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1. Silver

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INTRODUCTION

This review surveys the coordination chemistry of silver published during 1991. It follows a format similar to that used in the corresponding 1990 review [1]. Complexes are arranged in sections according to the oxidation state of the silver centre and, for silver(I), in subsections according to donor atom type. Section 1.4 covers selected cluster species; transition metal clusters containing one or two silver(I) phosphine units are not generally included in this review. Solid state compounds including oxides, phosphates and silicates are collected in Section 1.5.

An acknowledgement is due to the Cambridge Crystallographic Data Centre for providing atomic coordinates for structures which have been redrawn for this review; hydrogen atoms have generally been omitted from these structural figures.

Notes on the hazards and safe handling of silver(I) azide, silver(I) fulminate, silver(I) nitride, and silver(I) nitrate have been described [2]. Another paper of general interest addresses methods of silver recovery from waste AgCl. Methods include reduction by sodium borohydride or aqueous

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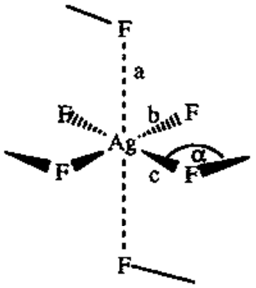
formaldehyde. The synthesis of silver(I) chloride from the recovered silver metal is also described [3].

1.1 SILVER(III)

The results of a comparative study of silver and gold trifluorides have been reported. Red diamagnetic AgF_3 is precipitated from solutions of $[AgF_4]^-$ in anhydrous hydrogen fluoride by adding a Lewis acid such as BF_3, PF_5 or AsF_5 (equ. (i)). The crystal structure of AgF_3 shows that the silver(III) centre resides in an elongated octahedral environment, (**1**); AgF_4-units are joined by symmetrically bridging fluorine atoms to produce helical chains. Silver trifluoride is thermodynamically unstable and loses F_2 when in contact with anhydrous hydrogen fluoride at 20°C (equ. (ii)). The product, Ag_3F_8, is a mixed Ag(II)Ag(III)-species with a magnetic susceptibility ($\mu_{eff} = 1.924\ (3)\ \mu_B$) that obeys the Curie-Weiss Law (4-280 K) [4].

$$[AgF_4]^- + L \rightarrow AgF_3 + [LF]^- \qquad (i)$$

$$3\ AgF_3 \rightarrow Ag_3F_8 + {}^1/_2\, F_2 \qquad (ii)$$



$a = 2.540\ (4)$ Å
$b = 1.863\ (4)$ Å
$c = 1.990\ (3)$ Å
$\alpha = 123.2\ (2)°$

(1)

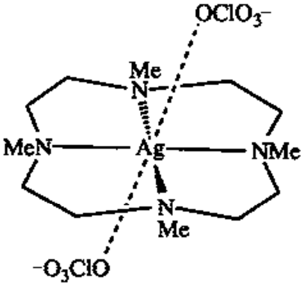
The reduction of $[Ag(OH)_4]^-$ by SCN^- ion for a concentration range of $5 \times 10^{-4}\ M \leq [SCN^-] \leq 0.25\ M$ has been investigated in aqueous alkaline media (25°C, $\mu = 1.2$ M) by stopped-flow spectrophotometry. For $[SCN^-] \leq 0.01$ M, the reaction is first order in each reactant and the overall rate constant is $21.7 \pm 0.3\ M^{-1}s^{-1}$, whereas at higher concentrations of SCN^-, the disappearance of silver(III) ions is pseudo-first order and the thiocyanate dependence is complex. Details of a proposed mechanism involving two electron redox steps are discussed [5]. Related work describes the kinetics and mechanism of the oxidation of the $edta^{4-}$ anion by $[Ag(OH)_4]^-$ to give iminodiacetate, glycinate, and glycolate ions. The overall rate equation is given in equ (iii) [6].

$$k_{obs} = \frac{(A + B[OH^-])[edta^{4-}]}{[OH^-] + C[edta^{4-}]} \qquad \text{(iii)}$$

$A = 4.38 \pm 0.57\ s^{-1}$ $B = 34.8 \pm 1.1\ dm^3mol^{-1}s^{-1}$ $C = 26.3 \pm 2.1$

1.2 SILVER(II)

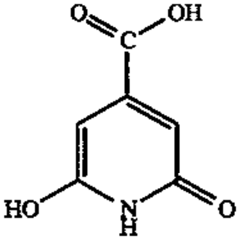
The structure of the silver(II) complex (**2**) has been determined. The molecules are centrosymmetric; two adjacent methyl groups are oriented above the macrocyclic ring and two below. The perchlorate ions interact significantly with the silver(II) centre [7].



