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COORDINATION CHEMISTRY REVIEWS

Silver 1995

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Contents

Introduction

This review is a representative, but not comprehensive, survey of the coordination chemistry of silver published in 1995 and follows the style of our 1994 survey [1]. It is based on searches of Chemical Abstracts, volumes 122, 123 and 124, Cambridge Structural Data Base, as well as individual searches of 12 major journals of the field. While organometallic complexes have been excluded, a few compounds containing silver–carbon bonds of general interest to coordination chemistry are presented in Section 3.8. Several figures in this review were redrawn from crystallographic coordinates available through the Cambridge Structural Data Centre.

A review, covering the literature up to 1991 and containing more than 600 structurally characterized inorganic and organometallic complexes of silver, appeared in 1995 [2].

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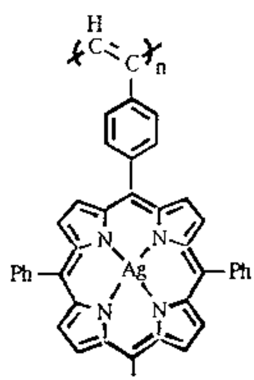
1. Silver(III)

A relatively long-lived $Ag^{III}_{(solv)}$ species, generated in anhydrous HF solutions of AgF_3 in the presence of strong F^--acceptor acids (AsF_5, SbF_5, BiF_5), has been put forward as the most powerful oxidant known. It is capable of oxidizing O_2 to O_2^+, as well as MF_6^- to MF_6, M = Ru, Pt. Compared to other electron oxidizers, the order of relative oxidizing power is $Ag^{III}_{(solv)}$ Å $Ni^{IV}_{(solv)} > PtF_6$ Å $RuF_6 > KrF^+ >$ $Ag^{II}_{(solv)}$ Å $O_2^+ > XeF^+$ Å AgF^+ [3].

In a kinetic study of the oxidation of azide by $[Ag^{III}(H_2TeO_6)_2]^{5-}$, the thermodynamic parameters have been determined for this reaction as well as for the one of the corresponding Cu^{III}-species. Both reactions proceed through the fast formation of a $[M^{III}\{TeO_4\}_2(OH)_3N_3]^{5-}$ intermediate, followed by a slow reaction with H_2O which, in the case of M = Ag, results in $[Ag^{I}\{TeO_4\}_2(OH)_4]^{7-}$ and N_3^+ a one-step two-electron process, and in the case of M = Cu, results in $[Cu^{II}\{TeO_4\}_2(OH)_4]^{6-}$ and N_3^+ in two one-electron steps [4].

A spectrophotometric kinetic study of the oxidation of oxalic acid and dioxalate by the Ag^{III} complex $[AgL](NO_3)_3$, L = ethylenebis(biguanidine), carried out in aqueous media, has suggested an outer-sphere mechanism with a two-electron transfer as the rate determining step [5].

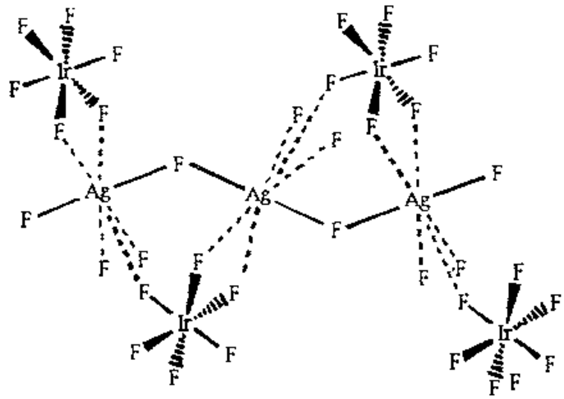
2. Silver(II)



(1)

A silver(II)-containing polyene (1) has been prepared from the corresponding substituted acetylene by polymerization with a Rh-catalyst; a thf-soluble and a thf-insoluble components have been isolated in ratio ~1:4. The ESR spectra of (1), both in solid state as well as in toluene solution, indicate the presence of exchange interaction among the Ag(II) centres [6].

The reaction of $AgMF_6$, M = Ir, Ru, Bi, Sb, with F_2 in anhydrous HF gave $(AgF^+)_n(MF_6^-)_n$, where AgF^+ could not oxidize M^V to M^{VI}. In contrast, the analogous reaction of $AgOsF_6$ yielded OsF_6, placing $(AgF^+)_n$ between OsF_6 and



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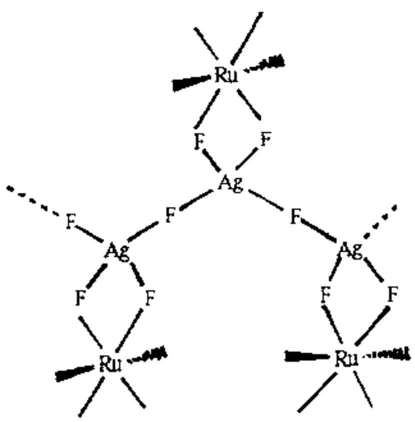

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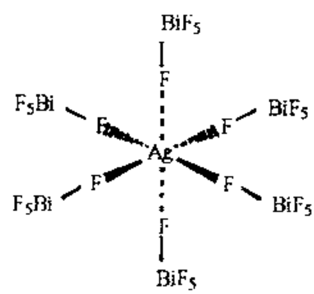
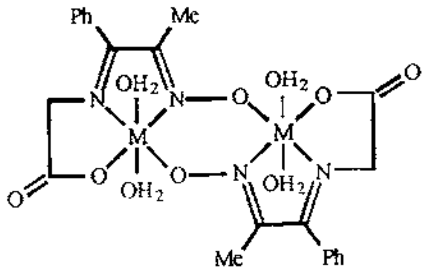


(4)

the other MF_6 compounds in terms of oxidizing potential. A more potent oxidant, $Ag^{II}_{(solv)}$, has been generated by treatment of $AgFAsF_6$ with AsF_5, or $AgAsF_6$ with O_2AsF_6 in anhydrous HF. $Ag^{II}_{(solv)}$ is capable of oxidizing O_2 to O_2^+ (at 195 K), $[IrF_6]^-$ to IrF_6, and C_3F_6 to C_3F_8 (see also Section 1) [3]. The structure of $(AgF^+)_n(IrF_6^-)_n$ (**2**) consists of chains with linear two-coordinate Ag atoms, which show, in addition, five equatorial long contacts with F atoms of the $[IrF_6]^-$ anions. The homologous $(AgF^-)_n(MF_6^-)_n$ salts, M = Sb, Bi, were found to belong to a different, as yet undetermined, structural type. A third motif has been encountered in the structure of $(AgF^-)_n(RuF_6^-)_n$ (**3**); the Ag atoms are in an approximately square planar environment with one pair of *cis*-F atoms acting as Ag–Ag bridges while the other pair of *cis*-F atoms bridge a Ag–Ru unit. A tetragonally distorted octahedral coordination of Ag has been found in the structures of $Ag(BiF_6)_2$ (**4**) and $AgRuF_6BiF_6$, where six F-atoms bridge between Ag and each of six BiF_6 or RuF_6-anions. While (**4**) obeyed the Curie–Weiss law, (**2**) and (**1**) showed low, and approximately temperature-independent, magnetic susceptibilities [7]. The reaction of UF_6 and AgF in anhydrous HF has been re-investigated and the new results support the formation of an intermediate red solid, proposed to be Ag_2UF_8, which subsequently decomposes to AgF_2 and $AgUF_6$ [8].



(**5**)

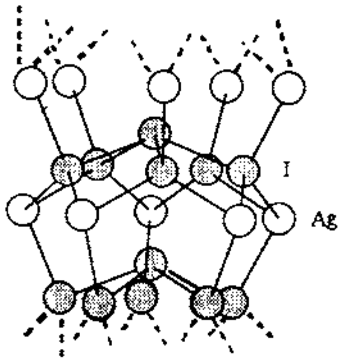
A silver(II) complex, $[Ag(bpy)_2](NO_3)_2$, prepared from $[Ag(bpy)_2](NO_3)$ by oxidation with $K_2S_2O_8$, has been used successfully for the redox titration of oxalic acid [9]. Two Ag(II) complexes of tetra-(3′-nitrophenyl)porphyrin and tetra-(3′-aminophenyl)porphyrin have been prepared and their ESR spectra reported along with those of the Cu(II) and Co(II) analogues [10]. The Ag(II) complex (**5**) of a Schiff base, characterized by elemental analysis, infrared and optical spectroscopies, has been proposed to have a dimeric structure based on its low magnetic moment of 1.63 BM and the presence of Ag–O and Ag–N stretches in the far-infrared [11].

3. Silver(I)

3.1. Complexes with halide and pseudohalide ligands

A new variation of the polymeric $(Ag_5I_6^-)_n$ cation has been identified in the structure of $(Ag_5I_6)_n(Ph_3PCH_2I)_n$ (**6**). The cationic polymer consists of alternating sheets of Ag_5-pentagons and I6-pentagonal pyramids, with three-coordinate Ag atoms at the apex of an AgI_3 trigonal pyramidal moiety [12]. A planar $[Ag_2I_4]^{2-}$ anion (**7**) with three-coordinate Ag-atoms has been reported in the structure of $[Bu_4N]_4[Ag_2I_4][W_6O_{19}]$ [13].

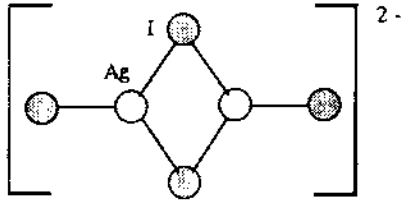
A continuing search for larger, even less-coordinating anions has lead to the syntheses of $[M(OTeF_5)6]^-$ M = Nb, Sb, and $[M(OTeF_5)_6]^{2-}$, M = Ti, Zr, Hf. Recrystallization of silver salts of these anions from dihaloalkane solvents and crystallographic characterization showed that in the structures of $[Ag(Cl_2CH_2)_3]_2[Ti(OTeF_5)_6]$ (**8**), $[Ag(Br_2CH_2)_3][Nb(OTeF_5)_6]$ (**9**) and $[Ag(1,2\text{-}Br_2C_2H_4)_3][Sb(OTeF_5)_6]$ (**10**), each Ag atom is coordinated by six dihaloalkane halogen atoms. In (**8**), three CH_2Cl_2 molecules are chelated to Ag with four



(6)

Ag - I = 2.837 Å (average)

I- Ag - I = 95.7 - 102.0°

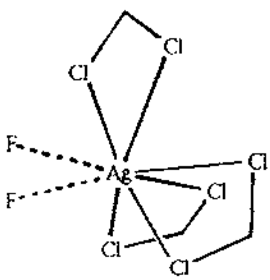


(7)

Ag - I = 2.679(2) Å

Ag - (μ- I) = 2.787(3), 2.807(3) Å

Ag . . . Ag = 3.112(4) Å

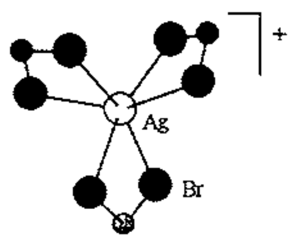


(8)

Ag - Cl = 2.656(3) - 3.049(4) Å

Ag - F = 3.029(8), 3.033(6) Å

Cl - Ag - Cl = 60.1(1), 60.8(1), 63.3(1)°



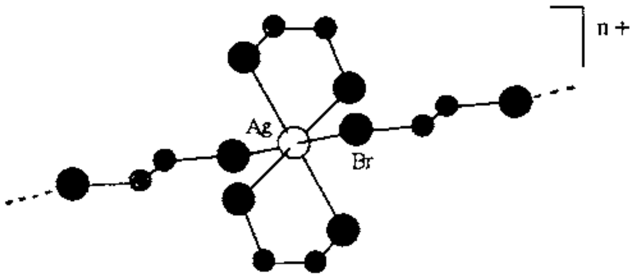
(9)

Ag - Br = 2.816(2) - 2.932(2) Å

Br - Ag - Br = 67.74(7) - 99.26(9)°

short, 2.656(3)–2.856(5) Å, and two long, 3.030(6) and 3.049(4) Å, Ag–Cl bonds leaving room for two additional long Ag···F interactions of 3.029(8) and 3.033(6) Å. In (**9**), the first structure of a coordinated dibromoalkane, the planes defined by the three chelate rings form angles of 80.6–99.4° to each other. The polymeric structure (**10**) contains bis-chelate $Ag(BrCH_2CH_2Br)_2$ planar moieties bridged by a third $BrCH_2CH_2Br$ molecule [14].

Some impressive two- and three-dimensional interpenetrating networks are known for the $[CdL_2\{Ag(CN)_2\}_2]$ and $[Cd(LL)\{Ag(CN)_2\}_2]$ systems, where L = monodentate *N*-donor, and LL = didentate *N*-donor. The use of small monodentate NH_3 has



(10)

Ag - Br = 2.702(1) - 3.081(2) Å

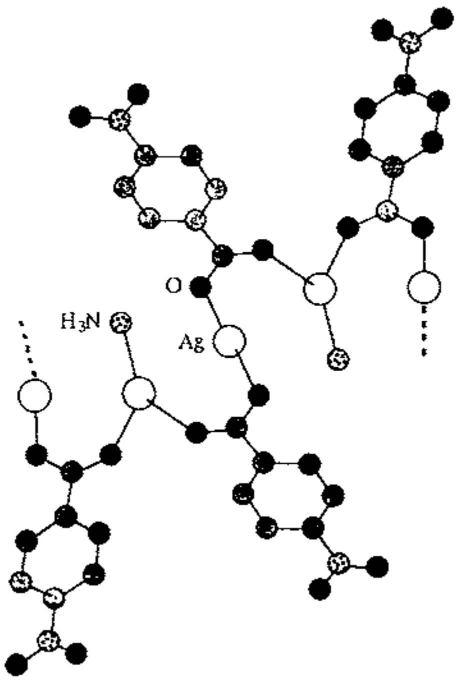
Br - Ag - Br = 82.86(4)° (chelate)

extended this work with a new structure, $[Cd(NH_3)_2\{Ag(CN)_2\}_2]_n$. It consists of two perpendicular interpenetrating two-dimensional networks, each formed by tetrahedral $Cd(NC\text{-}Ag\text{-}CN\text{-}Cd_{1/4})_4$ units, almost linear at the Ag-link [C–Ag–C = 175.5(2)°], but bent at the N-atoms [C–N–Cd = 154.8(8)°] [15].

3.2. Complexes with oxygen ligands

Eight publications have dealt with the crystallographic characterization of silver-carboxylate coordination polymers representing a wide variety of structural types. The structure of $Ag_2(p\text{-}NO_2\text{-}C_6H_4\text{-}CO_2)_2(NH_3)$ (**11**) consists of a zig-zag polymeric chain where Ag atoms are connected by a single p-benzoate bridge. One Ag atom is linearly coordinated by two O-atoms with the shortest Ag–O bond reported to date, 2.095(3) Å, while the other one is three-coordinate with two p-nitrobenzoate O-atoms and one ammonia molecule [16]. In contrast to (**11**), the coordination of NH_3 molecules to silver phthalate $Ag_2\{o\text{-}C_6H_4(CO_2)_2\}(NH_3)_2$ (**12**) terminates the potential growth of a polymer and results in a dimeric structure [17].

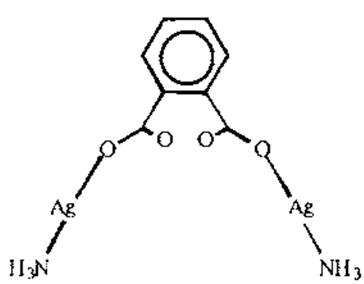
Dicarboxylate ligands have been successfully employed to construct two- and three-dimensional silver polymers. The structure of $Ag_4(glut)_2$ (**13**) consists of a planar arrangement of four silver atoms bridged by two glutarate dianions with Ag···Ag distance of 2.804(1) Å between carboxylate-bridged and 3.208(1) Å between non-bridged atoms of the same tetrameric unit. Longer Ag···O and Ag···Ag interactions between adjacent tetrameric molecules generate a two-dimensional structure [18]. The tetrameric units of (**13**) resulted from the *syn*-orientation of the glutarate carboxylates in the solid state, while the *anti*-orientation of the adipate carboxylates generated dimeric units in chain structures. Two neutral double-betaine ligands (*meso*-2,5-bis(trimethylammonio)adipate and *meso*-2,5-bis(pyridinio)adipate) have been used to form four two-dimensional structures, (**14**), (**15**), (**16**) and (**17**), all based on dimeric eight-membered silver-carboxylate rings. In (**14**) and (**15**), the Ag atoms are coordinated by three carboxylate-O atoms, two



(11)

Ag - O = 2.095(3), 2.319(3) Å

Ag - N = 2.154(5) Å

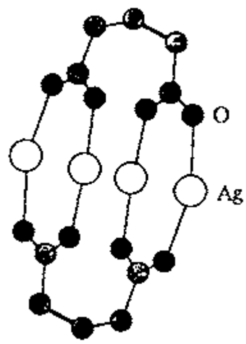


(12)

Ag - O = 2.134(2) Å

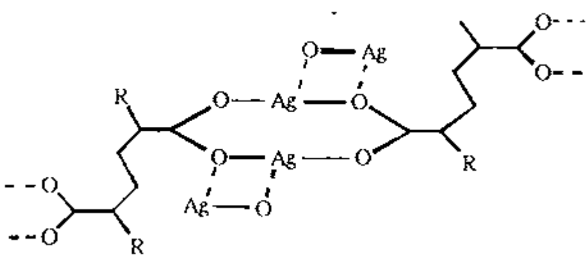
Ag - N = 2.116(3) Å

from the same dimeric unit and one more from a neighbouring unit, in a T-geometry, while the perchlorate counter-ions do not coordinate. In contrast, the solid-state structures of the corresponding nitrate polymeric salts show additional Ag–O con-



(13)

Ag - O = 2.107(7) - 2.223(8) Å

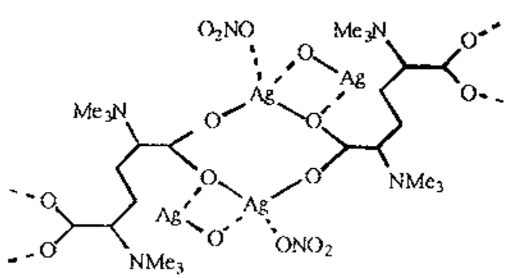


(14), R = py

Ag - O = 2.249(5) - 2.515(5) Å

(15), R = NMe_3

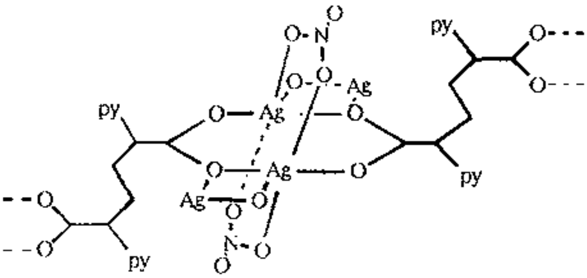
Ag - O = 2.225 (4) - 2.456(5) Å



(16)

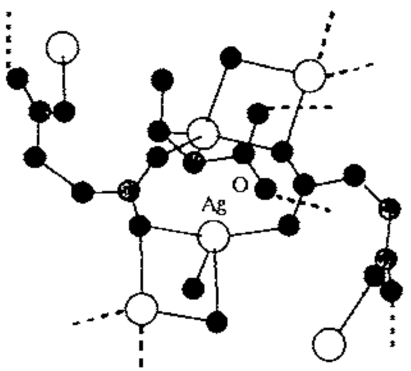
Ag - O = 2.250(3) - 2.567(4) Å

tacts to nitrate O-atoms. Four-coordinate trigonal pyramidal Ag atoms were found in (**16**) and five-coordinate square pyramidal ones in (**17**), the latter with nitrate ions in the unusual bridging coordination mode [19].



