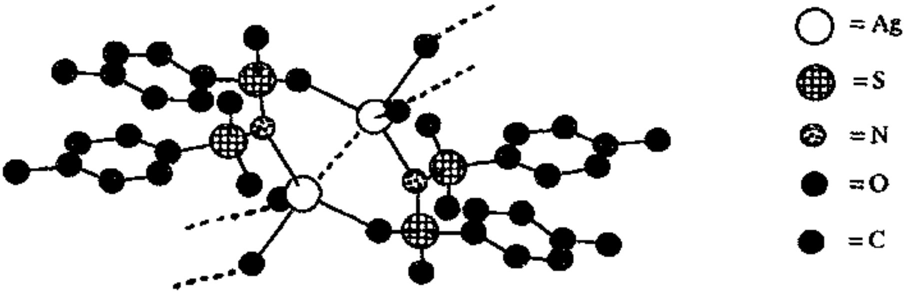


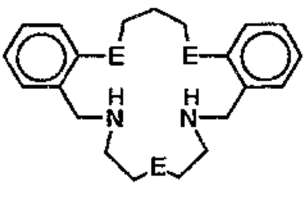
(82)

2.294(3) Å [98]. Five chlorosulfate complexes [(ClO$_3$S)AgL] (L = PPh$_3$, py, pyNO, 2,2′-bpy, acridine) have been studied by IR spectroscopy; a four-coordinate geometry for all five complexes has been suggested [99].



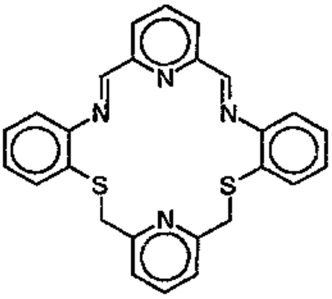
(83)

Stability constants have been determined potentiometrically for Ag$^+$ complexes of macrocyclic diaza-crown ethers and related bicyclic cryptands with mixed N/O/S-donor atoms in a variety of polar solvents. Examination of the calculated free energies of solvation and transfer show that, while Ag-solvation is the dominant effect, solvation of the complex cation in monocyclic crown-ethers as well as solvation of the free ligands in acidic solvents can be significant [100]. The obtained free energies are used along with potentiometrically and calorimetrically determined enthalpies of complexation to calculate the corresponding entropies. The thermodynamics of Ag$^+$ complexation with the crown-ethers and cryptands in polar solvents can be analysed into contributions of individual N/O/S-donor atoms [101]. The effect of systematic variation of element E with regard to the Ag^+/Pb^{2+} discrimination of the macrocyclic ligand **(84)** was studied by potentiometric titration methods. Among the six ligands examined, the one with a S_2N_2S-donor atom set favours silver by a factor of 10^9; $\log K(AgL) = 12.4$ [102].



E = O, NH, S

(84)

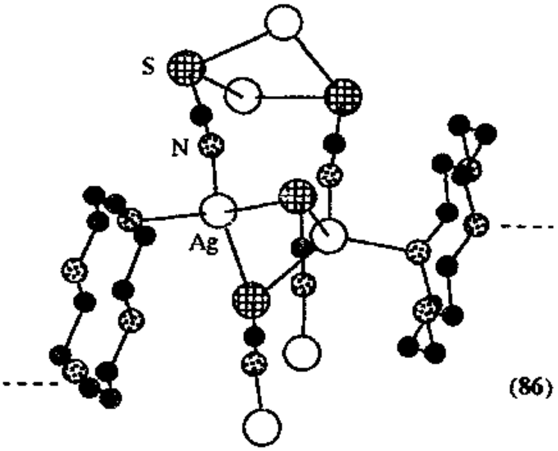


(85)

Metal complexes of the macrocyclic ligand **(85)** have been prepared by template condensation in the presence of Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+}. For the silver complex, the coupling $^3J(^1H\text{-}M)$ was not observable, a result attributed to fast exchange of this metal among the coordination sites of the hexadentate ligand [103]. The thermal decomposition of several $[(tu)AgL]^+$ complexes, including those with L = py, 2-pic, 3-pic, 4-pic, qu, iqu, pip, bpy and phen, was studied by TGA and DTA methods. The monodentate *N*-donor ligands dissociate at lower temperatures than tu, while tu dissociates before the didentate *N*-donors [104]. The thermal isomerization of a thermochromic silver dithiazonate complex was followed spectroscopically in three solvents at high pressure. The measured rates are independent of solvent polarity and decrease slightly with increasing external pressure; estimated activation volume, 7 $cm^3\ mol^{-1}$ [105].