Ag-N = 2.194 (3), 2.196 (3) Å

Ag-O = 2.889 (4) Å

(**2**)



(**3**)

Silver(II) ions form the red-brown complex $Ag(H_2L)_2$ where H_3L = citrazinic acid, (**3**). The complex reacts with other pyridine ligands, L', to give the mixed ligand complexes $Ag(H_2L)_2L'$ (dark brown) and $Ag(H_2L)_2L'_2$ (green) where L' = py, or 2-, 3-, and 4-picoline. The new complexes have been characterised by elemental analysis, infrared, electronic, and EPR spectroscopy, and magnetic moment measurements. The ligand H_2L^- functions in a bidentate manner and coordinates through one of the α-hydroxy groups and the heterocyclic *N*-donor. The silver(II) centre is in either a square planar or tetragonally distorted octahedral environment [8].

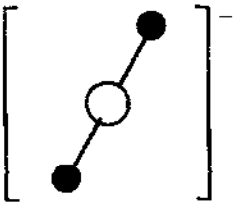
The electron transfer oxidation-reduction chemistry of *meso*-tetrakis(2,6-dichlorophenyl)-porphyrin, H_2L, and some of its metal complexes (including AgL) has been investigated by cyclic voltammetry and controlled-potential electrolysis. The results of ESR spectroscopic and magnetic moment measurements are also detailed [9]. When 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin, H_2L, is added to a silver colloid, (prepared by the reduction of $AgNO_3$ by $NaBH_4$), in 0.02 M phosphate buffer (pH = 7.3), a complex AgL is formed. SERS spectral data have been collected for the surface complex and have been compared with the resonance Raman spectrum of Ag(TTP) [10]. Two papers from the same group of researchers describe AgL complex formation when *meso*-tetrakis(4-sulfonatophenyl)porphyrin, H_2L is adsorbed on Ag_2O [11] and AgI [12] colloids. On Ag_2O, the adsorbed ligands undergo metal incorporation to eventually give (formally) the silver(II) complex, AgL. An intermediate is proposed on the basis of SERS spectral data [11]. Similar complex formation occurs on AgI, but when the ligand is absorbed on AgCl, H_4L^{2+} is observed in addition to AgL [12]. The results of an EXAFS study of poly[AgL] where H_2L is 5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphyrin have been represented; a comparison of spectral data for the complex with those of the discrete complex AgL indicates that there are similarities in structural features [13].

1.3 SILVER(I)

1.3.1 Complexes with halide and pseudo-halide ligands

The electronic structure of silver(I) chloride has been probed by use of *ab initio* Hartree-Fock methods. The results support the fact that the bonding in AgCl is strongly (but not exclusively) ionic in nature, and also confirm the importance of correlation effects [14].