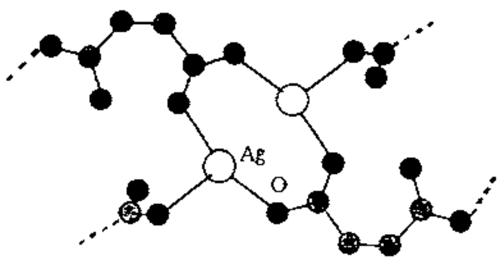
(17)

Ag - O = 2.393(3) - 2.496(3) Å



(18)

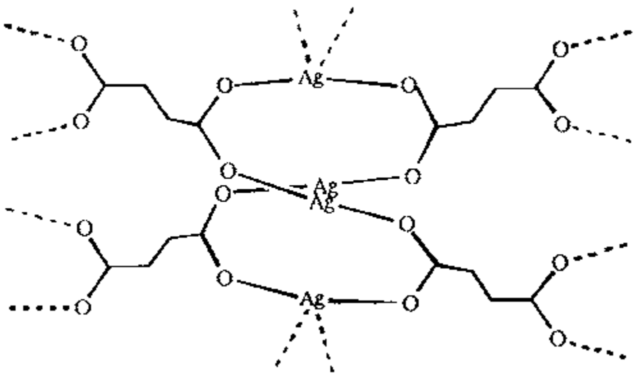
Ag - O = 2.185(3) - 2.387(3) Å



(19)

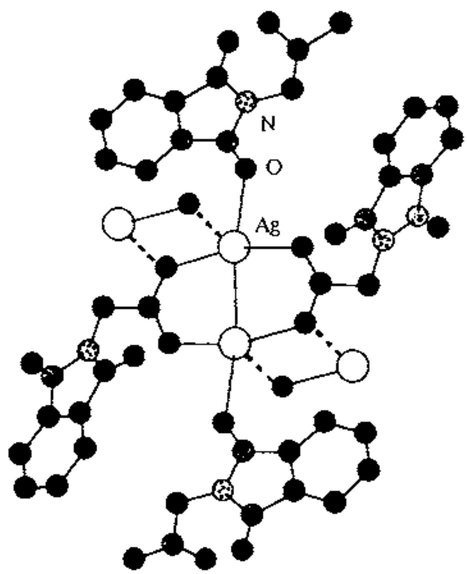
Ag - O = 2.233(2) - 2.426(2) Å

A two-dimensional polymeric structure (**18**) based on dimeric units of silver hydrogen maleate has been described. The typical Ag-carboxylate eight-membered rings, with Ag–O bonds of 2.233(2) and 2.283(2) Å are linked by Ag–O bonds of 2.426(2) Å to the dangling carboxylic acid group of their adjacent dimeric units. Silver maleate (**19**), on the other hand, forms a three-dimensional structure based again on dimeric, but heavily distorted, units. One of the maleate carboxylate groups participates in the formation of dimeric eight-membered rings. Interactions between Ag and O atoms of adjacent dimeric rings construct sheets. The second carboxylate group of each maleate serves to connect these sheets in the third dimension. An additional π-bonding interaction with the maleate ethylenic part distorts the coordination of half the silver atoms. The three-dimensional structure of silver fumarate (**20**) is based on an unusual figure-of-eight tetrameric building block. One of the carboxylate groups of each fumarate participates in the formation of one tetrameric ring, while the second carboxylate is part of the adjacent ring. The two Ag atoms



(20)

Ag - O = 2.158(4) - 2.533(5) Å

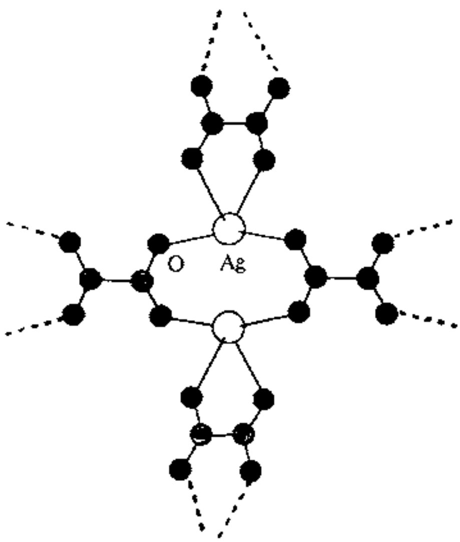


(21)

Ag - O = 2.225(2) - 2.612(2) Å

Ag - Ag = 2.8465(2) Å

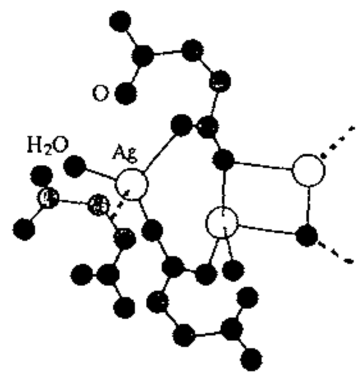
at the knot of the figure-of-eight tetrameric unit are two-coordinate, while the other two are bonded to two ring O-atoms and two O-atoms of adjacent rings [20]. A few more three-dimensional networks based on eight-membered silver-carboxylate rings have been characterized in the solid-state structures of some mono-, di-, and



(22)

Ag - O = 2.245(5) - 2.551(6) Å

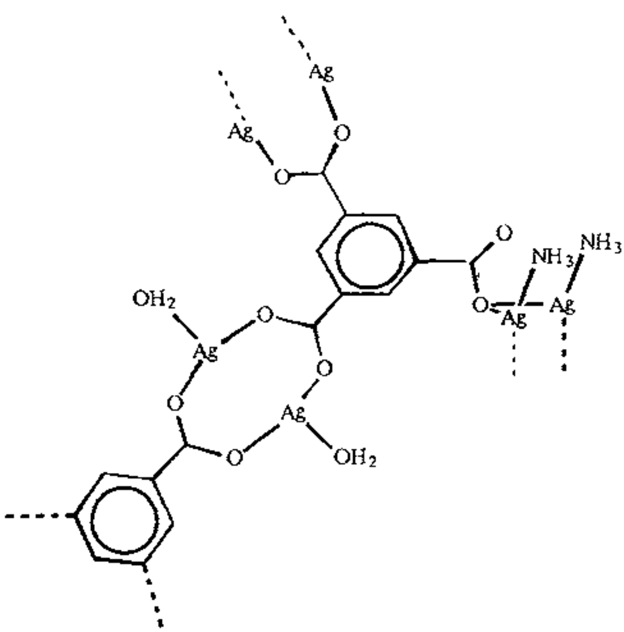
Ag . . . Ag = 2.945(1) Å



(23)

Ag - O = 2.185(5) - 2.619(5) Å

Ag . . . Ag = 3.0032(8) Å



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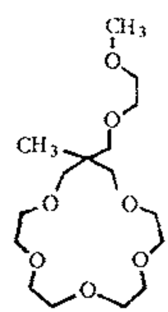
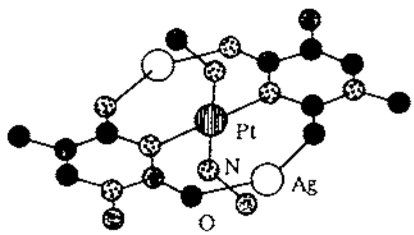


(25)

tricarboxylate silver complexes. Four-coordinate Ag-centres are present in the structures of *N*-phthaloglycinate (**21**), oxalate (**22**), and *cis*-butenedioate (**23**), silver complexes [21–23]. In addition, the later contains a Ag-alkene π-interaction. Coordinated H_2O and NH_3 molecules complete the three-coordination of the trimesic acid silver complex (**24**) [17].

Stability constants were determined conductometrically in aqueous solution at 25°C for the 1:1 complexes of the lariat ether (**25**) with metal cations. The order of selectivity, $Ag^+ > Na^+ > Tl^+ > K^+$, is the same as observed for an analogous crown ether without a side chain. For Ag^+ the measured stability constant was $1.12 \pm 0.02\ dm^3\ mol^{-1}$ [24]. The possible use of EDTA for the complexometric titration of silver has been examined in aqueous solutions. Highly neutralized $(EDTA)^{4-}$ precipitates Ag^+ as the $[Ag_4EDTA]$ complex which has been characterized by thermogravimetric analyses and potentiometric titration. Excess of titrant causes formation of the soluble $[AgEDTA]^{3-}$ complex. A conductometric titration of Ag^+ with $EDTA^{4-}$ showed a well defined end point corresponding to the precipitation of $[Ag_4EDTA]$ [25].



(**26**)

Ag - O = 2.259(8) Å

Ag - N = 2.149(9), 2.172(9) Å

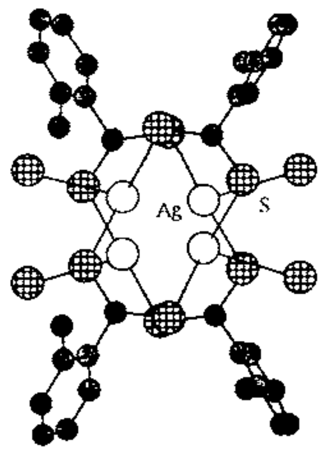
O - Ag - O = 139.3(3)°

N - Ag - N = 149.9(3)°

The first example of a trinuclear cytocine nucleobase forming a trinuclear Ag_2Pt complex has been reported. Two ligand molecules, *trans*-coordinated to the central Pt atom through their pyrazine N-atoms, form a metalloligand with two nitrogen and two oxygen atoms available for further coordination. Addition of silver salts to this metalloligand proceeds in a stepwise fashion, utilizing the two nitrogen atoms first and the two oxygen atoms last, yielding the head-to-head complex $[trans\text{-}Pt(NH_2Me)_2(\mu\text{-}L)_2Ag_2]^{2+}$ (**26**). While the $N_2Ag\cdots Pt$ and $O_2Ag\cdots Pt$ distances of 2.892(1) and 3.040(1) Å, respectively, indicate some metal–metal interaction, no Ag/Pt coupling was observed in the ^{195}Pt NMR spectrum of (**26**) [26].

Some silver complexes of isoorotic and 2-thioisoorotic acids with stoichiometries $Ag(H_2L)$, $Ag_2(HL)$ and $Ag(H_2L)(H_3L)$ have been prepared (along with their palladium and platinum analogues), and their antimicrobial activity has been tested [27].

3.3. Complexes with sulfur ligands



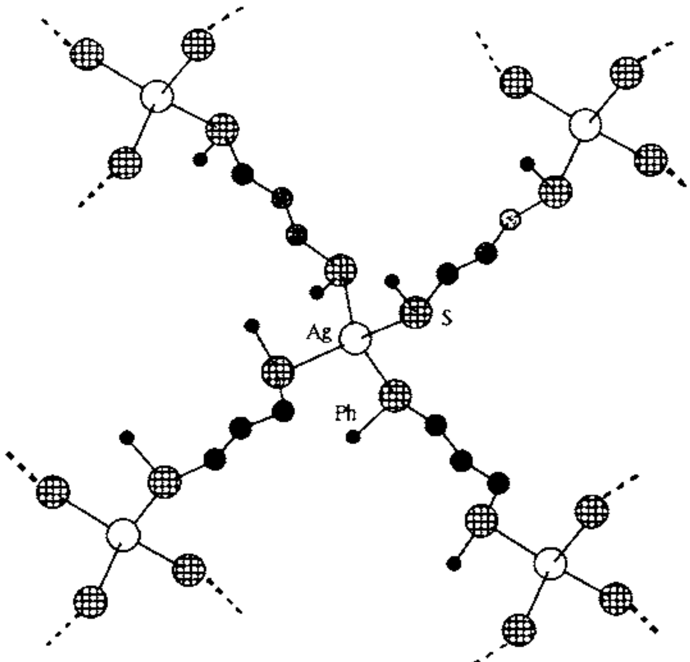
(27)

The insertion of CS_2 into the Ag–C bond of Ag(o-C_6H_4Me) gave a polymeric complex, $[Ag_4(S_2C\text{-}o\text{-}C_6H_4Me)_4]_n$ (**27**), with approximately planar AgS_3-coordination. Two dinuclear $Ag_2(S_2C\text{-}o\text{-}C_6H_4Me)_2$ units form a tetranuclear aggregate held together by Ag···Ag contacts of 3.088(3) and 3.216(3) Å, while long Ag–S interactions of 2.945(4) and 3.007 Å between consecutive tetramers make up the two-dimensional polymeric structure. Within the dimeric building blocks: Ag–Ag = 2.944(2) Å, Ag–S = 2.392(3)–2.402(5) Å, S–Ag–S = 155.6(2), 159.0(2)° [28].

The ligation properties of $RS(CH_2)_nSR$ ligands as a function of R and n have been probed by the study of two silver complexes of the potentially chelating dithioether ligands $RS(CH_2)_3SR$, (R = Me, Ph). Contrary to expectation, the $[Ag(PhSCH_2CH_2CH_2SPh)_2]^+$ complex (**28**) contains only ligands bridging between two silver atoms which are approximately tetrahedrally coordinated by four monodentate thioethers forming a three-dimensional polymeric structure. A different polymeric structure is found in $[Ag(MeSCH_2CH_2CH_2SMe)^+]_n$ (**29**) where the silver atoms are three-coordinate in a distorted trigonal environment and each dithioether ligand bridges three silver atoms using one monodentate and one didentate S-atom [29]. The ^1H and ^{109}Ag NMR spectra of (**28**) and (**29**) indicate that their solid-state polymeric structures do not persist in solution, while their $n = 2$ homologues appear to be monomeric chelated species (see Section 3.4 for some related diseleno- and ditelluroethers) [30].

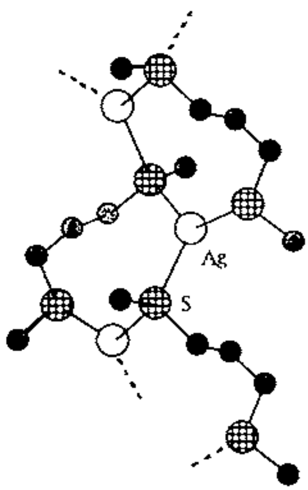
Oxidation of $1,1'\text{-}(PPh_2)_2Fc$ by elemental sulfur gives $1,1'\text{-}(SPPh_2)_2Fc$, which acts as a chelating ligand towards Ag and Au. In the Ag complex (**30**), the metal atom is in an almost perfectly linear environment. Coordination to the Ag atom brings about a torsion angle of 24° between the Cp-rings [31].

The reaction of $(NH_4)WS_4$, $AgNO_3$ and $(HOCH_2)_3CNH_2$ in 1:2:1 ratio in dmf yielded two forms of a polymeric material with chemical formula $[S_2WS_2Ag^-]_x[H_3NC(CH_2OH)_3^+]_x$. Recrystallization from dmf/Et_2O gave the single-



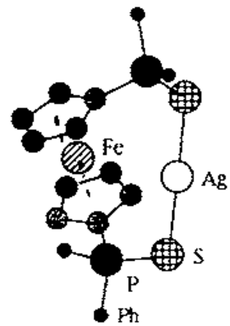
(28)

Ag - S = 2.572(2) - 2.623(3) Å



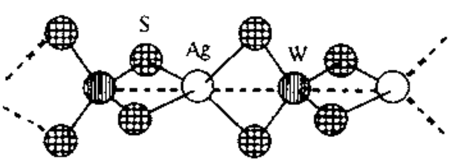
(29)

Ag - S = 2.475(3), 2.520(2), 2.560(3) Å



(30)

Ag - S = 2.381(1) Å

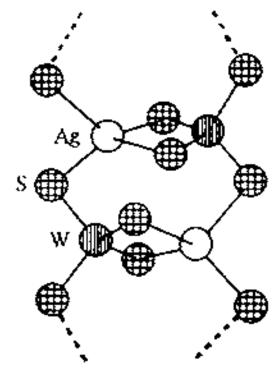


(31)

W . . . Ag = 2.915(6), 2.947(6) Å

Ag - S = 2.29(2) - 2.75(2) Å

S - Ag - S = 94.1(4) - 119.1(9)°



(32)

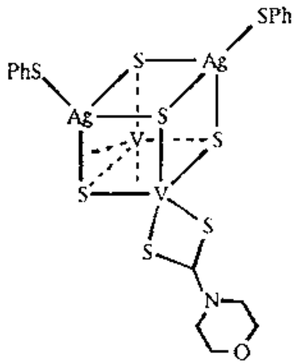
W . . . Ag = 2.980(2) Å

Ag - S = 2.538(8) - 2.613(8) Å

S - Ag - S = 92.1(2) - 126.7(2)°

chain material (**31**), while recrystallization from ETOH in the presence of H_2O gave the double-chain structure (**32**). In both forms, the silver atoms are in a distorted tetrahedral environment. In (**31**), the silver atoms are bridged to one tungsten atom by equivalent Ag–S bonds of 2.51(1) and 2.53(1) Å, and to the other by one short, 2.29(2) Å, and one long, 2.75 Å, bond. In (**32**), all Ag-S bonds are in the range 2.538(8)–2.613(8) Å [32].

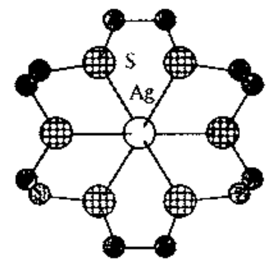
The cubane cluster $[V_2Ag_2(\mu_3\text{-}S)_4(OC_4H_8NCS2)_2(SPh)_2]^{2-}$ (**33**) was prepared from the reaction of $(NH_4)_3VS_4$, $Ag(PPh_3)_2NO_3$, $OC_4H_8NCS_2Na$, and PhSNa in dmf. It contains a $V_2Ag_2S_4$– cubane core with two PhS-groups bound terminally to



(33)

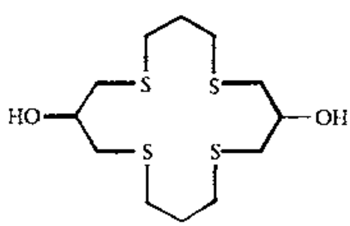
Ag - (μ^3 - S) = 2.480(5), 2.670(5) Å

Ag - SPh = 2.391(5) Å

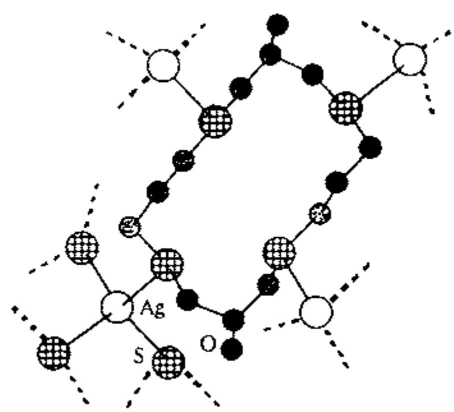


(34)

the silver atoms and the two dithiocarbamate ligands chelated to the vanadium atoms. The silver atoms are in a distorted tetrahedral AgS_4 environment with [33].