In the three-dimensional supramolecular structure of $Ag_2(SCN)_2$(cyclam) **(86)**, the silver atom is in a distorted tetrahedral environment formed by two S-atoms of the μ-SCN groups, one cyclam N-atom and a thiocyanate N-atom of the next $Ag_2(SCN)_2$ unit. Cyclam acts as a didentate ligand bridging two $Ag_2(SCN)_2$ units, placing the Ag-atoms in a roughly tetrahedral environment [106].

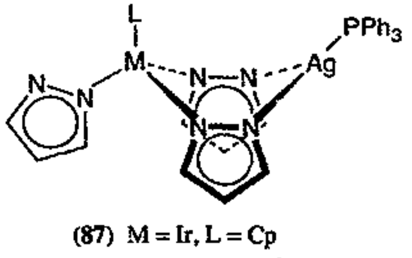
The dynamic behaviour of the Ag/Ir heterometallic di- and trinuclear complexes **(87)**, **(88)**, and **(89)** has been studied by variable temperature ^1H, ^{13}C, ^{15}N, ^{31}P, and ^{109}Ag NMR spectroscopy. Compound **(87)** shows an argentotropism ($\Delta H^‡ = 8.28$ kcal mol^{-1}, $\Delta S^‡ = -12.8$ eu) which renders the three pyrazoles equivalent as regards coupling to phosphorus, $^2J(^{31}P\text{–}^{15}N)$ 9.1 Hz. Similar behaviour has been observed for **(89)** ($\Delta H^‡ = 7.64$ kcal mol^{-1}, $\Delta S^‡ = -19.8$ eu). An inversion of the Ir–(μ-pz)$_2$–Ag ring is suggested as being responsible for the dynamic behaviour of **(88)**. Several heteronuclear coupling constants involving $^{107,109}Ag$ have been reported [107]. Advances in NMR spectroscopic line-shape theory allow improved determination of the activation energy (E_a) for the Ag–P bond cleavage in



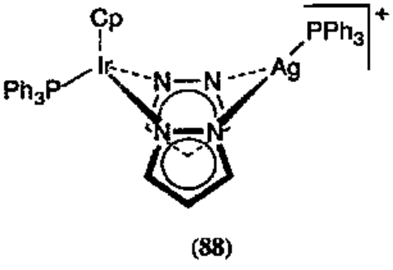
(86)

Ag–Ag = 2.975(1) Å
Ag–S = 2.615(1), 2.736(1) Å
Ag–N(cyclam) = 2.304(4) Å
Ag–N(thiocyanate) = 2.308(5) Å

[(η^6-cumene)Ru(μ-pz)$_3$AgPPh$_3$] **(90)**. Analysis of the ^{31}P NMR spectra showing dynamic behaviour between 213 and 328 K gives $E_a = 46 \pm 5$ kJ mol^{-1} (compared to the previous values of 38, 46 and 49 kJ mol^{-1}), $\Delta H^{\ddagger} = 44$ kJ mol^{-1} and $\Delta S^{\ddagger} = -26$ J K^{-1} mol^{-1} [108].