Three halo-anions of silver(I) have been isolated as their $[K(crypt\text{-}2,2,2)]^+$ salts; all have been structurally characterised. In $[AgCl_2]^-$, (4), the Ag-Cl distances of 2.330 (2) and 2.328 (2) Å are quite long. In $[Ag_2I_4]^{2-}$, (5), each silver(I) centre is displaced 0.123 Å from the plane defined by the three iodide ions which make up the trigonal coordination sphere of the metal ion; Ag-I distances are 2.672 (1) Å (terminal) and 2.789 (1) and 2.801 (1) Å (bridging) and the Ag---Ag separation is 3.557 (2) Å. The third anion is $[Ag_4Br_8]^{4-}$, (6); pertinent distances in (6) are $Ag\text{-}Br_{terminal}$ = 2.518 (2) Å, $Ag\text{-}Br_{\mu}$ = 2.651 (2), 2.631 (2), 2.722 (2), 2.696 (2), 2.799 (2) and 2.750 (2) Å, Ag---Ag = 3.65 (1) (twice) and 3.595 (2) Å [15]. The inclusion of an Na^+ ion into an Sn_xO_y-cage stabilised by organic substituents has been observed in $[(^iPrSn)_{12}O_4(OH)_{24}][Ag_7I_{11}].NaCl.H_2O.10dmso$; clearly, the relevance of this compound to this review is the presence of the counterion $[Ag_7I_{11}]^{4-}$. This anion is present in the lattice as a one-dimensional, twisted double chain, $^1_\infty\{[Ag_7I_{11}]^{4-}\}$ comprising face-sharing iodine tetrahedra. The positions of the iodine atoms are defined very precisely but the silver(I) ions are not as well located. The bulk structure suggests that the compound should show one-dimensional conductivity associated with the silver ions [16].



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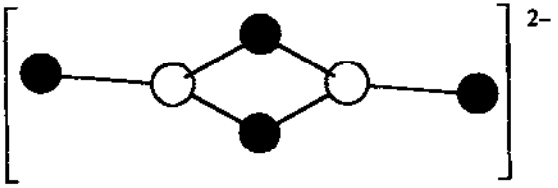

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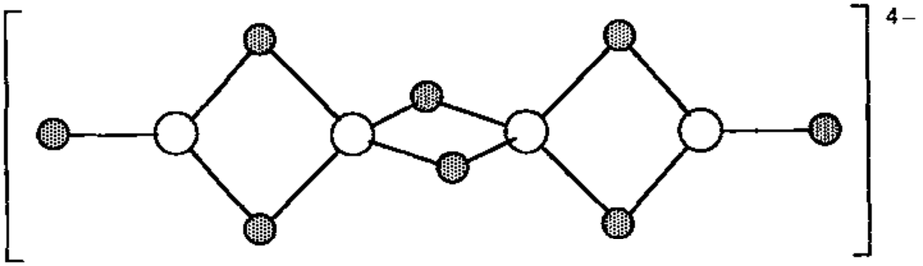
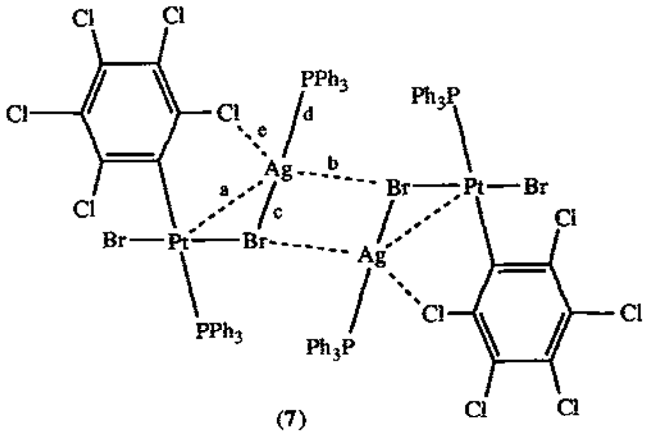


(6)

The reaction of triphenylphosphinesilver(I) perchlorate with [*trans*-$PtBr_2(PPh_3)(C_6Cl_5)]^-$ yields the dimeric complex $[(Ph_3P)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)]_2$, (7), in which the Pt–Ag interaction is supported by a single bromide bridging ligand [17]. The dimeric silver(I) complex $[Ag(\mu\text{-}I)(PPh_3)(py)]_2$ and the halo-complexes $Ag(PPh_3)_2X(py)$ (X = Cl or Br) are discussed in Section 1.3.3.