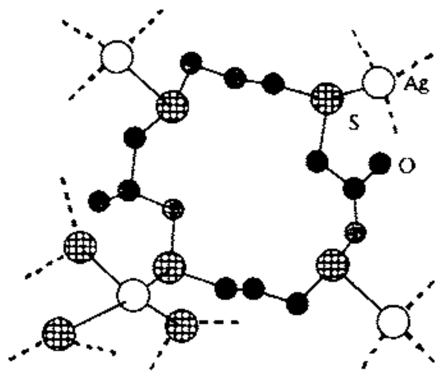
(35)



(36)

Ag - S = 2.600(4), 2.643(5) Å

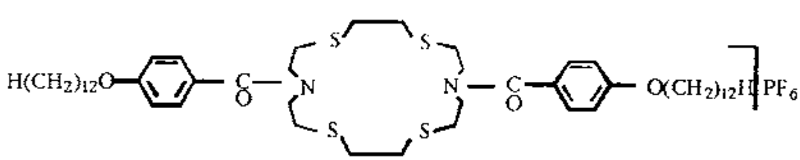
The large $\{Ag[18aneS_6]\}^+$ cation (**34**) has been used to stabilize polyiodide, I_x^- anions. From the reaction of $\{Ag[18]aneS_6\}BF_4$ with I_2, two crystalline products were obtained: one containing a $\{I_7^-\}_x$ three-dimensional network and the other discrete I_3^- anions. In both structures, the endo-bound cation is a trigonally compressed octahedron with S–Ag–S of Å80° for the chelate angles and Å100° for the non-chelate ones. However, the Ag–S bonds are equal, 2.754(2) Å, in the $[\{Ag[18]aneS_6\}I_7]_x$ structure and tetragonally elongated, Ag–S_{ax} = 2.8007(10) Å,



(37)

Ag - S = 2.546(7) - 2.697(6) Å

Ag–S_{eq} = 2.7255(7) Å, in the structure of {Ag[18]aneS_6}I_3 [34]. In contrast, the smaller S_4-macrocycle (**35**) coordinates to silver in an exodentate fashion, with four macrocycles coordinating to each distorted tetrahedral Ag and four Ag atoms bound to each macrocycle forming the polymeric structures (**36**) and (**37**). A nitrate counter-ion fills and flattens the void macrocycle in the structure of (**36**), while the acetate counter-ion of (**37**) forms hydrogen bonds between adjacent macrocycles. The smaller Cu^{2+} cation occupies a square-planar endo site in its corresponding complex with (**35**) [35].



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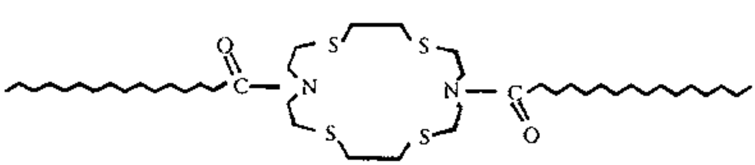
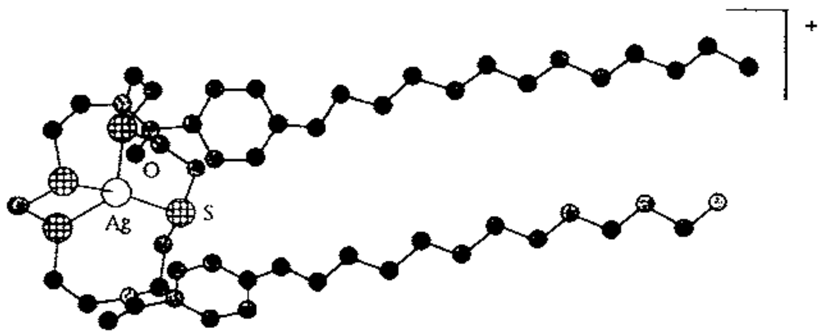


(39)

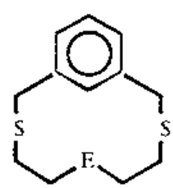
The non-mesogenic ligands (**38**) and (**39**), containing an N_2S_4-macrocycle, self-aggregate upon silver coordination to form mesomorphic structures. It has been proposed that the mesomorphic behaviour of the silver complex (**40**) is caused by



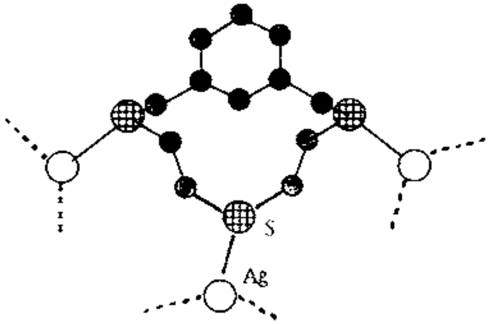
(40)

Ag - S = 2.474(5) - 2.674(5) Å

the segregation of its polar and apolar regions, resulting in an amphiphilic material. In the solid-state structure of (**40**) the Ag atom is in a flattened tetrahedral environment with S–Ag–S = 86.3(2)° for the five-membered chelates and S–Ag–S = 105.5(2), 108.9(2)° for the eight-membered chelates. The properties of (**40**) as well as those of the silver complex of (**39**), were examined by powder X-ray diffraction and differential scanning calorimetry [36,37].



(**41**) E = S
(**42**) E = O



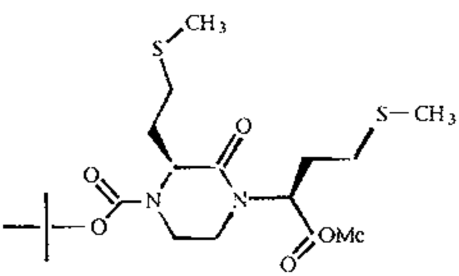
(**43**)

Ag - S = 2.530(5) - 2.556(5) Å

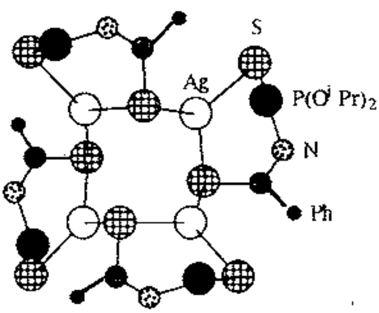
S - Ag - S = 106.3(2) - 135.9(1)°

A study of the AgL complexes of the macrocyclic ligands (**41**) and (**42**) has been undertaken in order to elucidate the factors which allow selective electrochemical recognition of silver cation by ion selective electrodes employing those ligands. The solid-state structure of (**43**) is a two-dimensional polymer where three Ag atoms are coordinated in a exodentate fashion by each molecule of (**41**), and three macrocycles coordinate to each Ag centre in a distorted trigonal planar arrangement. In solution, however, the endo coordination mode is preferred, except at the presence of excess silver, as indicated by solution ^{1}H and ^{13}C NMR spectroscopic studies [38].

Searching for water-soluble, thermally and light-stable materials with good antimicrobial activity, a Japanese group synthesized and studied the Na[AgHL] complex of the tribasic thiomalic acid, $HOOCCH(SH)CH_2COOH$, as well as the Na[AgL] and [AgHL] complexes of the dibasic thiosalicylic acid, o-HS-C_6H_4-COOH. Based on elemental, thermal, infrared, ESCA and ^{1}H, ^{13}C and ^{109}Ag NMR analyses, it has been proposed that all three materials are polymeric with two-coordinate Ag atoms and S-bound ligands [39,40]. Additional study of the Na[AgHL] thiomalate complex by electrospray ionization MS identified $Na_3Ag_4(HL)_4$ anions, indicating that cyclic tetrameric units constitute the $\{Na_4[Ag(HL)]_4\}_x$, $x = 6$–8, polymer [41].



(44)



(45)

Ag - S = 2.425(1) - 2.510(1) Å

S- Ag - S = 103.63(4) - 132.13(4)°

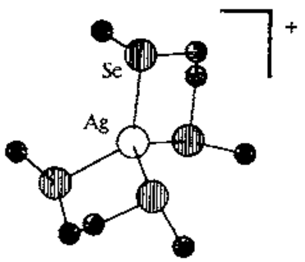
The silver complex of the piperazin-2-one derivative (**44**) was prepared and studied as a model of a non-heme metalloprotein. Molecular weight and FAB mass spectrometric data show a monomeric complex in solution, while the ^{13}C NMR shifts indicate coordination to silver through the two S-atoms [42]. The structure of the tetrameric complex (**45**) has been determined. It contains three-coordinate Ag atoms in a distorted trigonal planar environment [43].

Single crystals of the $AgLa_3GeS_7$ phase have been grown in a KBr flux and studied crystallographically. This material consists of trigonal-planar AgS_3 units stacked parallel to each other with an Ag···Ag separation of 2.920(1) Å, interconnected by $GeLaS_4$ distorted cubanes [44]. A quaternary sulfide, $BaSc_3AgS_6$, has been prepared by heating BaS, Sc, Ag, and S in an evacuated sealed tube. In the three-dimensional structure of this material the Ag-atoms occupy two distinct sites, one with trigonal-pyramidal AgS_4-geometry and Ag–S bonds in the range 2.406(6)–2.851(6) Å, and one with distorted square-pyramidal AgS_5-geometry and Ag–S bonds in the range 2.591(4)–2.781(4) Å [45]. (See Section 3.4 for some related selenide and telluride materials.)

Stability constants and enthalpies of formation for the $[AgL]^{2-}$ and $[AgL_2]^{5-}$

complexes, where $H_3L = HSCH_2CH(SH)CH_2SO_3H$, have been derived from potentiometric and calorimetric measurements [46].

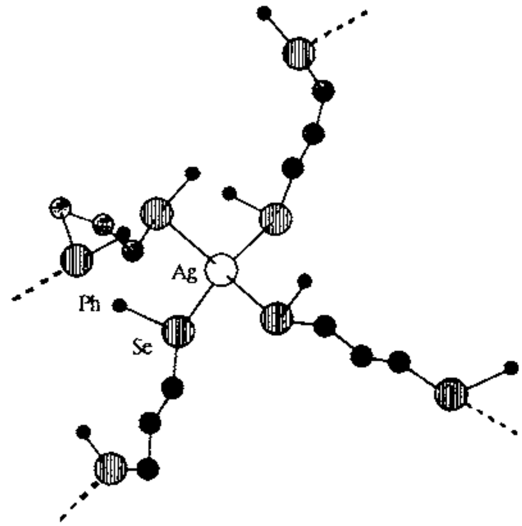
3.4. Complexes with selenium or tellurium ligands



(46)

Ag - Se = 2.610(1) - 2.638(1) Å

Se - Ag - Se = 89.61(5), 90.12(5)° (chelate)



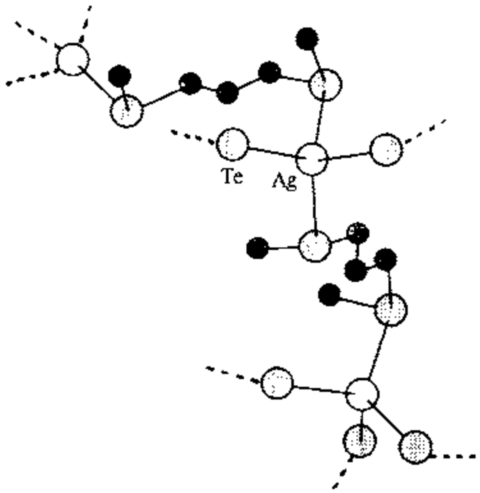
(47)

Ag - Se = 2.643(1) - 2.695(1) Å

Se - Ag - Se = 102.98(3) - 129.84(4)°

The diselenoether $RSe(CH_2)_nSeR$ forms the monomeric silver chelate (**46**) for $n=2$, R = Me, while a polymeric structure (**47**), analogous to its dithio homologue (**28**), is preferred for $n=3$, R = Ph. The silver atoms are in a distorted tetrahedral $AgSe_4$ environment in both (**46**) and (**47**) with Ag S bonds in the range of 2.610(1)–2.695(1) Å. Six silver–dichalcogenoether complexes $[Ag(RE(CH_2)_n\text{-}ER)_2]^+$, (E = Se, Te, $n=2$, 3, R = Me, Ph), examined by ^{77}Se, ^{125}Te and ^{109}Ag NMR spectroscopies showed no ^{77}Se–^{109}Ag or ^{125}Te–^{109}Ag coupling indicating labile behaviour of those ligands in solution [30].

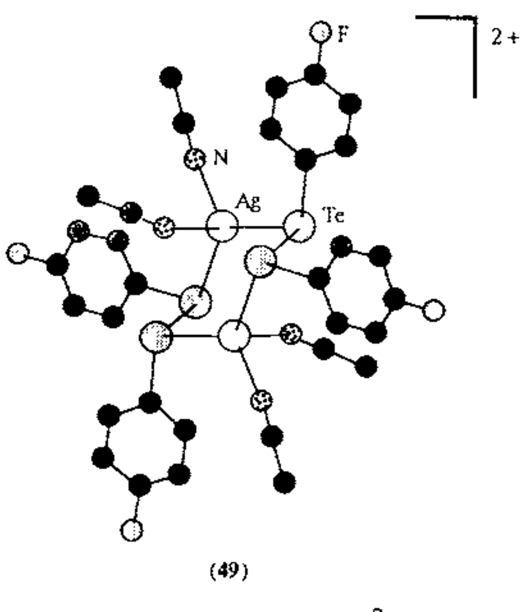
The coordination properties of some tellurium-containing ligands have been probed by the solid-state structural study of two silver complexes (**48**) and (**49**) formed by the reactions of $AgBF_4$ with $MeTe(CH_2)_3TeMe$ and $Te_2(p\text{-}F\text{-}C_6H_4)_2$. In the polymeric complex (**48**) the Ag atom is coordinated by four $MeTe(CH_2)_3TeMe$ ligands in a distorted tetrahedral geometry while each ditelluroether bridges two Ag atoms of a two-dimensional network. Solution ^{1}H, ^{13}C and ^{125}Te NMR spectroscopic results indicate that the polymeric structure is retained in solution. In the dimeric complex (**49**), two ditelluride $Te_2(p\text{-}F\text{-}C_6H_4)_2$ ligands bridge



(48)

Ag - Te = 2.785(2) - 2.837(2) Å

Te - Ag - Te = 99.48(7) - 122.51(8)°



(49)

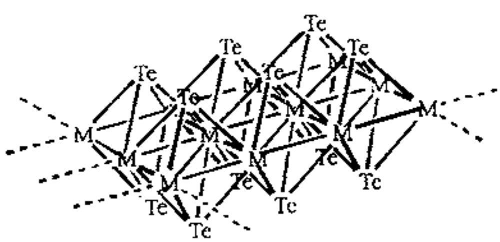
Ag - Te = 2.733(1), 2.736(1) Å

Te - Ag - Te = 120.49(3)°

the Ag atoms whose four-coordination is completed by two MeCN molecules. The related Te_2Me_2 ligand forms a polymeric Cu(I) complex [47].

Two silver selenophosphates, $A_2AgP_2Se_6$, A = K, Cs, have been prepared from the reaction of Ag in a $A_2Se/P_2Se_5/Se$ flux. The size of the counter-ion determines the Ag-coordination and the structure of the $(AgP_2Se_6^{2-})_x$ anionic polymer. While $K_2AgP_2Se_6$ is a three-dimensional network with distorted tetrahedral $AgSe_4$-coordination, (Ag–Se = 2.615(4)–2.797(4) Å), $CS_2AgP_2Se_6$ adopts a chain structure with distorted trigonal-planar Ag-atoms and Ag–Se = 2.545(2)–2.641(3) Å [48].

Ternary and quaternary metal telluride materials have been prepared from the metallic elements in telluride fluxes. The first ternary alkali metal silver telluride, $CsAg_5Te_3$, has been prepared from Ag in a $Cs_2Te/CaTe/Te$ flux. Its solid-state structure consists of Ag_5Te_3-three-dimensional network with tunnels occupied by Cs atoms. The silver atoms are located in either distorted tetrahedral or trigonally coordinated positions with Ag–Te bonds in the range of 2.743(4)–3.060(3) Å. $CsAg_5Te_3$ has a band gap of 0.65 eV [49]. Using the $K_2Te/BaTe/Te$ flux a layered silver telluride, $K_{0.33}Ba_{0.67}AgTe_2$, has been prepared. Alternating square nets of $(Te_2)^{4/3-}$ and puckered $(Ag_2Te_2)^{2-}$ networks with Ag-atoms in distorted tetrahedral $AgTe_4$- coordination, are separated by K^+ and Ba^{2+} cations; Ag–Te = 2.905(2) Å, Te–Ag–Te = 105.5(1)–111.50(6)° [50].



(50)

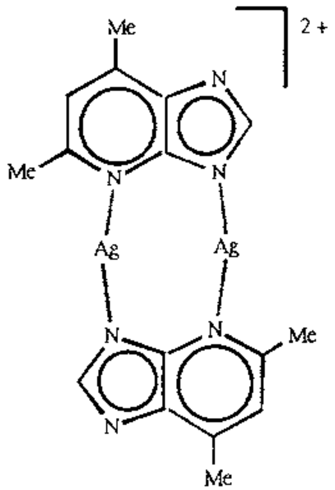
M = Ag/Fe

M - Te = 2.7853(4) Å

M - M = 3.1861(3) Å

The reaction of metallic Fe and Ag in a Cs_2Te/Te flux yielded a quaternary mixed-metal telluride containing two transition metals, $CsFe_{0.72}Ag_{1.28}Te_2$. The Fe and Ag atoms, which are disordered over the sites of a square lattice, are in a distorted tetrahedral environment with Fe/Ag–S = 2.7853(4) Å. Tellurium atoms cap the Fe/Ag lattice on both sides forming M:Te 1:1 layers (**50**) separated by Cs cations [51]. Similarly, from Zr and Ag in a Cs_2Te_3/Te flux, another quaternary material, $Cs_2ZrAg_2Te_4$, has been prepared. The $[ZrAg_2Te_4^{2-}]_n$ layers consisting of edge-sharing $AgTe_4$- and $ZrTe_4$-tetrahedra, are separated by Cs^+ cations; Ag–Te = 2.806(2), 2.817(2) Å, Te–Ag–Te = 106.34(7)–111.91(7)° [52].

3.5. Complexes with nitrogen ligands

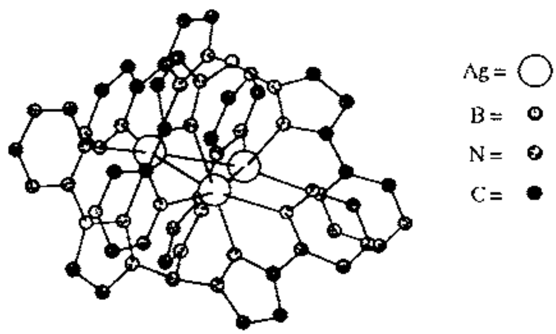


(51)

Ag - N = 2.210(2), 2.250(2) Å

Ag . . . Ag = 3.058(1) Å

N - Ag - N = 162.3(3)°



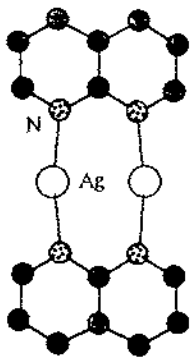
(52)

Ag - N = 2.264(9) - 2.44(1) Å

Ag - Ag = 2.977(1) Å

The question of Ag(I)–Ag(I) bonding interactions has been raised in three articles involving complexes with N-donor ligands. An Ag–Ag contact of 3.058(1) Å, measured in the structure of the dimeric triazolopyrimidine complex (**51**), has been shown by ab initio MO calculations to indicate a bonding interaction with Å30% the charge density of a Ag–N bond (of the same complex) [53]. A crystallographically characterized triangular Ag_3-aggregate, with Ag–Ag distances of 2.977(1) Å, encapsulated by two hexadentate $[HB(3\text{-}(2\text{-py})\text{-pz})_3]^-$ ligands, has been identified in the structure of the cationic complex $[Ag_3L_2]^+$ (**52**). One pyrazole N-atom and one pyridine N-atom of each ligand are coordinated to each Ag atom; each is coordinated by four N-atoms in total, with two Ag–Ag contacts completing a distorted octahedral environment [54]. An even shorter Ag–Ag contact of 2.780(1) Å has been encountered in the solid-state structure of $[Ag(\mu\text{-napy})]_2(NO_3)_2$ (**53**) (napy = 1,8-naphthyridine) where the nitrate ions interact weakly with the Ag-atoms [55].