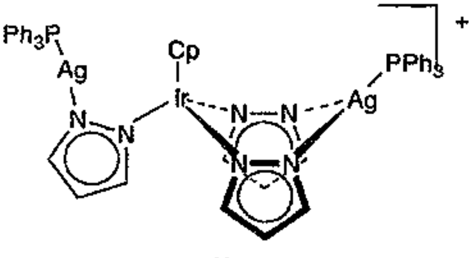
(87) M = Ir, L = Cp
(90) M = Ru, L = η^6-cumene



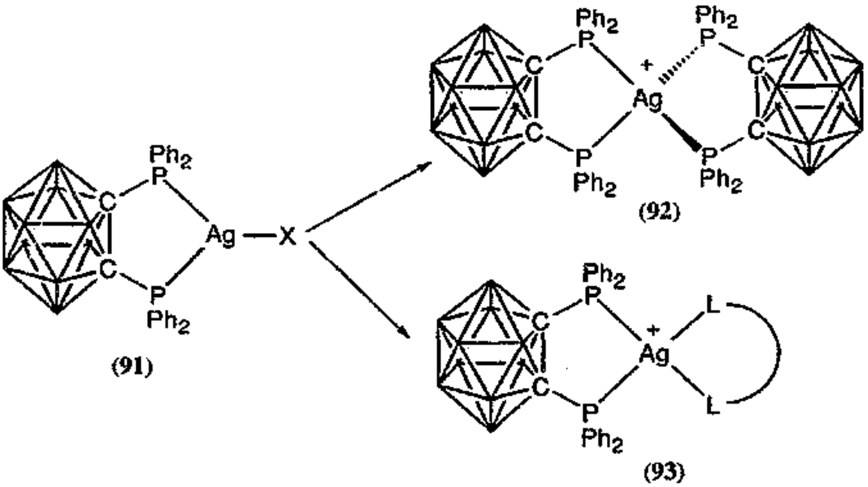
(88)

Three- and four-coordinate mononuclear complexes are prepared with the chelating diphosphane ligand (Ph$_2$P)$_2$C$_2$B$_{10}$H$_{10}$ and characterized by elemental analysis, conductivity, ^{1}H and ^{31}P NMR and IR spectroscopy. The anion X(= ClO$_4$, NO$_3$) of **(91)** can be replaced by a variety of monodentate or chelating ligands to give new complexes **(92 and 93)**. Of these, the L–L = phen or CH$_2$(PPh$_2$S)$_2$ complexes have been structurally characterized [109].

The trinuclear complex **(94)**, whose structure has been determined by partial



(89)

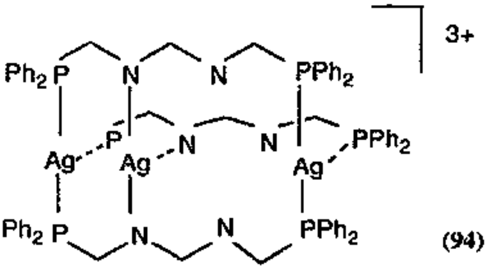


(91)

(92)

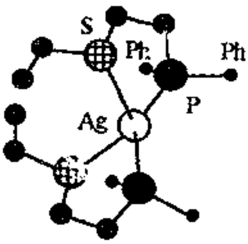
(93)

X-ray analysis, shows an intraligand emission with lifetime of 5 μs on excitation at 330–370 nm in acetonitrile at room temperature [110].



(94)

The crystal structure of $[AgL_2]ClO_4$ **(95)** with the chelating ligand $Ph_2P(CH_2)_2SEt$ has been described. The Ag-atom, located on a two-fold axis, is in a distorted tetrahedral AgS_2P_2 environment [111].



(95)

Ag–S = 2.694(2) Å
Ag–P = 2.456(2) Å
P–Ag–P = 148.9(1)°
S–Ag–S = 112.0(1)°
S–Ag–P = 82.5(1), 115.5(1)°