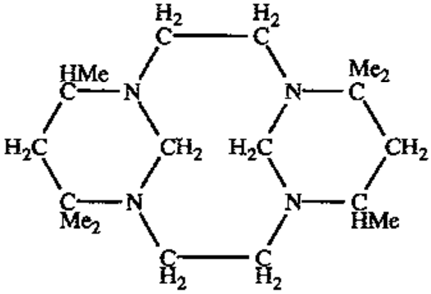


a = 2.918 (1) Å
b = 3.109 (1) Å
c = 2.606 (1) Å
d = 2.389 (3) Å
e = 3.007 (3) Å

(7)

The extraction of $K[Ag(CN)_2]$ and its gold(I) analogue by dicyclohexano-18-crown-6 in various media has been studied; the silver(I) ion extracts less well than does the gold(I) ion [18]. The thermal stability of $[Ph_2I][Ag(CN)_2]$ has been investigated as part of a study of this and related cyano complexes; changes in morphology of the sample as a function of temperature have been detailed [19].

An inclusion complex is formed when $K[Ag(SCN)_2]$ interacts with the ligand, L, (**8**). The compound exhibits $[Ag_2(SCN)_4]_n$ chains which follow the direction of the crystallographic *b*-axis; the shortest contact between the silver(I) centre and L is 4.424 (3) Å. Each $Ag_2(SCN)_4$ unit possesses a centre of symmetry and important distances are Ag-S = 2.871 (1), 2.476 (1) and 2.526 (1) Å, and Ag-N = 2.307 (5) Å [20]. The crystal structure of an orthorhombic form of silver(I) dicyanamide has been elucidated. It consists of infinite $-(Ag-N{\equiv}C-N-C{\equiv}N-)_n-$ chains which run parallel to the crystallographic *a*-axis. The structure is similar to that previously determined for the trigonal form of the compound, with the exception that the 3_1 axis in the trigonal form is replaced in the orthorhombic modification by a 2_1 axis. Pertinent bond parameters in silver(I) dicyanamide are Ag-N = 2.14 (2) and 2.08 (2) Å, C≡N = 1.17 (3) and 1.16 (3) Å, C-N = 1.28 (3) and 1.29 (3) Å, and ∠N-Ag-N = 177 (1)° [21].



(**8**)

1.3.2 *Complexes with silver-carbon bonds*

The reaction of silver(I) perchlorate with two equivalents of the ylide $Ph_3P{=}CHC(O)NMe_2$ in Et_2O gives the complex $[Ag\{CH(PPh_3)C(O)NMe_2\}_2][ClO_4]$ in high yield. The product, unlike the reagents, is insoluble in Et_2O and precipitates from the reaction mixture. The complex $[Ag\{CH(PPh_3)C(O)NMe_2\}_2][ClO_4]$ has been characterised by elemental analysis, ^1H and ^{31}P NMR and IR spectroscopy, and conductance measurements. Related gold(I) and gold(III) complexes have also been reported [22].

The first silver(I) carbonyl complex to be isolated is $Ag(CO)\{B(OTeF_5)_4\}$ and this borate is described in Section 1.3.6.

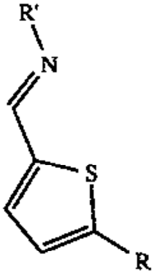
1.3.3 Complexes with nitrogen donor ligands

An investigation of the solvation of silver(I), copper(I) and copper(II) ions in aqueous acetonitrile has been carried out. Results support the fact that silver(I) ions, like copper(I) ions, are preferentially solvated by MeCN; this is in contrast to the preferential solvation of the divalent ions by water [23]. The molecular structure of an orthorhombic form of silver(I) dicyanamide was descibed in Section 1.3.1 [21].

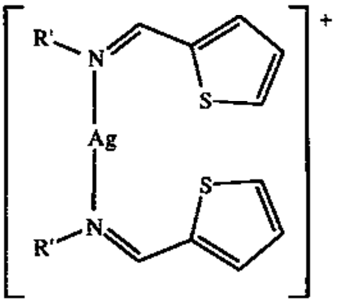
The crystal structure of $Ag_3SeO_3N.3NH_3.2H_2O$ has been determined. There are two independent silver(I) centres bonded to the nitrogen atom of the amidoselenate group; these groups are connected by the silver ions to give an infinite polymeric chain. The third silver(I) ion is present as $[Ag(NH_3)_2]^+$ [24].