Two silver atoms can be encapsulated by the cryptand (54), L, forming the complex $[Ag_2L][O_3SCF_3]$ which has been characterized by ^1H NMR spectroscopy. To this end, the chemical shifts of the aromatic protons have been particularly informative, as has the coupling to $^{107,109}Ag$, the latter observed only at 233 K. Comparisons with the Cu(I) cryptates of (**54**) and related cryptands have been

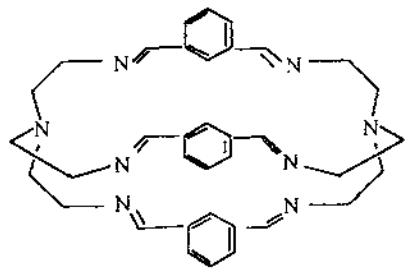


(53)

Ag - N = 2.204(3), 2.213(3) Å

N - Ag - N = 164.8(1)°

Ag - Ag = 2.780(1) Å



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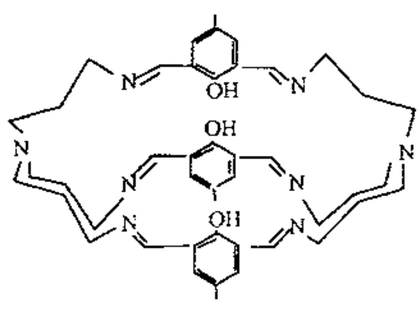

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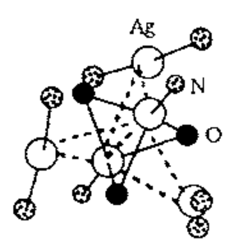
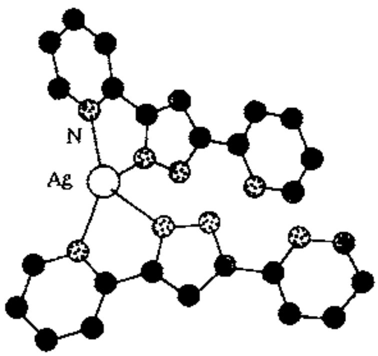


(56)

discussed [56]. A cryptand larger than (**54**) and containing three additional phenoxo *O*-donor functions (**55**), has been found to encapsulate an Ag_5-aggregate. The $[Ag_5L][BF_4]$ cryptate has been prepared on the Ag-template from the [2+3] condensation of $N(CH_2CH_2CH_2NH_2)_3$ with 2,6-$(HCO)_2$-4-Me-C_6H_2OH. The Ag_5-core (**56**) of the complex is in a trigonal bipyramidal arrangement with the apical Ag atoms bridged by the three phenoxo oxygen and the bridgehead nitrogen atoms [Ag–O = 2.445(6)–2.623(7) Å, Ag–N = 2.265(7), 2.286(8) Å] while the equatorial Ag atoms are approximately linearly coordinated by two side-arm nitrogens with Ag–N = 2.126(9)–2.167(9) Å [57].

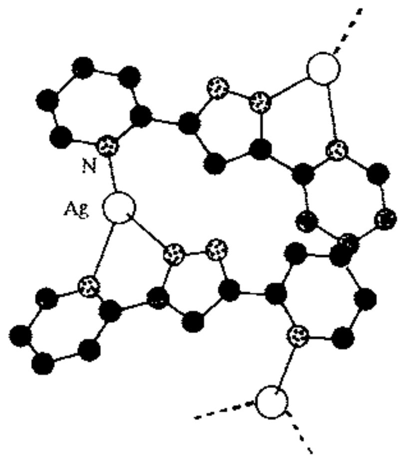
Two different crystalline products have been isolated from reactions of $AgClO_4$ with the potentially tetradentate ligand 3,5-$(2\text{-py})_2$pzH in different solvents. The 1:2 reaction in pentane has yielded the mononuclear AgL_2 complex (**57**) where each ligand acts as a single chelate to a silver atoms in a trigonal pyramidal



(57)

Ag - N = 2.25(1) - 2.485(9) Å

N - Ag - N = 70.7(4) - 72.3(4)° (chelate)

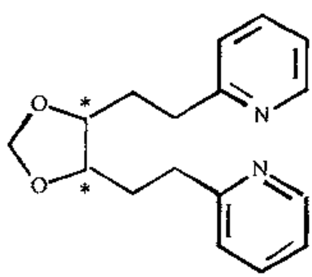


(58)

Ag - N = 2.213(3) - 2.388(3) Å

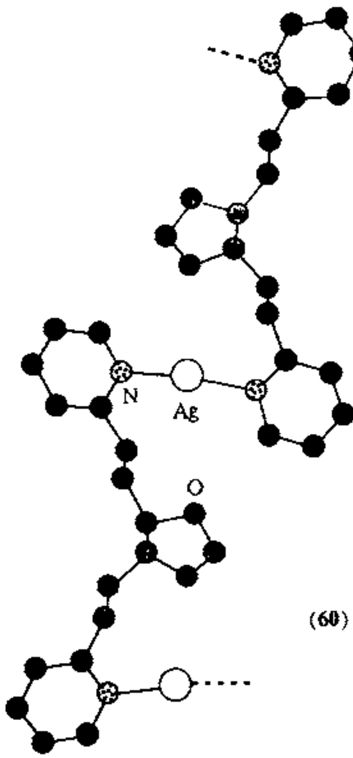
N - Ag - N = 71.6(1)° (chelate)

N_4-geometry. Two such mononuclear complexes are linked by hydrogen-bonds. In contrast, the 1:1 reaction in MeOH has produced a polymeric $(AgL)_n$ complex (**58**) where each ligand acts as a chelate to one silver atom and as a monodentate py-donor to the next, while the silver atoms are in a trigonal planar N_3 environment. In a related Cu(II) complex the 3,5-(2-py)$_2$pzH ligand is a bis-chelate N_4-donor [58].

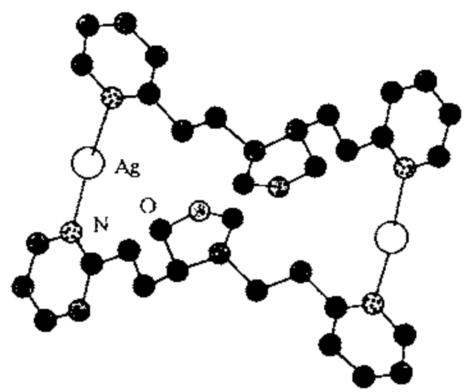


(59)

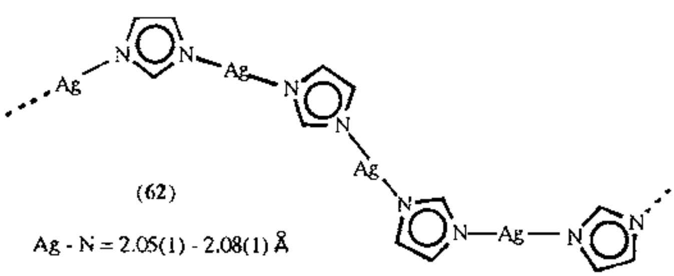
Different products in each case have been obtained from the reaction of silver triflate with the racemic mixture or with enantiomerically pure (*R,R* or *S,S*) forms of ligand (**59**). With the former, the dimeric *meso*-complex (**60**) has been isolated, while with the latter, the *R,R* or *S,S*-forms, respectively, of the polymeric $[AgL^-]_n$ catenate (**61**) have been characterized. The polymeric structure is not maintained in solution as 1:1 mixtures of *R,R*- and *S,S*-(**61**) in MeOH produce the dimeric *meso* form (**60**), indicating molecular recognition of the enantiomeric forms of (**D**) with the assistance of Ag-cations [59].



(60)



(61)

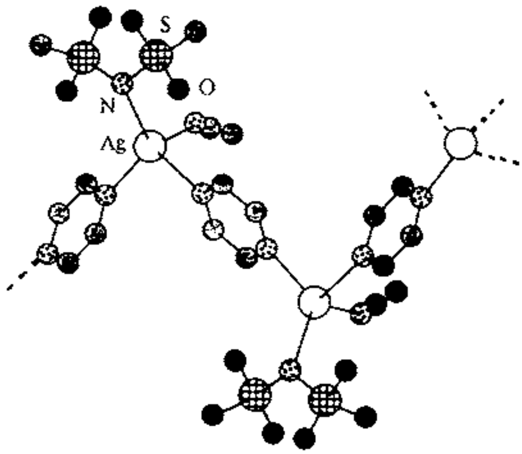


(62)

Ag - N = 2.05(1) - 2.08(1) Å

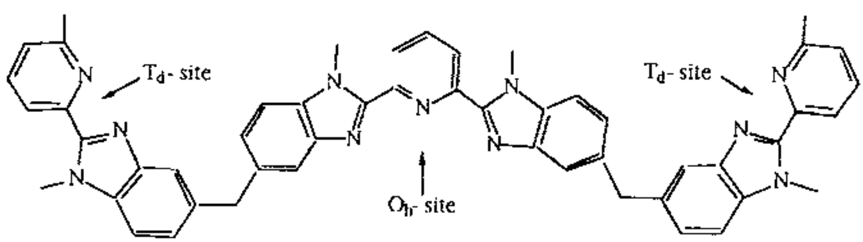
N - Ag - N = 167.6(1), 171.8(8)°

Ab initio techniques have been employed for the structure determination of polymeric silver–imidazolate (**62**) from X-ray powder diffraction data from a conventional source. The one-dimensional polymer (**62**) consists of $(\text{Ag-imz})_n$ parallel chains with alternating *cis*, *trans* arrangement of the imidazole rings with respect to the polymer backbone and interchain Ag· · ·Ag distances of 3.161(4) Å. Molecular mechanics calculations confirmed that the determined conformation represents a thermodynamic minimum [60]. The structure of a one-dimensional polymer (**63**) with a silver–pyrazine backbone has been reported. The four-coordination of the Ag atom is completed by one MeCN and one $N(SO_2Me)_2$ ligands [61].

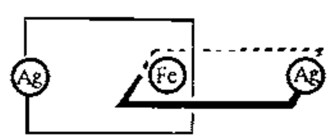


(63)

Ag - N = 2.324(2), 2.340(2) Å



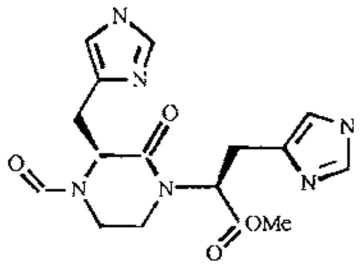
(64)



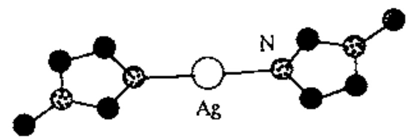
(65)

The segmental ligand (**64**), containing a tridentate (octahedral) and two didentate (tetrahedral) bites, forms a $[Ag_2FeL_2]^{4-}$ [2]catenate complex (**65**). The Fe(II)-centre is located in an octahedral *mer*-site between two (**64**) molecules and each Ag-centre in a tetrahedral site formed by two didentate bites of the same ligand, with average Ag–N bond lengths of 2.311 Å. Two forms of this [2]catenate have been characterized: the *meso*-(P,M) and the racemic mixture of the (P,P) and (M,M) forms.

The ^{1}H NMR spectra of (**65**) reveal a rapid interconversion of the P and M enantiomers [62].



(**66**)

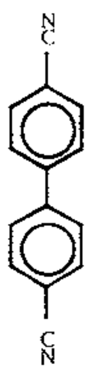


(**67**)

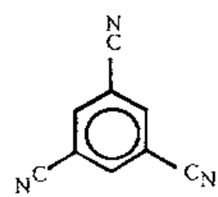
Ag - N = 2.099(3) Å

The silver complex of the piperazin-2-one derivative (**66**) has been prepared and studied as a model of a non-heme metalloprotein. Molecular weight and FAB mass spectrometric data show a monomeric complex in solution, while the ^{13}C NMR shifts indicate that both imidazole side-chain groups are coordinated to silver [42].

A linear two-coordinate Ag(*N*-MeIm)$_2$ complex cation (**67**) (*N*-MeIm = *N*-methylimidazole) has been characterized in the crystal-structure of {Fe(OEP)(*N*-MeIm)$_2$][Ag(*N*-MeIm)$_2$][PF$_6$] [63].

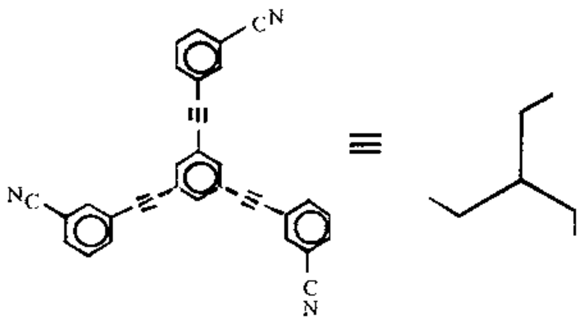


(**68**)

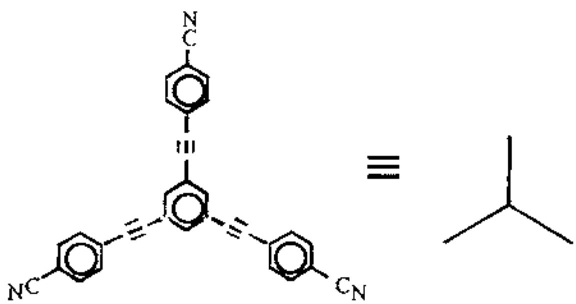


(**69**)

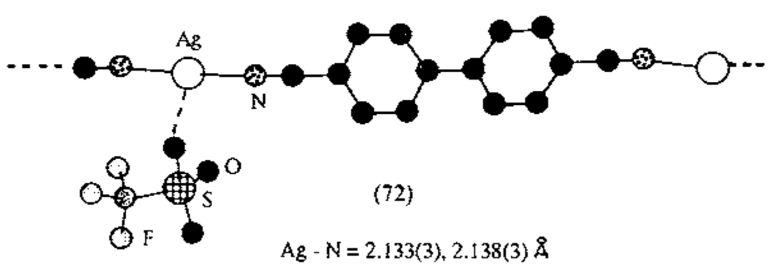
Supramolecular architecture continues to be a very active field of research and several contributions come from the area of silver complexes with *N*-donor ligands acting as spacers. Some one-, two- and three-dimensional polymeric structures have been constructed using rigid nitrile ligands, such as (**68**)–(**71**), as connectors between silver atoms. Crystallization of (**68**) with AgO_3SCF_3 from benzene gave the one-dimensional material (**72**) with silver atoms almost linearly coordinated by two nitriles and one long Ag· · ·triflate interaction preventing higher coordination of the Ag atom. In contrast, crystallization of (**68**) with $AgPF_6$ from toluene or ethanol allowed four-coordination of silver (**73**) giving a three-dimensional network of nine interpenetrated diamondoids—the highest degree of interpenetration known [64].



(70)



(71)

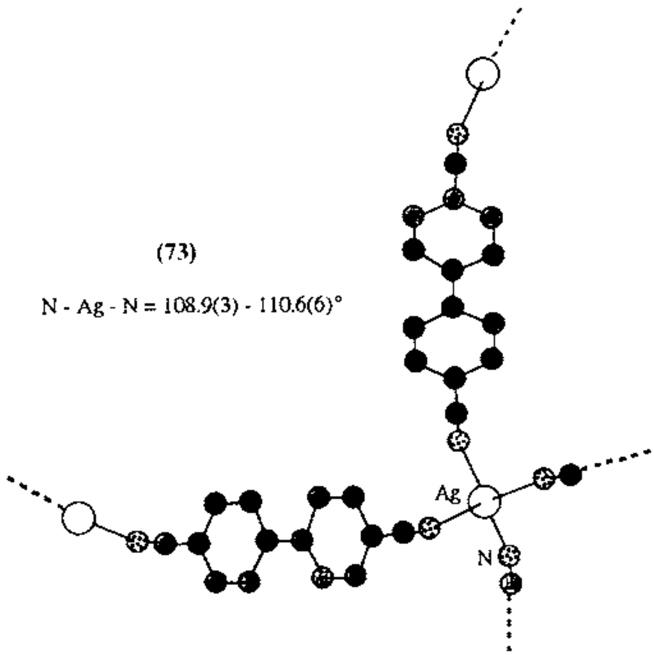


(72)

Ag - N = 2.133(3), 2.138(3) Å

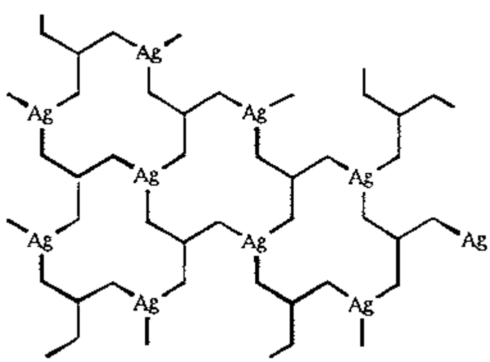
N - Ag - N = 174.4(1)°

Recrystallization of the tridentate ligands (**69**) or (**70**) with AgO_3SCF_3 resulted in the two-dimensional honeycomb structures (**74**) and (**75**), respectively, both of which are based on three-coordinate Ag-centres. Triflate ions fill-up the space between layers in the structure of (**74**), while the much larger voids of (**75**) are occupied by benzene molecules, which were shown by TGA to be reversibly removed [65,66]. A three-dimensional structure of six interpenetrating lattices, obtained from the recrystallization of (**71**) with AgO_3SCF_3, also contained benzene molecules which could be exchanged without lattice damage [65]. Similar to ihe nitrile rods

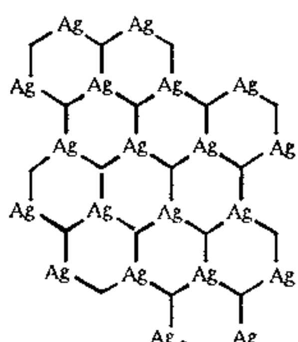


(73)

N - Ag - N = 108.9(3) - 110.6(6)°



(74)

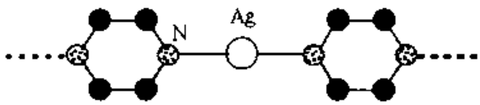


(75)

Ag - N = 2.261 Å

N - Ag - N = 114.9, 122.0°

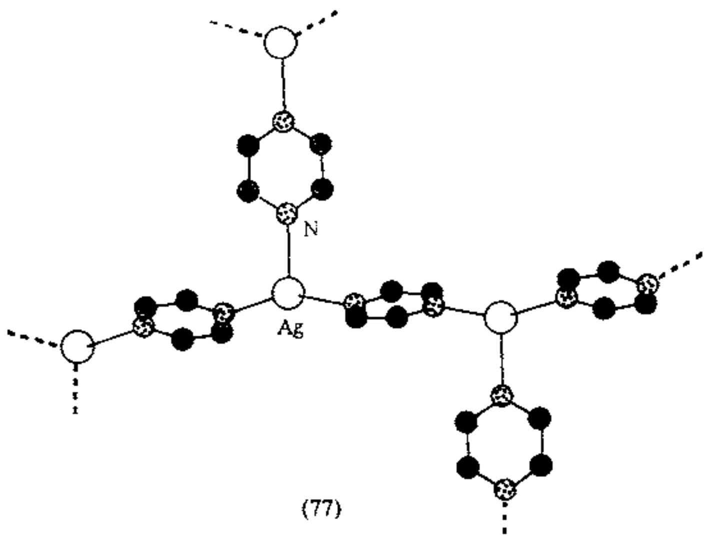
mentioned above, linear pyrz ligands (pyrz = pyrazine) have also been employed for the self assembly of polymeric materials. Varying the reaction conditions and stoichiometry, one-, two-, and three-dimensional structures, containing two-, three-, four-, five-, and six-coordinate Ag atoms, have been prepared. A linear $\{Ag(pyrz)^{+}\}_n$ polymer (**76**) has been crystallized from a stoichiometric mixture of $AgBF_4$ and



(76)