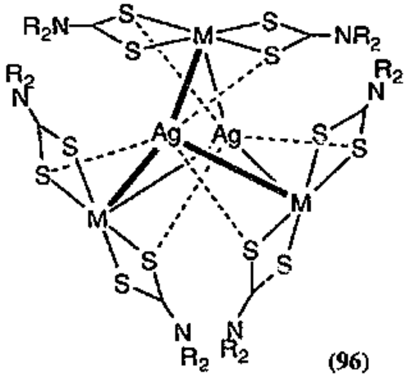
5. Complexes with silver–metal bonds

11 complexes of the general formula $[M_3(S_2CNR_2)_6Ag_2]X_2$ (M = Pd, Pt, R = Et, Pr^i, Pr, Bu; X = BF_4, ClO_4) have been prepared by 2:3 addition of AgX to $M(S_2CNR_2)_2$, and three of them—$[Pd_3(S_2CNEt_2)_6Ag_2][ClO_4]_2$, $[Pd_3(S_2CNPr^i_2)_6Ag_2][BF_4]_2$, and $[Pt_3(S_2CNPr^i_2)_6Ag_2][BF_4]_2$ (**96**)—have been structurally characterized. To each Ag-atom are coordinated three S-atoms from the three $M(S_2CNR_2)_2$ moieties in a triangular fashion; long Ag–S bonds are accompanied by short Ag–M distances, and vice versa (see Table 3). The XPS binding energies of $Pt(4f_{7/2})$, $Pd(3d_{5/2})$, $Ag(3d_{5/2})$ and $S(2p_{3/2})$ suggest electron donation from Pt (or Pd) and S towards Ag, while NMR spectroscopic data ($^1J(^{195}Pt,^{107,109}Ag)$ 194 and ≈200 Hz) point to significant Pt–Ag bonding interactions. Some analogous $[M_3(S_2CNR_2)_6Cu_2]X_2$ complexes have also been reported and compared to those of silver [112]. Electrospray-MS proves valuable in the solution study of this new class of metal–metal bonded dithiocarbamates. Not only the existence of $[Pt_3(S_2CNR_2)_6Ag_2]^{2+}$ cations, R = Et, Pr, Bu, in $MeOH/MeCN/CH_2Cl_2$ solutions, but also the global scrambling of ligands is evident in mixed ligand systems by the presence of fragments in the mass spectrum corresponding to all possible permutations of the three different dithiocarbamates [52].

The reaction of $Ag(Br_5CB_9H_5)$ (**10**) with $IrCl(CO)(PPh_3)_2$ (described in Section 4.1) does not give the expected Cl-metathesis product but the metal–metal

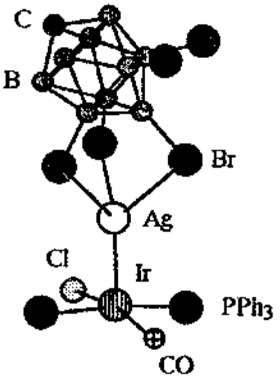
Table 3
Selected bond lengths for $[M_3(S_2CNR_2)_6Ag_2]^{2+}$

M, R	Ag–S (Å)	Ag–M (Å)
Pd, Et	2.305(6)–2.337(6)	3.073(2)–3.287(3)
Pd, Pr^i	2.468(3)–2.764(3)	2.928(1)–3.001(1)
Pt, Pr^i	2.702(3)–2.707(3)	2.895(1)–2.911(1)



(96)

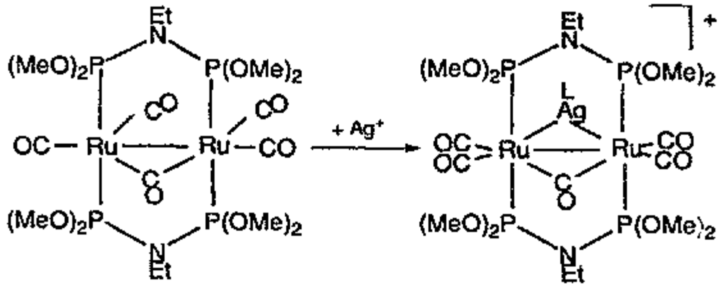
bonded adduct (97) containing an Ir→Ag donor–acceptor bond. The Ag-atom is in a tetrahedral environment comprising three bromine atoms of the η^3-pentabromocarborane and the Ir-atom [12].