The decomposition of a bis(ethylenediamine)silver(I) complex has been used as a method of producing uniform silver particles of average diameter 0.52 ± 0.10 μm. The method involves the aging of a solution of $AgNO_3$ (1.0×10^{-3} M), the ligand, en, (1.0 M), and nitric acid (0.25 M) at 100°C. The results of XPS studies are discussed [25].

The 1:2 reactions of $Ag(O_3SCF_3)$ with ligands, L, of type **(9)** (R = H, Me, $^{t}BuMe_2Si$; R' = ^{i}Pr, ^{t}Bu, $CH_2{}^{t}Bu$, (*S*)-CHMePh) yield stable complexes of formula $[AgL_2][O_3SCF_3]$. For R = H and R' = (*S*)-CHMePh, the product has been structurally characterised. In $[AgL_2]^+$, **(10)**, the silver(I) centre is in a linear environment, coordinated by one *N*-donor of each ligand. The two sulfur atoms are turned toward the silver ion but the Ag---S distances are very long and do not indicate significant bonding interactions. The solution properties of the complex have been investigated by use of ^{1}H, ^{19}F, and ^{109}Ag NMR spectroscopy; again, evidence points to the coordination sphere being predominantly that of the *N*-donor atoms [26].



(9)



R' = (*S*)-CHMePh

Ag–N = 2.147 (11),
2.174 (11) Å

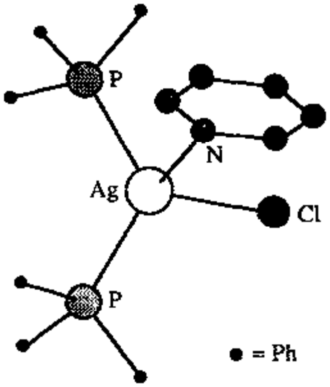
Ag----S = 3.017 (3),
3.036 (7) Å

(10)

The crystal structures of the silver(I) complexes $Ag(PPh_3)_2Cl(py)$, **(11)**, $Ag(PPh_3)_2Br(py)$, and $[Ag(\mu\text{-}I)(PPh_3)(py)]_2$, **(12)**, have been redetermined. Previously, the chloro- and bromo-complexes had been assigned to the $P2_1/m$ space group and the iodo-complex to the $C2/m$ space group; these have now been reassigned in $P2_1/a$ and $C2/a$ respectively. Selected structural parameters for the three complexes are listed in Table 1 [27].

Table 1 Selected bond distances and angles in the complexes $Ag(PPh_3)_2Cl(py)$, **(11)**, $Ag(PPh_3)_2Br(py)$, and $[Ag(\mu\text{-}I)(PPh_3)(py)]_2$, **(12)**.

Parameter	$Ag(PPh_3)_2Cl(py)$ X = Cl	$Ag(PPh_3)_2Br(py)$ X = Br	$[Ag(\mu\text{-}I)(PPh_3)(py)]_2$ X = I
Ag-X / Å	2.517 (2)	2.636 (2)	2.876 (1), 2.851 (1)
Ag-N / Å	2.593 (4)	2.572 (7)	2.335 (7)
Ag-P / Å	2.477 (2), 2.474 (2)	2.473 (3), 2.483 (3)	2.438 (2)
Ag----Ag / Å			2.956 (1)
Ag-X-Ag / deg			61.87 (3), 62.46 (3)
X-Ag-X / deg			117.83 (3)



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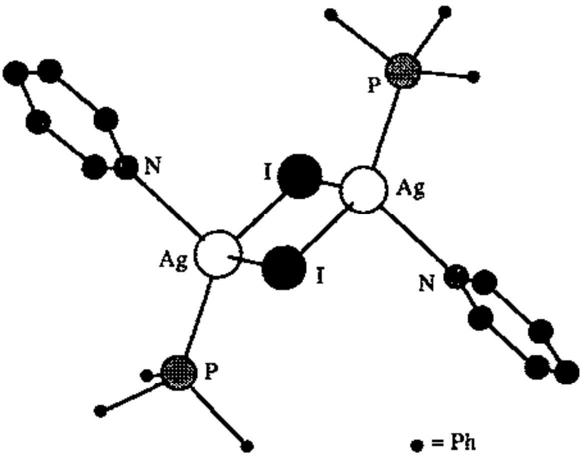
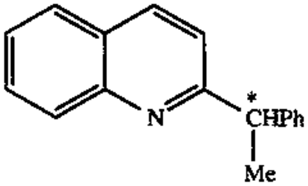
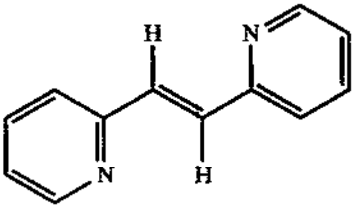