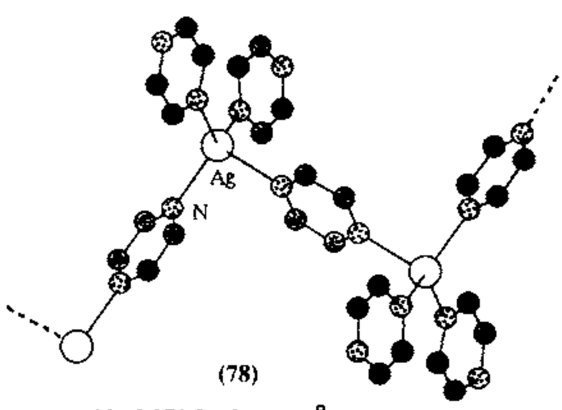
Ag - N = 2.193(3) Å

N - Ag - N = 173.6(2)°



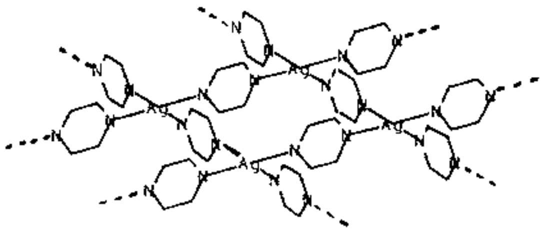
(77)

Ag - N = 2.239(3) - 2.419(3) Å



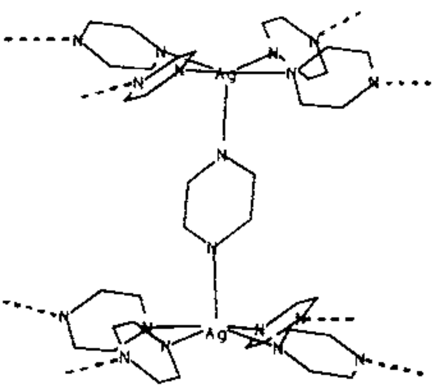
(78)

Ag - N = 2.276(5) - 2.410(5) Å



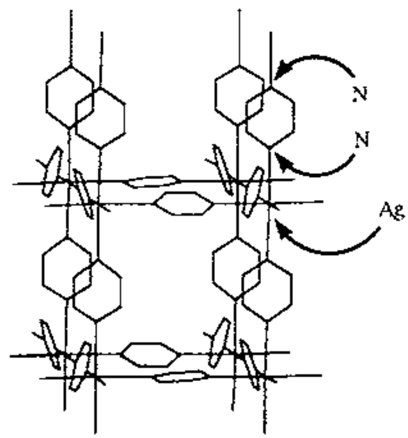
(79)

Ag - N = 2.32(2), 2.45(2)Å



(80)

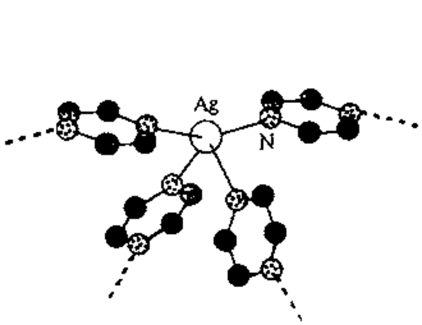
Ag - N = 2.44(2), 2.454(9)Å



(81)

Ag - N = 2.481(7) - 2.519(8)Å

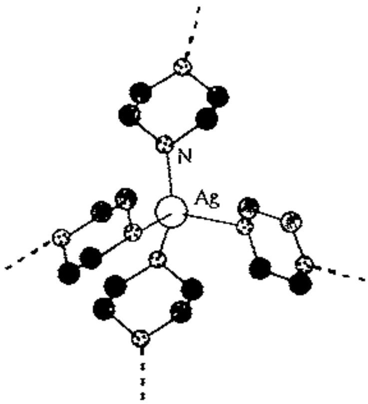
pyrz in EtOH. In the presence of excess pyrz, (**76**) is converted into a material of $[Ag_2(pyrz)_3^{2+}]_n$ composition (**77**) which has been encountered in one two- and one three-dimensional forms, the latter with a triply interpenetrated lattice. Both forms, however, contain three-coordinate Ag-atoms with two short and one long Ag–N bonds of geometry intermediate between T-shaped and trigonal planar. A mixture of (**76**), (**77**) and (**78**) has been obtained from a pyrz/$AgBF_4$ 4:1 ethanolic solution. (**78**) is a one dimensional polymer with a zig-zag Ag(pyrz)-backbone containing four-coordinate Ag atoms with two terminal and two bridging pyrz ligands [67]. Layering of an ethanolic $AgPF_6$ solution with a solution of pyrz in a chlorinated solvent (CH_2Cl_2, $CHCl_3$, or CCl_4) with a pyrz/Ag ratio of 2:1 to 3:1, a two-dimensional layered material $[Ag_2(pyrz)_5][Ag(pyrz)_2][PF_6]_3$, with unusual Ag-coordination, has been prepared. It consists of alternating layers with $[Ag(pyrz)_2]$ (**79**) and $[Ag_2(pyrz)_5]$ (**80**) composition, separated by solvent molecules and the counter-ions. While layer (**79**) consists of a square-grid of square planar Ag atoms (with long axial interactions to the PF_6 counter-ions), layer (**80**) is made



(82)

Ag - N = 2.292(3), 2.306(3) Å N - Ag - N = 155.8(1)°

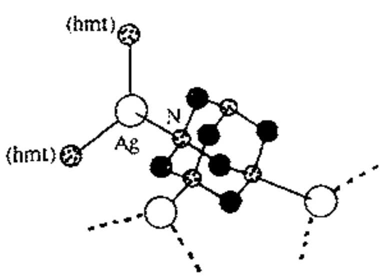
Ag - N = 2.389(3), 2.510(3) Å N - Ag - N = 95.7(1)°



(83)

Ag - N = 2.316(8) - 2.439(6) Å

up of two such grids cross linked by pyrz bridges, so that the Ag atoms are five-coordinate square pyramidal. Under the same conditions, but using $AgSbF_6$ instead of $AgPF_6$, a three-dimensional lattice (**81**) of octahedral Ag atoms and $Ag(pyrz)_3$ composition has been characterized [68]. A four-coordinate see-saw geometry has been observed in the two-dimensional $[Ag(pyrz)_2][PF_6]$ (**82**) structure assembled from $AgPF_6$ and pyrz in H_2O/EtOH. Similarly, employing the flexible ppz ligand (ppz = piperazine), a two-dimensional $[Ag(ppz)_2][BF_4]$ network (**83**) of distorted tetrahedral Ag atoms has been constructed [69].

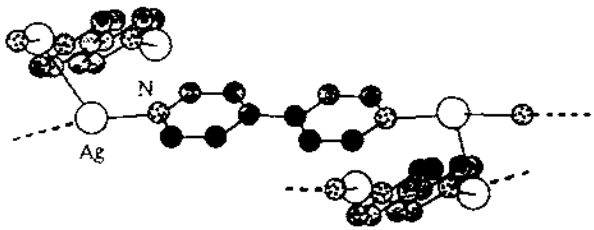


(84)

Ag - N = 2.362(2) Å

N - Ag - N = 119.52(1)°

Crystallization of $AgPF_6$ with the potentially tetradentate ligand hmt gave a $[AgL^+]_n$ polymer (**84**) where the silver ions are in a trigonal planar environment and hmt is tridentate. The channels of the three-dimensional structure (**84**) are filled by $[PF_6]^-$ counter-ions and H_2O molecules which can be removed reversibly by heating [70].

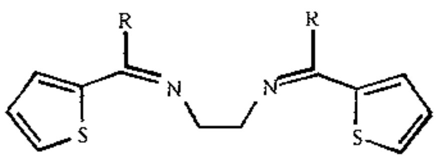


(85)

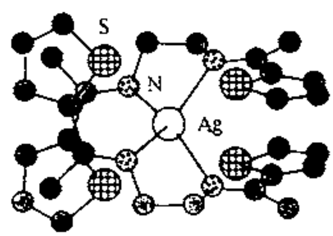
Ag - N = 2.163(6) Å

Ag - Ag = 2.970(2) Å

Recrystallization of 1:1 or 1:2 mixtures of $AgNO_3$ and 4,4′-bpy gave $[AgL^1]_n$ linear polymeric chains (**85**) interconnected by Ag–Ag bonds of 2.970(2) Å on alternate sides and forming a triply interpenetrated network. This arrangement places the Ag atoms in an unusual T-shaped geometry defined by two 4,4′-bpy ligands and the Ag–Ag bond [71].



(86)



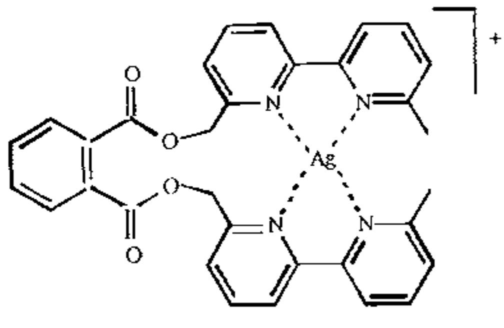
(87)

Ag - N = 2.329(3) Å

The N_2S_2-donor ligand (**86**) forms ML_2 chelate complexes with Ag(I) and Cu(I) where only the N-atoms coordinate to the metal. The solid-state structure of its Ag complex (**87**) shows the metal atom to be in a flattened four-coordinate geometry with N–Ag–N angles of 77.3(1)° and 112.8(1)° for the chelate and non-chelate N-atoms, respectively. Solution NMR spectroscopic studies indicate a tetrahedral coordination geometry supporting the view that the solid-state flattening is forced by the packing of the thiophene groups. Comparison has been made with the isostructural Cu(I) complex [72].

Some silver sulphonamide complexes, of interest with regard to their antiseptic properties, have been proposed to contain Ag–N bonds on the basis of their infrared spectra [73].

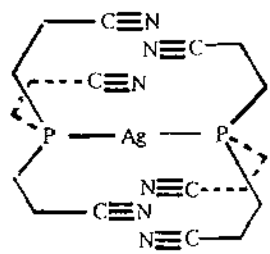
The mononuclear complex (**88**) has been prepared from the free ligand and $AgClO_4$ and characterized by ^1H and ^{13}C NMR spectroscopies and FAB-MS techniques [74].



(88)

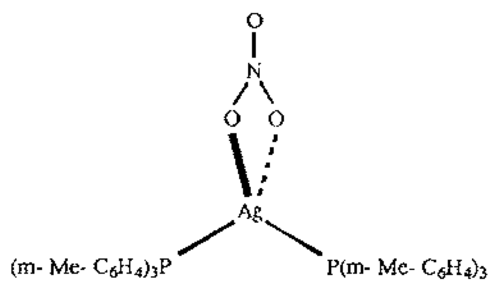
A trinuclear Ag_2Pt complex (**26**) containing one two-coordinate nitrogen-bound Ag atom has been described in Section 3.2 [26].

3.6. Complexes with phosphorus ligands



(89)

Ag - P = 2.3832(9) Å



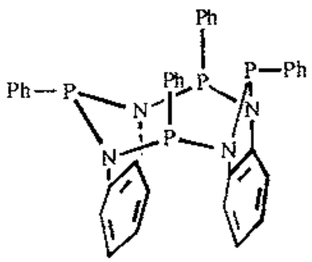
(90)

Ag - P = 2.4128(8) Å   P - Ag - P = 138.11(2)°

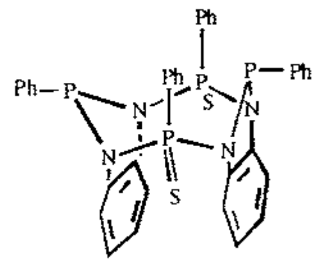
Ag - O = 2.516(3) Å   O - Ag - O = 50.25(9)°

High-resolution solid-state CP-MAS ^{31}P NMR spectroscopy has been shown to be a good structural probe for silver phosphine complexes as the P/Ag coupling constant is sensitive to the lengths and angles of Ag–P bonds. For the two-coordinate linear complexes $[(Ph_3P)_2Ag]NO_3$ and $[\{(NCCH_2CH_2)_3P\}_2Ag]NO_3$ (**89**) as well as for the four-coordinate (through long Ag–nitrate contacts) complex $[\{(m\text{-Me-}C_6H_4)_3P\}_2Ag]NO_3$ (**90**), coupling constants $^1J(^{31}P-^{107}Ag) = 467$, 496, 453 ± 6 Hz and $^1J(^{31}P-^{109}Ag) = 524$, 564, 517 ± 6 Hz have been measured, respectively. In complex (**89**), the phosphine ligand $P(CH_2CH_2CN)_3$ adopts a conformation in which it encapsulates the metal atom corresponding to a Toliman cone angle of 175° [75,76].

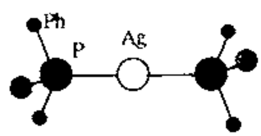
A heterodimetallic complex, $(PhCC)_2Pt(\mu\text{-dpmMe})_2AgCl$, has been prepared from the reaction of $[Pt(dpmMe)_2]Cl_2$ with AgCl as a 4:1 mixture of two isomers, as evident by its ^{1}H NMR spectrum, in contrast to its similarly prepared, $(PhCC)_2Pt(\mu\text{-dpmMe})_2HgCl_2$ analogue which is present in solution as a single isomer. In the ^{31}P NMR spectrum of the Pt/Ag-complex, $^1J(^{31}P-^{107}Ag)=382$ Hz and $^1J(^{31}P-^{109}Ag)=441$ Hz [77].



(91)

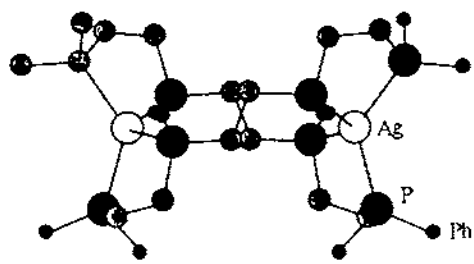


(92)



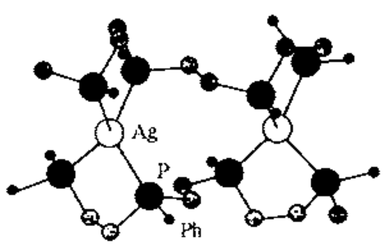
(93)

Ag - P = 2.4106(9) Å



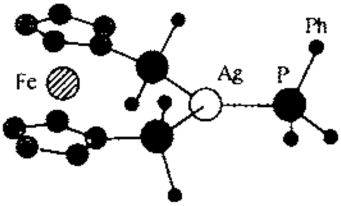
(94)

Both cyclotetraphosphazane ligands (**91**) and (**92**) form mononuclear AgL$^+$ complexes identified by FAB-MS. The former, containing two endo- and two exo-oriented phosphine electron-pairs, utilizes only the exo-site in its silver complex: $J(^{31}P-^{107}Ag)=316$ Hz, $^1J(^{31}P-^{109}Ag)=366$ Hz. In contrast, (**92**), having the exo-sites occupied by S atoms employs the endo ones towards silver coordination: $^1J(^{31}P-^{107}Ag)=341$ Hz, $^1J(^{31}P-^{109}Ag)=392$ Hz [78]. The crystal structure of $[Ag(PMePh_2)_2]ClO_4$ (**93**) containing a crystallographically linear two-coordinate silver atom has been reported [79].



(95)

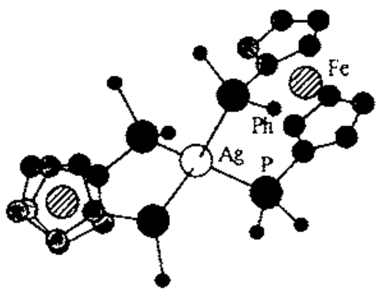
The use of poly(tertiary)phosphines towards the synthesis of helicates has been investigated for the first time. The reaction of $AgClO_4$ and (*S,S*)-(+)-$Ph_2P(CH_2)_2P(Ph)(CH_2)_2P(Ph)(CH_2)_2PPh_2$ in MeOH gave Λ-(−)-$[Ag_2\{(R,R)\text{-}L\}_2]^{2+}$. Two co-crystallized conformers of this complex, a double-helix (**94**) and a side-by-side helix (**95**), have been characterized crystallographically [80].



(96)

Ag- P(dppf) = 2.431(1), 2.480(1)Å

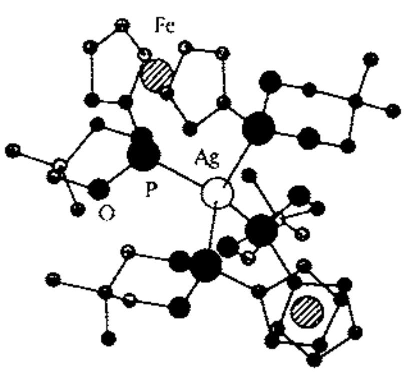
Ag- PPh_3 = 2.424(1)Å



(97)

Ag- P (dppf) = 2.561(2), 2.584(2)Å

Ag- PPh_3 = 2.549(2), 2.602(2)Å



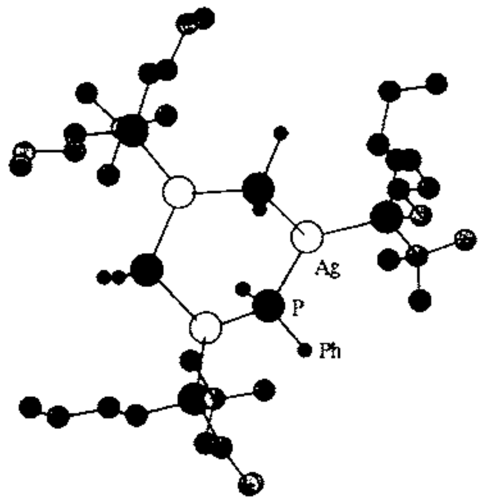
(98)

Ag - P = 2.450 - 2.460 Å

P - Ag - P = 98.2, 99.9° (chelate)

The reaction of dppf with $AgClO_4$ gave the complex Ag(dppf)(ClO_4) for which a dimeric structure with chelating dppf and bridging perchlorate ligands has been proposed on the basis of FAB-MS and molecular weight measurements. Various *P*-, *S*-, and *N*-donor ligands can replace the perchlorates leading to new dppf-containing complexes characterized by FAB-MS, ^1H and ^{31}P NMR spectroscopies and conductivity measurements. Two of those, (**96**) and (**97**) containing, respectively, three- and four-coordinate AgP_3 and AgP_4 centres, have been structurally characterized.

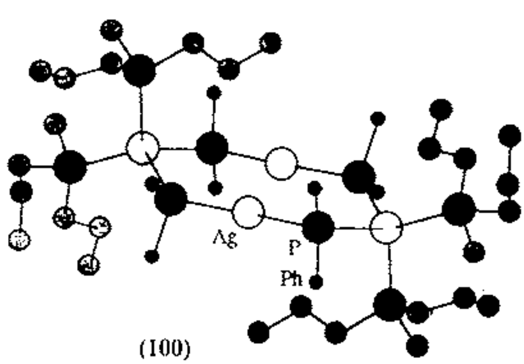
(See Section 3.9 for a related AgP_2N_2 complex [81]. Related to (**97**) is the Ag-complex (**98**) of a neopentylidenediphosphonito-substituted ferrocene ligand, containing a tetrahedral Ag-atom [82].