(97)

Ag–Ir = 2.631(5) Å
Ag–Br = 2.752(8)–2.973(6) Å

Addition of Ag-salts to a solution of (98) gives trinuclear heterodimetallic complexes (99) which are characterized by their IR and ^{31}P NMR spectra. The presence of a single doublet ^{31}P-resonance [$^2J(^{31}P^{107,109}Ag)$ 13.6 Hz (L = py) or 13.9 Hz (L = MeCN)] points to a symmetrical $Ru_2(\mu\text{-}AgL)$ unit in solution, analogous to the crystallographically determined structure of the corresponding $Ru_2(\mu\text{-}AuPPh_3)$ complex [113]. Two complexes, $[PtAgCl_2(C_6F_5)PPh_3]_x$ (8) and $(PPh_3)Ag(\mu\text{-}Cl)PtCl(C_6F_5)PPh_3$ (9), containing Ag–Pt bonds have been described in Section 4.1 [11].

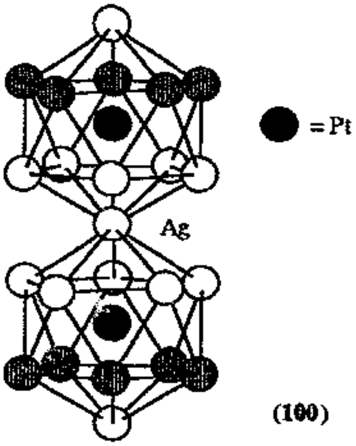


(98) (99)

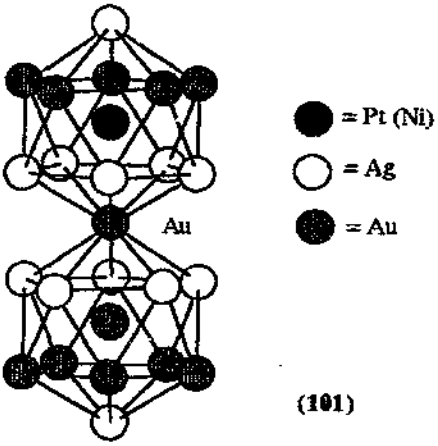
6. Silver clusters

Two articles describe large ternary M–Au–Ag clusters prepared from smaller preassembled units. A Pt–Au–Ag supracluster $Pt_2(AuPPh_3)_{10}Ag_{13}Cl_7$ (**100**) has been prepared by the addition of $Ag(PPh_3)(NO_3)$ and NaCl to a $PtAu_7$-cluster and characterized by elemental analysis, FAB–MS, IR and ^{31}P NMR spectroscopy, and X-ray crystallography. Its biicosahedral structure consists of two $Ag(Au_5)Pt(Ag_5)Ag$, Pt-centred icosahedra, sharing an Ag-vertex. The Ag–Ag, Ag–Au, and Au–Au bonds range from 2.807(9) to 3.040(8) Å, while the Pt–Ag and Pt–Au bonds are between 2.682(5) and 2.839(4) Å. Cyclic voltammetry shows irreversible multielectron oxidation of (**100**) [114]. Vertex-sharing biicosahedral $MAu_{12}Ag_{12}$ (M = Pt, Ni) supraclusters are prepared by reduction of lower-nuclearity clusters as shown in

$$[(Ph_3P)_8Au_8M][NO_3] + (Ph_3P)_4Ag_4Cl_4 + NaBH_4 \rightarrow \underset{(101)}{[(Ph_3P)_{10}Au_{12}Ag_{12}MCl_7]Cl} \tag{iii}$$

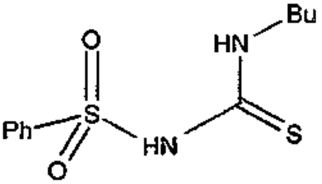


(**100**)



(**101**)

In (**101**), the biicosahedron is made up of M-centred $Ag(Au_5)M(Ag_5)Au$ and Au-centred $Ag(Au_5)Au(Ag_5)Au$ icosahedra sharing the Au-vertex, with metal–metal bond strengths in the order $M\text{–}Au < M\text{–}Ag < Au\text{–}Au \leq Au\text{–}Ag < Ag\text{–}Ag$. The site preferences of these "cluster-of-clusters" assemblies are explained on the basis of bond strength vs. charge accumulation considerations, which are supported by EHMO calculations [115]. *N*-Butyl-*N'*-benzenesulfonylthiourea (**102**) forms three 1:1 complexes with silver, distinguished by their luminescent properties. One of them is isotypical to an analogous Cu(I) complex which has been shown crystallographically to contain a Cu_6 octahedral cluster core [116].