(99)

Ag- PPh_2 = 2.465(2)- 2.502(1)Å

Ag- PR_3 = 2.447(2)- 2.453(1)Å



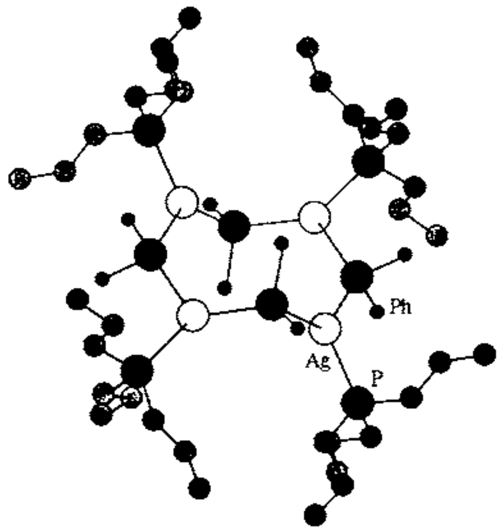
(100)

$Ag_{(2c)}$- PPh_2 = 2.390(2), 2.391(2)Å

$Ag_{(4c)}$- PPh_2 = 2.535(2), 2.548(2)Å

$Ag_{(4c)}$- PR_3 = 2.481(2), 2.506(2)Å

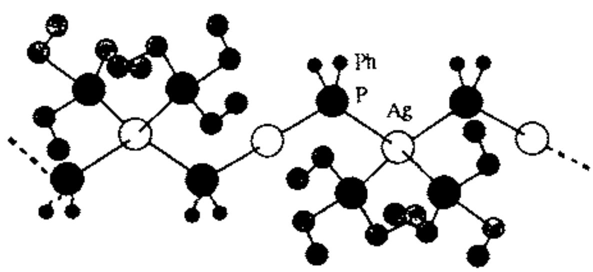
Some trimeric, tetrameric and polymeric complexes containing (μ-PPh_2) bridges have been prepared from the reaction of AgCl and Ph_2PSiMe_3 in the presence of tertiary phosphines whose nature determines the nuclearity and structure of the



(101)

Ag- PPh_2 = 2.436(1)-2.5266(2)Å

Ag- PR_3 = 2.451(2), 2.453(2)Å



(102)

$Ag_{(2c)}$- PPh_2 = 2.398(4), 2.408(4)Å

$Ag_{(4c)}$- PPh_2 = 2.592(5), 2.609(4)Å

$Ag_{(4c)}$- PR_3 = 2.522(6), 2.558(5)Å

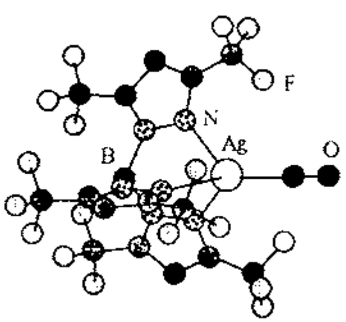
products. The trinuclear $Ag_3(\mu-PPh_2)_3(PBu_2{}^tBu)_3$ (**99**) contains a twisted Ag_3P_3 ring with P–Ag–P angles of 111.30(5)-113.66(4)° and the three-coordinate Ag atoms are in approximately trigonal planar geometries. Three-coordinate Ag atoms make up the tetranuclear $Ag_4(\mu-PPh_2)_4(PPr_3)_4$ (**100**) as well. The P–Ag–P angles within the eight-membered Ag_4P_4 ring range from 115.64(5)° to 122.89(4)°. In the also tetranuclear $Ag_4(\mu-PPh_2)_4(PMePr_2)_4$ (**101**), the eight-membered Ag_4P_4-ring contains alternating two- and four-coordinate (P–Ag–P = 163.12(5)° and 98.02(7)°, respectively) Ag atoms. The one-dimensional $[Ag_2(\mu\text{-}PPh_2)_2(PEt_3)_2]_n$ polymer (**102**) is composed of alternating crystallographically linear and approximately tetrahedral [P–Ag–P = 117.3(1)°] Ag atoms [83].

3.7. Complexes with antimony ligands

The crystal structure of $CeAgSb_2$, prepared by the reaction of Ce, Ag, and Sb in a NaCl/KCl flux, has been reported. In the alternating cerium antimonide and silver antimonide layers, the Ag-atoms are tetrahedrally coordinated by four Sb-atoms with Ag–Sb = 2.866 Å, while the closest Ag···Ag contact is 3.085 Å [84].

3.8. Complexes with carbon ligands

An analysis of the Ag–CO bonding in "non-classical" Ag carbonyls has been carried out on the basis of Fenske–Hall calculations and the results have been compared to those of Zr(IV) carbonyls. The non-classical behaviour of the C–O stretching frequency trends has been attributed to uncompensated CO-to-metal σ-donation due to the very weak metal-to-ligand π-back donation [85]. The Ag–CO bond dissociation energies for $Ag(CO)_x^+$ complexes, $x = 1$–4, has been found by collision-induced dissociation mass spectrometry to be 0.92, 1.13, 0.57, and 0.47 eV, respectively, verifying earlier predictions by ab initio calculations [86].

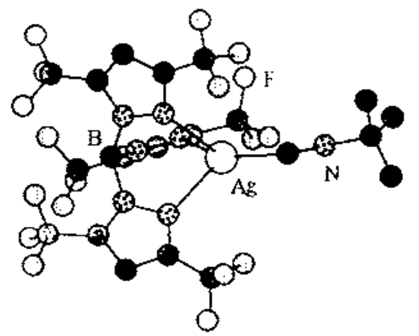


(103)

Ag - C = 2.037(5) Å

C - O = 1.116(7) Å

Ag - C - O = 175.6(6)°



(104)

Ag - C = 2.059(4) Å

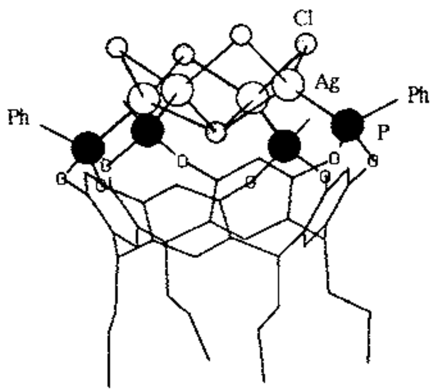
C - N = 1.139(5) Å

Ag - C - N = 173.7(4)°

Addition of CO, or BuNC, to $[HB\{3,5\text{-}(CF_3)_2pz\}]Ag$ has lead to the isolation and characterization of the corresponding adducts, to $[HB\{3,5\text{-}(CF_3)_2pz\}]Ag$–CO (**103**) and to $[HB\{3,5\text{-}(CF_3)_2pz\}]Ag$–CNBu (**104**), respectively. The presence of the strongly electron-withdrawing CF_3 – groups on the ligand is the reason for the short

Ag C bonds and the high IR stretching frequencies: $\nu(CO)=2162$ (in hexane), 2178 cm (solid) and $\nu(CN)=2214\ cm^{-1}$ measured for (**103**) and (**104**) [87].

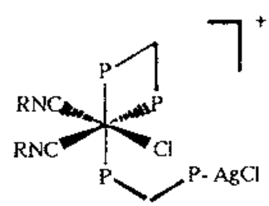
3.9. Complexes with mixed donor-atom ligands



(105)

Ag - (μ-Cl) = 2.56(1) - 2.62(1)Å

Ag - (μ⁴-Cl) = 2.69(1) - 2.76(1)Å



(106)

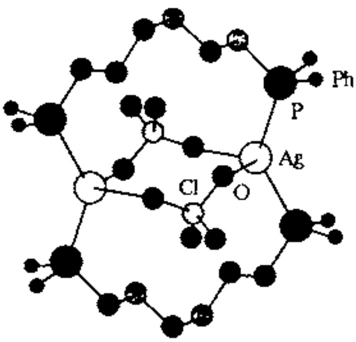
A derivatized calixresorcinarene with a P_4-donor-set, forms a complex containing a $Ag_4(\mu\text{-}Cl)_4$ moiety in a crown configuration which can bind reversibly an additional μ_4-Cl ion placing the Ag atoms in a distorted tetrahedral Cl_3P-coordination (**105**). Extended Hückel calculations have shown that the μ_4-Cl atom is covalently bound to the Ag_4-square. The μ_4-position can be occupied by a variety of ions, but preferential encapsulation of iodine has been observed.

Structural and anion inclusion selectivity comparisons between (**105**) and its Cu_4 homologue have been discussed [88].

Addition of silver, or mercury, salts to a ruthenium complex containing dangling phosphines of monodentate dppm ligands has lead to the isolation of mixed-metal complexes, $[(RNC)_2Cl(dppm)Ru(\mu\text{-}dppm)AgCl]^+$ (**106**); these have been characterized by NMR spectroscopy and showed a value of $^1J(^{31}P-^{107,109}Ag)=683$ Hz [89].

A thorough vibrational study of some copper–halide–PMe_3 complexes along with the $Ag_4I_4(PMe_3)_4$ cubane complex, has allowed the assignment of ν(M X) and ν(M P) bands in the near-IR and Raman spectra. The 81 and 112 cm^{-1} IR bands as well as the 117 cm^{-1} Raman band have been assigned to ν(Ag I), while the Raman bands at 28 and 156 cm^{-1} have been assigned to a cage deformation and a ν(Ag P) stretch, respectively [90].

Five articles have dealt with the chelating versus bridging coordination mode of diphosphine ligands and the anion-receptor properties of their copper and silver

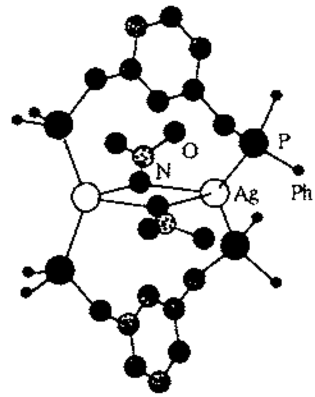


(107)

Ag - P = 2.416(2), 2.419(2) Å

Ag - O = 2.639(4), 2.712(6) Å

P - Ag - P = 134.33(5)°



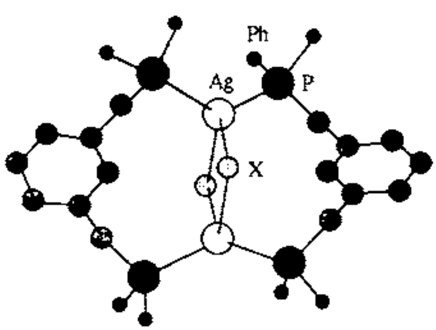
(108)

Ag - P = 2.439(6) - 2.454(6) Å

Ag - O = 2.44(2) - 2.69(2) Å

P - Ag - P = 134.2(2), 138.0(2)°

Ag . . . Ag = 4.175(2) Å



(109) X = Cl

Ag - P = 2.470(6) - 2.510(7) Å

Ag - Cl = 2.671(5) - 2.758(7) Å

P - Ag - P = 126.2(2), 129.5(2)°

Ag . . . Ag = 3.753(3) Å

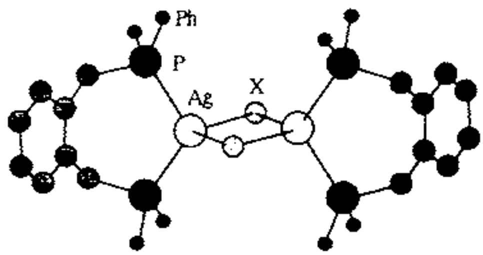
(110) X = I

Ag - P = 2.496(6) - 2.511(6) Å

Ag - I = 2.879(2) - 2.916(2) Å

P - Ag - P = 115.5(2), 117.0(2)°

Ag . . . Ag = 3.295(2) Å



(111) X = Cl

Ag - P = 2.446(1), 2.450(2) Å

Ag - Cl = 2.576(2), 2.627(2) Å

P - Ag - P = 111.83(6)°

Ag . . . Ag = 3.238(1) Å

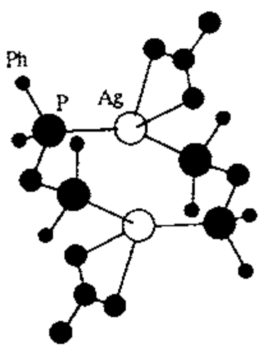
(112) X = I

Ag - P = 2.487(1), 2.493(2) Å

Ag - I = 2.824(1), 2.892(1) Å

P - Ag - P = 109.84(6)°

Ag . . . Ag = 3.218(1) Å



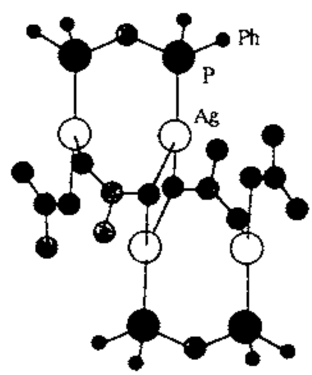
(113)

Ag - P = 2.437(3), 2.473(3) Å

Ag - O = 2.547(7), 2.611(3) Å

P - Ag - P = 146.1(1)°

O - Ag - O = 50.4(2)°

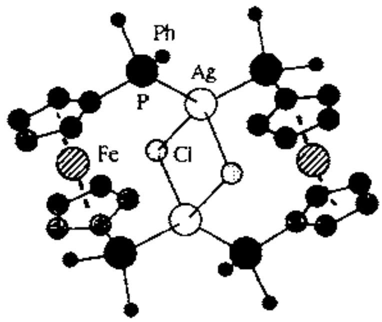


(114)

Ag - P = 2.363(4), 2.390(4) Å

Ag - O = 2.23(1) - 2.48(1) Å

complexes. In the dimeric complex $[Ag\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}(ClO_4)]_2$ (**107**) the bridging eight-atom diphosphine ligands hold the metal atoms at a Ag · · · Ag distance of 5.318(2) Å which is sufficiently wide to accommodate two didentate μ-ClO_4 ions [91]. Similarly, a seven-atom diphosphine bridge separates the two Ag atoms of $[Ag\{\mu\text{-}Ph_2PCH_2(m\text{-}C_6H_4)CH_2PPh_2\}(NO_3)]_2$ (**108**) by a distance of 4.175(2) Å, bridged by two monodentate nitrates. When Cl or I atoms take the place of the nitrates, (**109**) and (**110**), the silver atoms are pulled closer together at distances

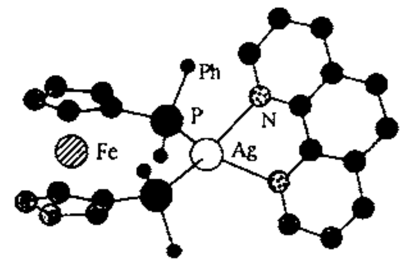


(115)

Ag - P = 2.461(1), 2.474(1) Å

Ag - Cl = 2.667(2), 2.677(2) Å

P - Ag - P = 129.93(4)°



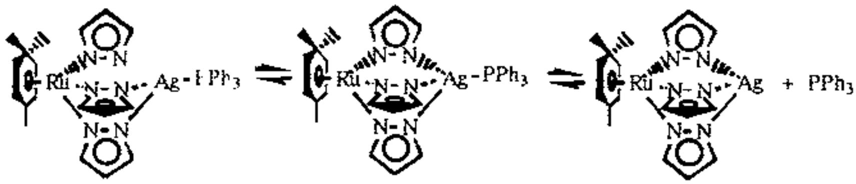
(116)

Ag- P = 2.411(1), 2.407(1) Å

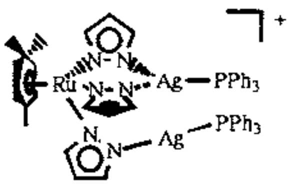
Ag- N = 2.343(3), 2.361(3) Å

of 3.753(3) and 3.295(2) Å, respectively. A related, but shorter, six-atom diphosphine ligand, chelates to silver in the also dimeric complexes $[\{Ph_2PCH_2(o\text{-}C_6H_4)CH_2PPh_2\}Ag(\mu\text{-}X)]_2$, X = Cl or I, (**111**) and (**112**), where the two silver phosphine moieties are held together by the μ-X groups and the Ag-atoms approach to 3.238(1) and 3.218(1) Å, respectively [92]. One dinuclear and one tetranuclear silver dppm-acetate complexes have been reported, their nuclearity depending on the Ag:dppm ratio of the reaction mixture. The dinuclear $[Ag(\mu\text{-dppm})(AcO)]_2$ (**113**) which formed in a 1:1 mixture, or in the presence of excess dppm, contains four-coordinate Ag-atoms with weakly chelating acetates. From a 2:1 mixture, on the other hand, the tetranuclear complex $[Ag_2(\mu\text{-dppm})(\mu\text{-AcO})_2]_2$ (**114**) with two monodentate and two didentate μ-AcO groups, was isolated. Upon addition of dppm, (**114**) was converted to (**113**) [93]. The characterization of a silver complex of the metalloligand dppf in the bridging coordination mode has been reported. Complex $[Ag(\mu\text{-dppf})(\mu\text{-Cl})]_2$ (**115**) bears some structural similarity to (**111**), but with approximately trigonal planar Ag atoms at a Ag··· Ag distance of 4.073 Å bridged by two weakly bound chlorides [94]. The chelating mode of dppf coordination has been encountered in the mononuclear Ag(dppf)(phen) complex (**116**), prepared from the reaction of $Ag(dppf)(ClO_4)$ and phen, and containing a four-coordinate Ag centre in a distorted tetrahedral geometry (see also Section 3.6) [81].

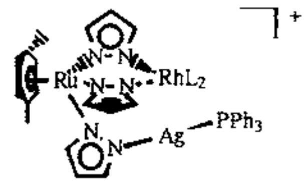
Heterodimetallic and heterotrimetallic complexes can be prepared with the metalloligand anion $[(\eta^6\text{-}p\text{-cumene})Ru(pz)_3]^-$ which chelates to metals in a similar fashion to trispyrazolylborates. The Ru/Ag complex (**117**) contains one dangling pyrazolate arm which can be used towards further coordination to form the Ru/Ag_2 and Ru/Ag/Rh complexes (**118**) and (**119**). Variable temperature ^{31}P NMR spectroscopic observations have been accounted for by Ag-whizzing around the three pyrazolate



(117)

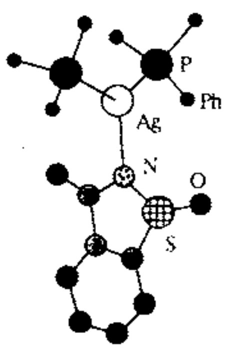


(118)



(119)

N-atoms of (**117**) and a dissociation equilibrium of the phosphine, while in (**118**) both Ag-atoms appear to be whizzing, exchanging their two- and three coordinate positions. Similar behaviour has been recorded for the corresponding Cu and Au complexes [95].



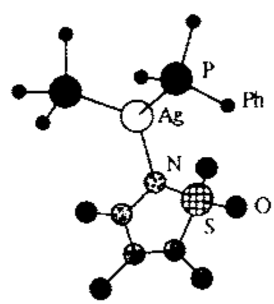
(120)

Ag - P = 2.432(3) - 2.454(3) Å

Ag - N = 2.270(8), 2.285(8) Å

P- Ag - P = 129.72(9), 131.24(9)°

P - Ag - N = 113.9(2) - 114.7(2)°



(121)

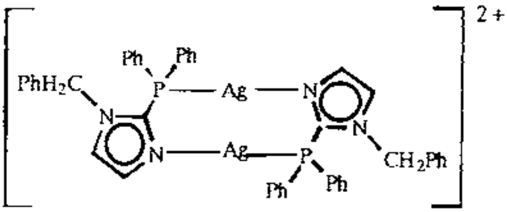
Ag - P = 2.434(2), 2.468(2) Å

Ag - N = 2.259(7) Å

P - Ag - P = 125.97(8)°

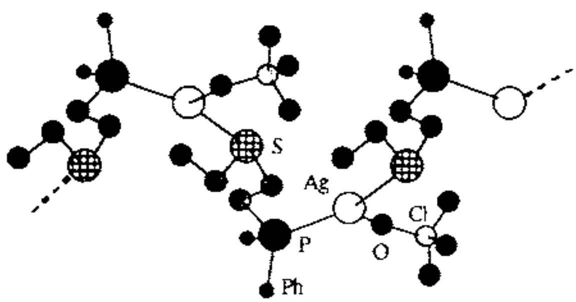
P - Ag - N = 111.4(2), 121.5(2)°

The crystal structures of two bis(phosphine)silver complexes of an isothiazolone and a benzisothiazolone, (**120**) and (**121**), containing trigonal-planar Ag-atoms in P_2N-coordination, have been described [96].



(122)

Three coordination modes have been encountered in the chemistry of two *P,N*-donor ligands with different P–N bites. The ^{1}H and ^{31}P NMR spectroscopic study of dimeric $[M_2(\mu\text{-BzIm})_2]^{2+}$ (M = Ag, Au) has shown that both complexes consist of a single isomer, but, while the gold complex is static in solution, that of silver (**122**) is fluxional with its two conformations frozen at 253 K and distinguished by their different P/Ag coupling constants: $^{1}J(^{31}P-^{107}Ag) = 464$ and 643 Hz [97]. The larger, potentially didentate ligand $Ph_2P\text{-}CH_2CH_2\text{-}(2py)$ forms a two-coordinate P-bound, $[AuL_2]^+$ complex, but four-coordinate $[ML_2]^+$ chelates for M = Cu, Ag. ^{1}H, ^{13}C and ^{31}P NMR spectroscopic studies have shown that the Δ and Λ enantiomeric forms of the Cu and Ag complexes are in a dynamic equilibrium involving the cleavage/formation of M–N bonds, while in the presence of excess L, the Ag-complex forms three- and four-coordinate P-bound $[AgL_3]^+$ and $[AgL_4]^+$ complexes with dangling pyridine tails [98].



(123)

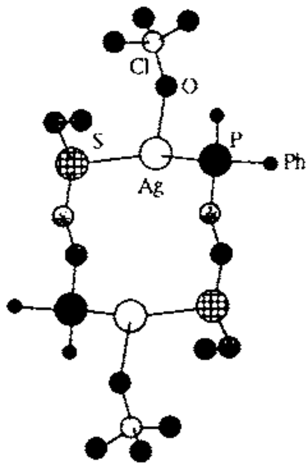
Ag - P = 2.39(1) Å

Ag - S = 2.43(1) Å

Ag - O = 2.51(3) Å

P - Ag - S = 154.5(4)°

The $[AgL_n]^+$ complex formation for $L = Ph_2PCH_2SPh$, $Ph_2P(CH_2)_2SR$ (R = Me, Et, Ph) has been studied in propylene carbonate. Potentiometric and calorimetric determination of the thermodynamic quantities of these reactions, corroborated by ^{31}P NMR spectroscopic data, have indicated that while Ph_2PCH_2SPh behaves as a monodentate *P*-donor, the larger $Ph_2P(CH_2)_2SR$ ligands are *P,S*-donor chelates in their $[AgL]^+$ and $[AgL_2]^+$ complexes, but, they too, become monodentate *P*-donors in $[AgL_3]^+$. Dinuclear $[Ag_2L]^{2+}$ complexes with $\mu\text{-}Ph_2P(CH_2)_2SR$ ligands have also been identified. The crystal structure of $[Ag_2\{\mu\text{-}Ph_2P(CH_2)_2SEt\}_2](ClO_4)_2$ consists of co-crystallized open-chain polymeric (**123**) and dimeric (**124**) forms of this complex, with Ag-atoms in a planar three-coordinate PSO-environment, taking into account the coordinated ClO_4-counter-ions [99].



(124)

Ag - P = 2.37(1) Å

Ag - S = 2.48(1) Å

Ag - O = 2.59(3) Å

P - Ag - S = 139.9(5)°

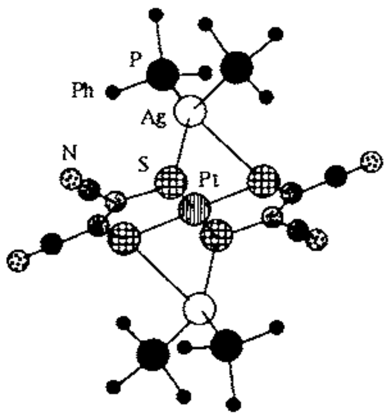
(125)

The [AgL](BF_4) complex of the open-chain P_2S_2-ligand (**125**) has been studied by MS, and IR and NMR spectroscopies. At 300 K, the ^{31}P and ^{109}Ag NMR spectra suggest a static behaviour of the phosphines, but fast exchange of the thioether atoms, which is frozen at 220 K; $^1J(^{31}P-^{107}Ag)=445$ Hz, $^1J(^{31}P-^{109}Ag)=510$ Hz. An X-ray study of the corresponding [CuL](PF_6) complex has confirmed its monomeric nature [100].

Some mixed Ag/M complexes (M = Ni, Pd, Pt) have been prepared by complexation of two $[Ag(PR_3)_2]^+$ fragments between two chelated mnt-ligands (mnt = maleonitriledithiolate) of the $[M(mnt)_2]^{2-}$ anions placing the Ag-atoms in a distorted tetrahedral P_2S_2-environment. While the Ag–M distances in (**126**), (**127**) and (**128**), which are shorter than the sum of the van der Waals radii imply a bonding interaction, the UV spectra and cyclic voltammograms of the Ag/M-complexes are indistinguishable from those of $[M(mnt)_2]^{2-}$ and the ^{31}P and ^{195}Pt NMR spectra do not support the presence of a Ag–M bond [101].

The hexanuclear $Ag_4W_2S_8(AsPh_3)_4$ complex (**129**), containing a $Ag_4W_2S_6$ prismane core, has been characterized and studied with regard to its NLO properties. The silver atoms, which are in a tetrahedral S_3As environment, have binding energies of 368.60 ($3d_{5/2}$) and 374.70 eV ($3d_{3/2}$), determined by XPS. Cyclic voltammetric scans of (**129**) revealed a reversible couple at −0.09 V along with two more irreversible processes. The optical properties of (**129**) have been studied with a 7 ns pulsed laser at 532 nm showing a third-order NLO susceptibility of 1.7×10^{-10} esu [102].

In order to investigate the ligation mode of the reported binding of formates to the surfaces of copper and silver catalysts, the solid-state structure, IR, and CP-MAS ^{13}C and ^{31}P NMR spectra of $(Ph_3P)_2AgO_2CH$ (**130**) and

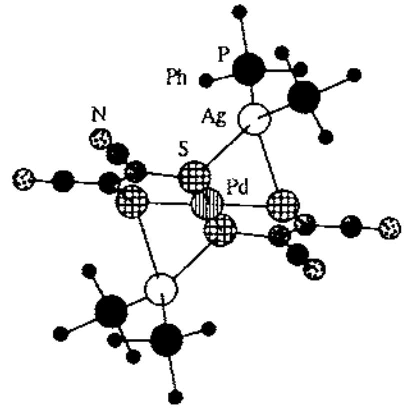


(126)

Ag - P = 2.443(3), 2.509(3) Å

Ag - S = 2.728(3), 3.093(3) Å

Ag . . . Pt = 2.996(1) Å

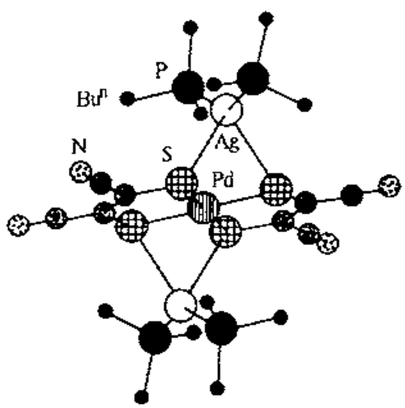


(127)

Ag - P = 2.457(2), 2.500(1) Å

Ag - S = 2.798(2), 2.861(2) Å

Ag . . . Pd = 3.030(1) Å

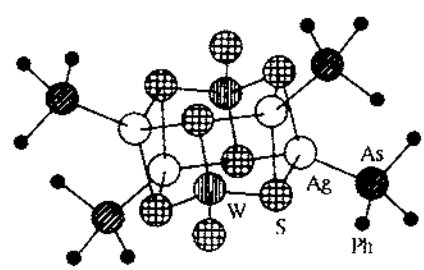


(128)

Ag - P = 2.418(1), 2.444(1) Å

Ag - S = 2.824(1), 3.083(1) Å

Ag - Pd = 3.0421(4) Å



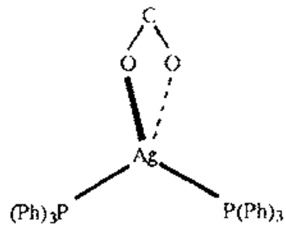
(129)

Ag - S = 2.519(3) - 2.691(3) Å

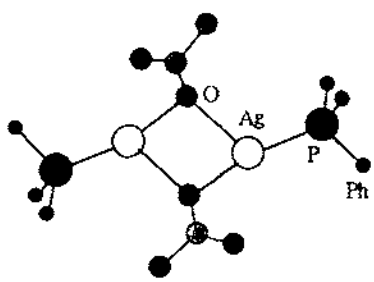
Ag - As = 2.511(2), 2.533(2) Å

Ag - W = 2.979(1), 3.008(1) Å

$(Ph_3P)_2AgO_2CH_2HCO_2H$ (**131**) have been studied. The hydrogen bonded network and long Ag···O interactions brought about by the interstitial formic acid molecules, cause a significant widening of the P–Ag–P angle of (**131**), manifested in the



	(130)	(131)
Ag - P =	2.4261(7) Å	2.426(2) Å
Ag - O =	2.425(3) Å	2.550(7), 2.713(8) Å
P - Ag - P =	127.37(3)°	147.86(7)°
O - Ag - O =	52.4(1)°	49.5(2)°



(132)

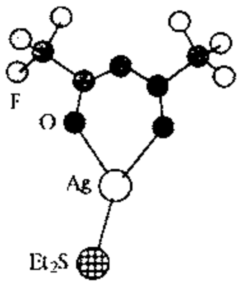
Ag - P = 2.341(3), 2.346(3) Å

Ag - O = 2.190(8), 2.69(1)

2.210(9), 2.570(9) Å

P/Ag coupling constants $^1J(P\text{-}Ag) = 432, 517$ Hz for (**130**) and (**131**), respectively [103]. The crystal structure of related dimeric $[(Ph_3P)Ag(OAc)]_2$ (**132**) containing three-coordinate Ag-atoms has been reported [104].

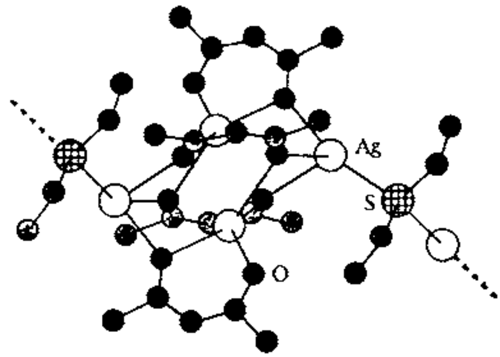
Searching for suitable reagents and optimum compositions for aerosol-assisted CVD of Ag/Pd films, the reaction between $Ag(hfac)(SEt_2)$ (**133**) and $Pd(hfac)_2(SEt_2)$ has been investigated. The stability of $Pd(hfac)_2(SEt_2)$ appears to be the driving force of the reaction whose other product is $[Ag(hfac)]_4(SEt_2)$ (**134**). Solution NMR spectroscopic experiments indicate that (**134**) is monomeric with equivalent hfac ligands, contrary to the solid-state structure which shows a one-dimensional polymer with the Ag-atoms in an unusual distorted square pyramidal O_4S-environment. Also unusual, is the ligation of hfac, with half the hfac anions in



(133)

Ag - O = 2.33(2) Å

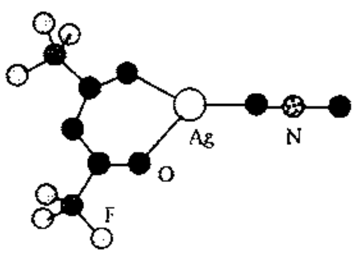
Ag - S = 2.47(9) Å



(134)

Ag - O = 2.251(7) - 2.596(9) Å

Ag - S = 2.441(2) Å

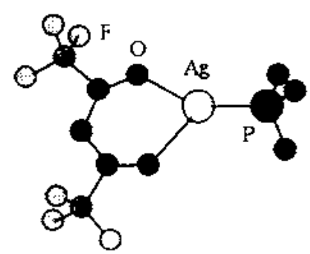


(135)

Ag - O = 2.250(6), 2.309(6) Å

Ag - C = 2.043(9) Å

O - Ag - C = 127.5(3), 151.5(3)°

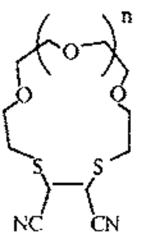


(136)

Ag - P = 2.311(3) - 2.326(4) Å

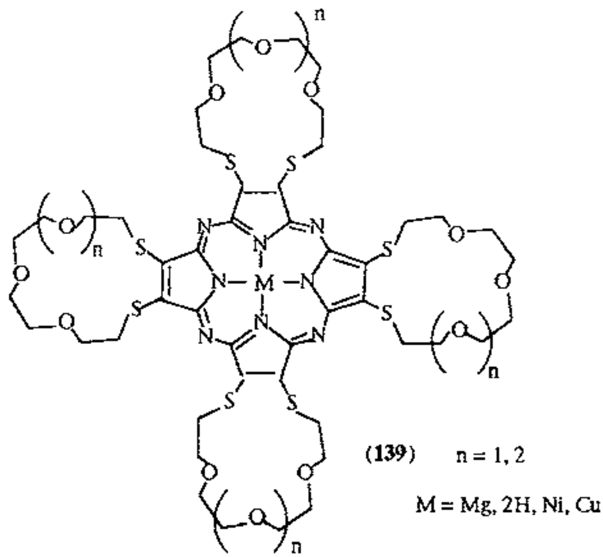
Ag - O = 2.268(8) - 2.309(8) Å

a μ^4-η^2,η^2- and half in a μ-η,η^2-mode. The parent complex Ag(hfac)(SEt_2) (**133**) has the expected three-coordinate silver structure [105]. Following up a lead that isonitrile complexes of copper, gold and platinum showed good CVD of the corresponding metal films, the (hfac)M(CNMe), M = Cu, Ag, complexes have been prepared and studied. The mononuclear silver complex (**135**) containing an isonitrile and an asymmetrically chelated hfac, has a ν(C–N) IR stretch at 2231 cm^{-1} (higher than the free ligand) even though no C/Ag coupling has been observed in ^{13}C NMR spectrum. Complex (**135**) is volatile [sublimes at 363 K (10^{-3} Torr)] and in the presence of hydrogen deposits silver films, without detectable impurities, at 523 K [106]. Monomeric in solution and in the solid state, as evident by the crystal structure of (hfac)$AgPMe_3$ (**136**) are also the related complexes (hfac)$AgPR_3$ and (fod)$AgPR_3$ (R = Me, Et; fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato) which can be sublimed without decomposition (tested by TGA) and leave quantitatively a silver residue upon thermolysis at 413–453 K. Under H_2, pure silver films have been deposited by CVD from these precursors. The low-melting complexes (hfac)$AgPEt_3$ and (fod)$AgPEt_3$ are the first liquid precursors for CVD of silver [107].



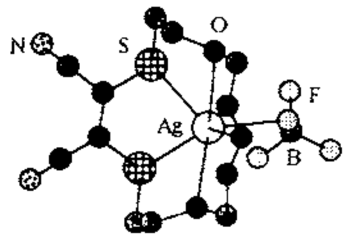
(137) n = 1

(138) n = 2



(139) n = 1, 2

M = Mg, 2H, Ni, Cu

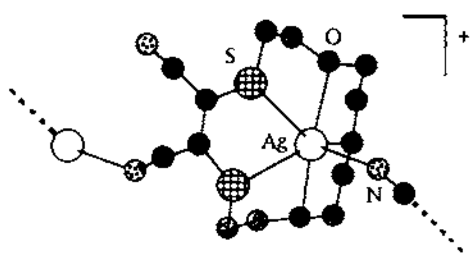


(140)

Ag - S = 2.718(2), 2.732(2) Å

Ag - O = 2.399(5), 2.579(6), 2.705(6) Å

Ag - F = 2.456(1) Å



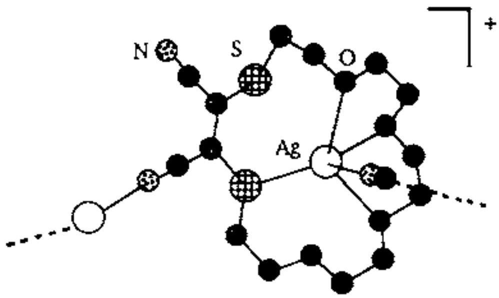
(141)

Ag - S = 2.683(2), 2.711(2) Å

Ag - O = 2.516(7), 2.682(7), 2.802(6) Å

Ag - N = 2.276(6) Å

An improved synthesis of the mixed-O/S crown ether (**137**) and (**138**) has been followed by its cyclization to yield the substituted tetraazaporphyrin (**139**). All the complexes (**137**)–(**139**) are efficient towards silver encapsulation. The Ag–(**137**) complex is encountered in two forms; one in which the Ag atom is coordinated by the S_2O_3-set of the macrocycle, in an approximately square-pyramidal geometry.

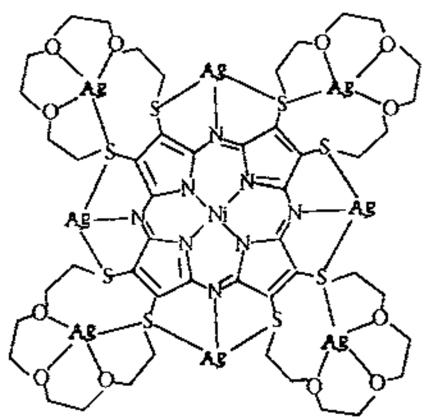


(142)

Ag - S = 2.533(3) Å

Ag - O = 2.50(1) - 2.86(1) Å

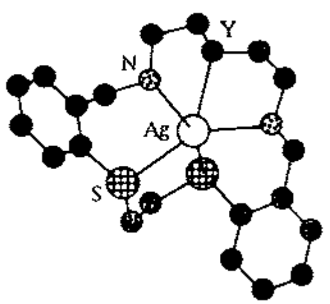
Ag - N = 2.31(1) Å



(143)

crown ether	meso - pocket
Ag - S = 2.50(1) - 2.60(1) Å	Ag - S = 2.65(1) - 2.88(1) Å
Ag - O = 2.39(3) - 2.69(3) Å	Ag - N = 2.37(3) - 2.43(3) Å

with a $[BF4]^-$ anion occupying the axial site *trans* to a S-atom (**140**), and one in which a nitrile group of the adjacent crown ether occupies the axial site forming a polymer (**141**). A similar polymeric structure has been determined for the Ag–(**138**) complex (**142**) where the Ag atoms are bound to the SO_4-set of the crown ether (one S atom remains uncoordinated) and the links between units are provided by additional coordination of peripheral nitriles to Ag atoms of the adjacent unit. In MeOH solution, the polymeric structure of (**141**) and (**142**) is disrupted and the macrocycles are symmetrically coordinated to the metal, as evident by ^{13}C NMR spectroscopy, while in MeCN the solvent scavenges Ag from the macrocycle [108]. Spectroscopic studies have indicated that in $CHCl_3$/MeOH solution of >10:1 $AgBF_4$: (**139**), M = Ni, the crown ether groups bind four Ag-atoms in an endocyclic fashion. However, the X-ray analysis (**143**) has revealed that four more Ag-atoms are bound in the *meso*-pockets in the solid state, utilizing two exodentate S-atoms of the crown ether groups along with the *meso* N-atoms of the porphyrazin in only the second example of *meso*-pocket coordination [109].