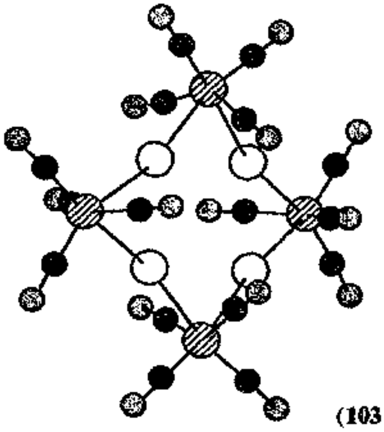


(102)

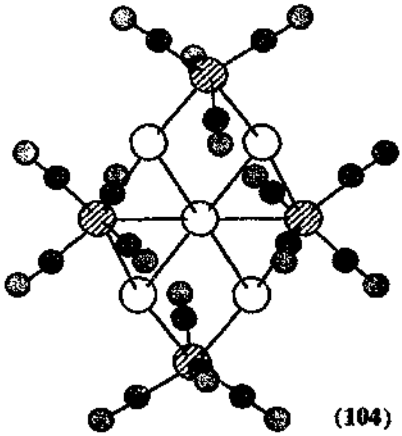
The products of the following consecutive reactions can be isolated by appropriate adjustment of the Ag^+ and $[Fe(CO)_4]^{2-}$ ratio:

$$Ag^+ + 2\{Fe(CO)_4\}^{2-} \rightarrow [Ag\{Fe(CO)_4\}_2]^{3-} \qquad \text{(iv)}$$

$$2Ag^+ + 2[Ag\{Fe(CO)_4\}_2]^{3-} \rightarrow [Ag_4\{\mu-Fe(CO)_4\}_4]^{4-}\ \mathbf{(103)} \qquad \text{(v)}$$



(103)



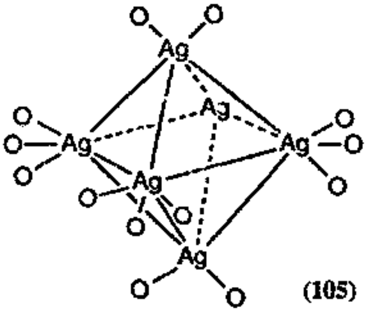
(104)

○ = Ag ▨ = Fe ● = C ● = O

$$Ag^{+} + [Ag_4\{\mu-Fe(CO)_4\}_4]^{4-} \rightarrow [Ag_5\{\mu-Fe(CO)_4\}_2\{\mu_3-Fe(CO)_4\}_2]^{3-}\ \textbf{(104)} \qquad \text{(vi)}$$

The planar Ag_4Fe_4 and Ag_5Fe_4 cluster cores of **(103)** and **(104)** are constructed with long peripheral Ag–Ag distances of 3.017(1)–3.334(1) Å and shorter Ag–Ag bonds of 2.795(1) Å between central and peripheral atoms, as well as Ag–Fe bonds ranging from 2.570(2) to 2.727(1) Å. Weak Ag–CO interactions are observed. An explanation of the chemistry of **(103)**, **(104)** and related clusters is given on the basis of EHMO calculations on those materials [117].

Three-dimensional Ag_5SiO_4 is prepared from the hydrothermal reaction of Ag powder and amorphous SiO_2. Its structure consists of Ag_6-octahedra **(105)** in which the Ag-atoms are coordinated by two or three O-atoms of the silicate anions. In terms of electron counting, this structure is better described as $[Ag_6]^{4+}(Ag^{+})_4(SiO_4^{4-})_2$ where the two excess electrons of the Ag_6-cluster occupy the a_1 skeleton orbital [118].



(105)

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