(**144**) Y = O

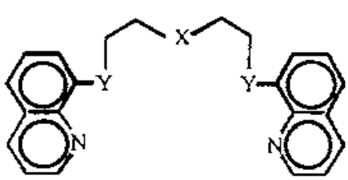
(**145**) Y = N

(**146**) Y = S

Ag - S = 2.652(3) - 2.713(2) Å

Ag - O = 2.631(4) Å

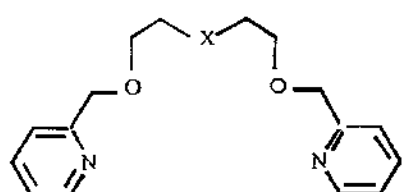
Ag - N = 2.353(4) - 2.552(6) Å



(**147**)

Y = O, S

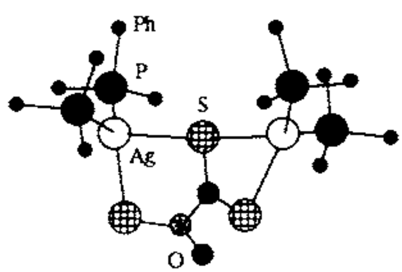
X = O, NPh, CH_2



(**148**)

X = O, NPh, CH_2

Silver recovery continues to be an active area of research. The development of macrocyclic hosts which discriminate between silver and lead has been the focus of five articles, while three more articles have dealt with acyclic polyether complexing agents. In an effort to improve the understanding of the factors which influence this discrimination, twenty 17-, 18-, and 19-membered macrocyclic ligands containing five S/N/O heteroatoms have been examined with regard to the stability of their respective silver and lead complexes. Three Ag-complexes (**144**), (**145**) and (**146**) of the macrocycles with the higher Ag-over-Pb selectivity have been studied crystallographically revealing that all five heteroatoms are bound to the Ag-atoms in the solid state. The corresponding Pb-complexes require additional coordination by two perchlorate counter-ions [110]. An improved one-step template method for the synthesis of diaza-crown ethers has been reported and the thermodynamic stability constants for two of their Ag-complexes have been determined: log$K$ = 5.26, 7.8 for the 4,10-diaza-18-crown-6 and 4,13-diaza-18-crown-6, respectively [111]. The Ag-cation transport, in a CH_2Cl_2 liquid membrane system, by some bis(monoaza-crown-15); lend bis(monoaza-crown-18) systems has been studied and transport rates of 0.1–4.3×10^{6} mol h^{-1} have been measured [112]. Some 12-, 15- and 18-membered azacrown ethers have been functionalized by a high-pressure reaction in which heteroaromatic groups are attached to the azacrown N-atom. The resultant lariat ethers showed good Ag-extraction selectivities attributed to cooperation of the endocyclic coordination sites with the newly introduced side arms [113]. Two 18-crown-6 O_4N_2- and O_5N-macrocycles, containing a triazole or phenol functions in the macrocycle and pyridine side arms, have also shown selectivity towards the binding of Ag^+ over alkali metal cations [114]. Nine acyclic polyethers, (**147**) and (**148**), have been prepared and studied with regard to their metal extraction efficiency. All showed preferential extraction of the soft cations, Cu^+, Ag^+, and Hg^{2+}, while Ag extractability was enhanced by addition of picrates [115]. Eight more polyether molecules of the general formula R-$ECH_2ECH_2ECH_2ECH_2E$-R, R = Ph, $PhCH_2$, E = O/S, have been examined with regard to their silver-complexing ability and selectivity by potentiometric methods. Complexation enthalpies in the range of -0.50 to -91.75 kJ mol^{-1} have been calculated with the less favourable value corresponding to the all-oxygen polyether and increasing with the number of thioether S-atoms [116]. Spectrophotometric determination of stability constants for complexes of several metal cations with hydrazone derivatives of cyclic and acyclic dithiamonoaza, tetrathiaza, and tetrathiamonoaza polyethers showed a high silver selectivity of the latter [117].



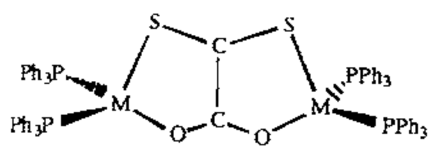
(**149**)

Ag - (μ - S) = 2.680(2), 2.725(2) Å

Ag - S(end- on) = 2.645(3) Å

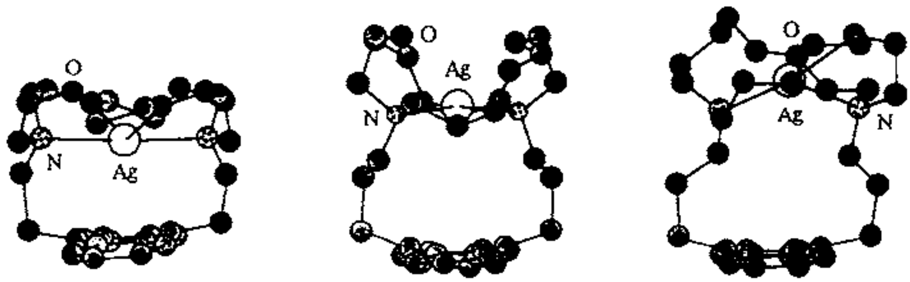
Ag - S(side - on) = 2.545(3) Å

Ag - P = 2.447(3) - 2.516(2) Å



(**150**) M = Cu, Ag

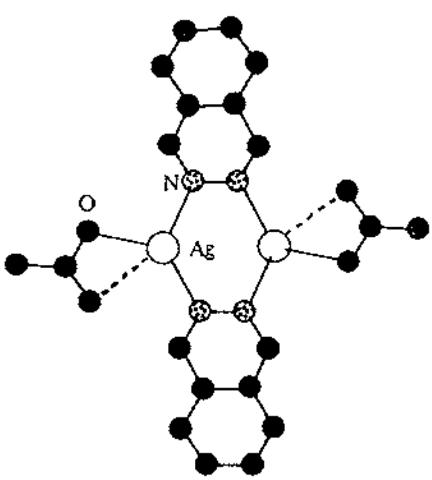
The structures of three Ag and Cu complexes of trto (trithiooxalte) and i-dto (1,1-dithiooxalate) have been determined in order to probe the preferences of these ligands with regard to the end-on or side-on ligation modes. In $\{(Ph_3P)_2Ag\}_2(\mu$-trto) (**149**) both side-on five-membered [S–Ag–S = 81.82(9)°] and end-on four-membered [S–Ag–S = 66.87(8)°] chelate rings, utilizing only the *S*-donor sites, have been found. Symmetrical coordination of the metal atoms to two side-on, *S,O*-donor sites was preferred in the isostructural Cu and Ag complexes $\{(Ph_3P)_2M\}_2([\mu$-i-dto) (**150**) [118].



(**151**) (**152**) (**153**)

The coordination of Ag^+ in the N_2O_4-18-crown-6 moiety of 9, 10-anthraceno[2.2.2]cryptands modulates the light emission properties of the anthracene ring. Two systems, with two- or three-atom links between the anthracene and 18-crown-6 parts, have been studied. The first one, (**151**), with Ag-anthracene distance of 3.01 Å, shows no fluorescence, while the second one. (**152**) and (**153**) (two conformations), with a distance of 4.46 or 5.14 Å, emits a two-component spectrum with peaks at 455 and 490 nm [119].

Some LAgF and L_2AgF complexes, where L = *O*-, or *N*-donor ligands, have been prepared, characterized by elemental analysis, conductivity measurements and IR spectroscopy, while their thermal stability has been studied thermogravimetrically [120].



(**154**)

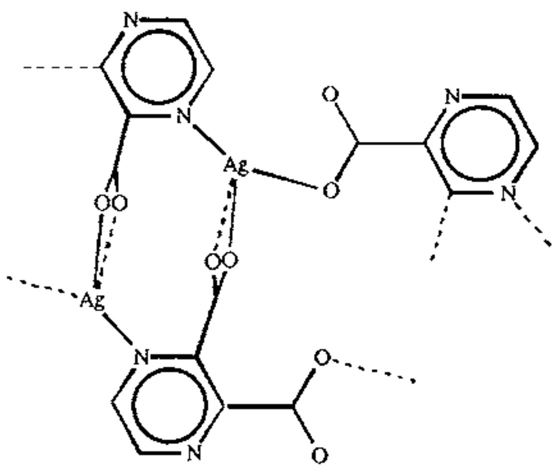
Ag - N = 2.25(1), 2.30(1) Å

Ag - O = 2.37(1) Å

Ag . . . Ag = 3.392(2) Å

N - Ag - N = 126.9(4)°

The crystal structure of polymeric $\{[Ag(\mu\text{-phz})(OAc)\}_2]_n$ (**154**), has been reported (phz = phthalazine). It consists of dimeric silver-phthalazine six-membered rings linked by Ag··· O interactions of 2.63(1) Å with the dangling acetate O-atom



(155)

Ag - O = 2.333(6), 2.376(5) Å

Ag - N = 2.249(6) Å

[121]. One more polymer has been characterized in the structure of silver pyrazine-2,3-dicarboxylate (**155**) containing three-coordinate Ag-atoms [17].

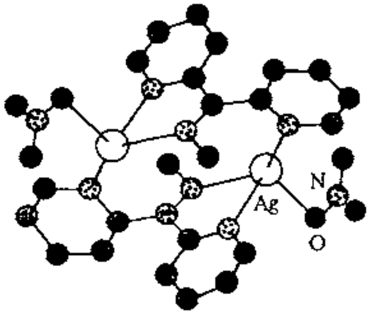
The crystal structure of $[AgL(NO_3)]_2$ (**156**) represents the first report of metal complex of the di-2-pyridyl ketone oxime ligand. Complex (**156**) contains Ag-atoms in a distorted tetrahedral N_3O-environment, including a coordinated monodentate nitrate ion [122].

Trans-1,2-dimethyldiaziridine forms a polymeric $[LAg(NO_3)]_n$ complex (**157**), where alternating diaziridines of opposite configuration provide the links between Ag-atoms which are in a distorted tetrahedral N_2O_2-environment with asymmetrically chelating nitrates [123].

The isostructural anions $[Ag_2Te(TeS_3)_2]^{2-}$ (**158**) and $[Ag_2Te(TeSe_3)_2]^{2-}$ (**159**) have been prepared from the reactions of silver salts with K_2Te and S, or K_2Se_3 and Te. They consist of Ag_2Te triangles capped on both sides by the heterochalcogenide anions $(TeS_3)^{2-}$ or $(TeSe_3)^{2-}$. The Ag-atoms are three-coordinate in a TeS_2- or $TeSe_2$-environment, respectively [124].

4. Complexes with silver–metal bonds

Surveying the reaction chemistry of anionic $[cis\text{-}Rh(C_6F_5)_2L_2]$ complexes, a heterodimetallic Ag/Rh compound has been prepared from the reaction with $(Ph_3P)Ag(ClO_4)$. For $L = P(OPh)_3$, the air, light, and thermally unstable $cis\text{-}((PhO)_3P)_2(C_6F_5)_2RhAg(PPh_3)$ (**160**) has been isolated and characterized by



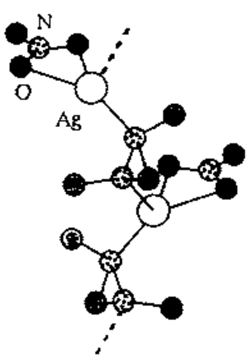
(156)

Ag - N = 2.282(4) - 2.396(5) Å

Ag - O = 2.459(5) Å

N - Ag - N = 68.4(1), 99.9(1), 131.8(2)°

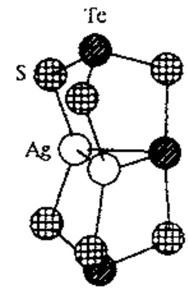
N - Ag - O = 97.7(2), 104.7(1), 123.4(2)°



(157)

Ag - N = 2.30(2), 2.34(2) Å

Ag - O = 2.50(2), 2.59(2) Å



(158)

Ag - Te = 2.788(3), 2.803(4) Å

Ag - S = 2.412(8) - 2.474(9) Å

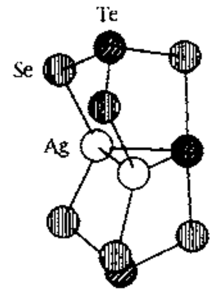
S - Ag - S = 141.0(3), 146.2(3)°

S - Ag - Te = 106.4(2) - 108.5(2)°

solution ^1H, ^{19}F and ^{31}P NMR ($^1J(^{31}P-^{109}Ag)=663$ Hz, $^1J(^{31}P-^{107}Ag)=574$ Hz) as well as crystallographically. Complex (**160**) contains an unsupported Rh–Ag (donor–acceptor) bond with a two-coordinate silver and distorted squarepyramidal Rh-atom. Similar reactions for L = CO, cod, resulted in mononuclear products [125].

The synthesis and structural characterization of a Ag–Hg bonded trinuclear complex $[AgHg_2(dppm)_3]^{3+}$ (**161**) has been reported. In the presence of elemental mercury, a 1:1:3 mixture of $Hg(O_3SCF_3)_2$, $Ag(O_3SCF_3)$ and dppm in CH_2Cl_2 gave the subvalent complex (**161**) in almost quantitative yield [126].

Some tetranuclear Ag_4, Cu_4, and Ag_2Cu_2 isostructural "butterfly" complexes, supported by μ-mercaptothiazoline ligands, have been prepared from the corresponding $[M_4L_4]_n$ polymers by stoichiometric addition of phosphine, arsine, or pyridine. The solid-state structures of the Ag_4- and Ag_2Cu_2-complexes, (**162**) and (**163**), respectively, showed the "wing tip" Ag-atoms in a PS_2N-environment, while the



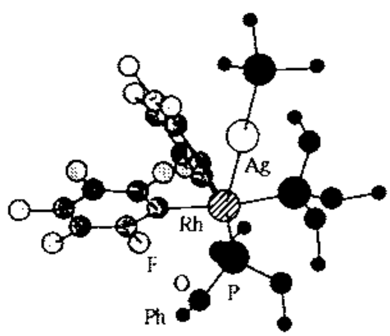
(159)

Ag - Te = 2.742(3), 2.745(3) Å

Ag - Se = 2.538(3) - 2.565(3) Å

Se - Ag - Se = 129.3(1), 132.3(1)°

Se - Ag - Te = 112.74(9) - 114.0(1)°

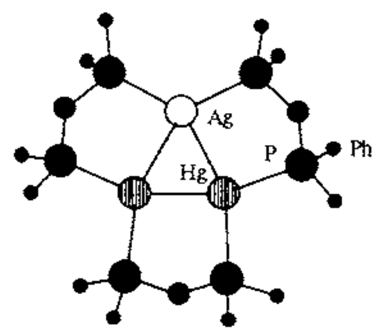


(160)

Ag - Rh = 2.635(1) Å

Ag - P = 2.368(3) Å

P - Ag - Rh = 172.41(8)°



(161)

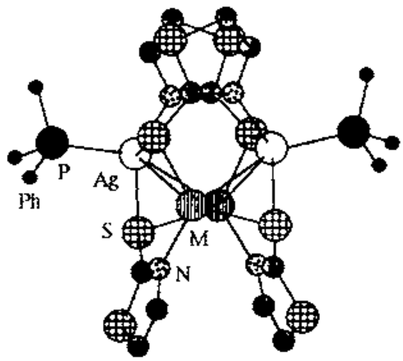
Ag- P = 2.470 (6), 2.487(6) Å

Ag- Hg = 2.805(2), 2.853 (2) Å

central Ag-atoms of (**163**) has a S_2N-coordination, both in addition to central-"wing tip" metal–metal contacts [127].

5. Silver-containing clusters

As part of a series of articles devoted to the study of Ag/Fe-clusters, the diamagnetic $[Ag_{13}\{Fe(CO)_4\}_8]^{3-}$ (**164**) has been prepared by controlled oxidation of



(162) M = Ag

Ag - P = 2.523(3) Å

Ag - N = 2.287(9) Å

Ag - S = 2.433(3) - 2.728(3) Å

Ag - Ag = 3.083(1) - 3.110(1) Å

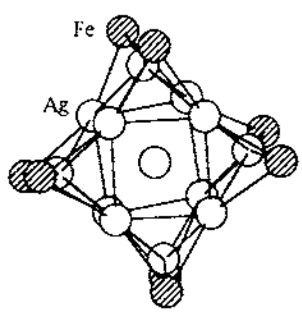
(163) M = Cu

Ag - P = 2.440(2) Å

Ag - N = 2.242(5) Å

Ag - S = 2.571(2), 2.577(2) Å

Ag - Cu = 2.948(1) Å



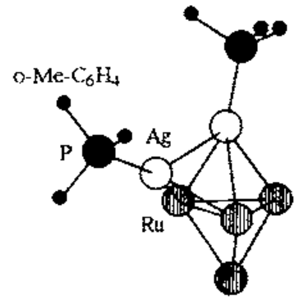
(164)

Ag - Ag = 2.842(1) - 3.046(1) Å

Ag - Fe = 2.679(2) - 2.755(2) Å

$[Fe(CO)_4]^{2-}$ by Ag^+ and characterized crystallographically; it consists of a centred Ag_{13}-cuboctahedron with the triangular faces capped by Fe-atoms. A reversible one-electron reduction to paramagnetic $[Ag_{13}\{Fe(CO)_4\}_8]^{5-}$, as well as a further irreversible reduction to $[Ag_{13}\{Fe(CO)_4\}_8]^{5-}$, have been identified by cyclic voltammetry at −0.37 and −0.65 V (versus SCE), respectively [128].

The Ru/Ag-clusters $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(o\text{-}Me\text{-}C_6H_4)_3\}_2]$ and $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(\mu\text{-}dppf)_2]$ have been prepared by addition of silver salts and

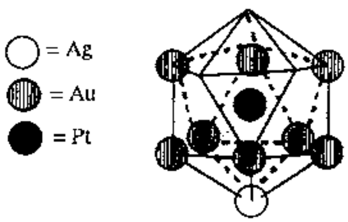


(165)

Ag - Ru = 2.862(2) - 3.045(2) Å

Ag - Ag = 2.867(2) Å

Ag - P = 2.466(5), 2.494(5) Å

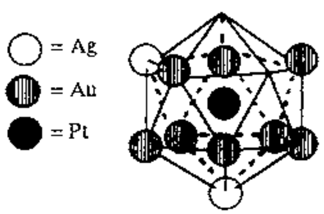


(166)

Ag - Pt = 2.703(3) Å

Ag - Au = 2.773(7) - 3.106(6) Å

Ag - O_3N = 2.47(5), 2.52(4) Å



(167)

Ag - Pt = 2.784(7), 2.810(7) Å

Ag - Au = 2.784(7) - 3.390(8) Å

Ag - O_3N = 2.18(10) - 2.72(4) Å

the appropriate phosphine ligand to $[Ru_4(\mu\text{-H})_2(CO)_{12}]^{2-}$. The solid-state structure of the former, (**165**), has been determined showing a trigonal-bipyramidal Ru_4Ag-core with the second Ag-atom capping one of the three Ru_2Ag-faces, while the μ_3-hydrides cap the remaining two Ru_2Ag-faces. In solution, the two Ag-atoms are involved in an intramolecular exchange for which a free energy of activation of 40 ± 1 kJ mol^{-1} has been calculated for $[Ag_2Ru_4(\mu_3\text{-H})_2(CO)_{12}(\mu\text{-dppf})_2]$ from variable temperature ^{31}P NMR spectroscopic data. The phosphines have also shown dynamic behaviour with the $P(o\text{-Me-}C_6H_4)_3$ ligands exchanging intermolecularly, while the dppf ligand undergoes configuration inversion at the P-atoms. Similar structural and dynamic behaviour results have been obtained for analogous Ru/Cu and Ru/Au clusters [129,130].

Two new trimetallic hydrido clusters have been prepared from the reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ and $AgNO_3$ under H_2. Both 10-atom $[Pt(H)(AgNO_3)(AuPPh_3)_8](NO_3)$ (**166**) and 11-atom $[Pt(H)(AgNO_3)_2(AuPPh_3)_8](NO_3)$ (**167**) clusters are based on an icosahedral framework of metal atoms with the vacant vertices accommodating hydrides. The Ag-atoms occupy sites of high connectivity and are also coordinated by nitrates. The solution ^1H, ^{31}P ^{195}Pt NMR spectroscopic data are in agreement with the solid-state structure determination: for (**166**), $^1J(^1H-Ag) = 19.7$ Hz, $^3J(^{31}P-Ag) = 19$ Hz, $^1J(^{195}Pt-^{107}Ag/^{109}Ag) = 425/487$ Hz, and for (**167**), $^3J(^{31}Pt-Ag) = 19$ Hz, $^1J(^{195}Pt-^{107}Ag/^{109}Ag) = 405/465$ Hz [131].

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