(12)

The reaction of (+)-(*RS*,*RC*)-1-phenylethyl-2-quinolyl sulfoxide with EtMgBr in thf gives (–)-(**13**). The formation of $[(–)\text{-}(\mathbf{13})H][ClO_4]$ in the presence of silver(I) perchlorate has been reported, but attempts to crystallise this compound led instead to $[AgL_2][ClO_4]$ where ligand L is (–)-(**13**). The two quinolyl groups are coordinated via the *N*-donors but the two donors provide a non-linear environment for the silver(I) ion; Ag-N = 2.195 (4) and 2.192 (5) Å, ∠N-Ag-N = 151.6 (2)°. Weak cation-anion interactions are observed with Ag-O = 2.98 (1) and 2.97 (1) Å and it is suggested that these are made possible as a consequence of the obtuse N-Ag-N bond angle [28].

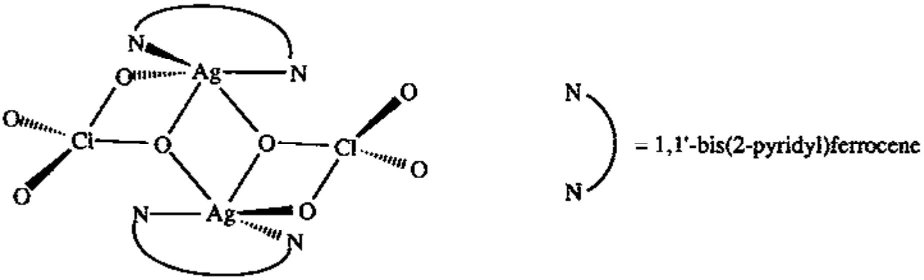


(–)-(13)



(14)

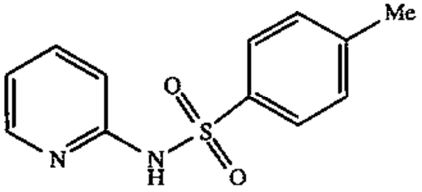
A potentiometric titration method has been used to study the complexation of silver(I) ions with several pyridines and piperidines, and with the aliphatic amines $^{n}BuNH_2$, $^{t}BuNH_2$ and $^{i}C_5H_{11}NH_2$ in dmso ($T = 20 \pm 2°C$). The complex stabilities are related to the strengths of the bases. Bonding in the complexes is discussed and it is shown that the heterocyclic ligands exhibit both σ-donor and π-dative interactions [29]. The polymeric complex $\{AgL(ClO_4)\}_\infty$ forms when a methanol solution of *trans*-1,2-bis(2-pyridyl)ethene, L, **(14)**, is added to a methanol solution of $AgClO_4$. In the IR spectrum, a characteristic absorption at 1631 cm^{-1} is assigned to $\nu_{C=C}$. The molecular structure of the complex $\{AgL(ClO_4)\}_\infty$ has been determined and is described as containing macrocations $\{[AgL]^+\}_\infty$. The silver centres are well separated from the perchlorate anions in the crystal lattice. Each silver(I) centre is in an approximately linear environment and the ligands form the rigid backbone of the polymeric chain; the Ag-N distances are 2.158 (3) and 2.166 (3) Å and ∠N-Ag-N = 169.6 (1)° [30].



(15)

The air-stable, red complex $[AgL(ClO_4)]_2$ where L = 1,1'-bis(2-pyridyl)ferrocene has been prepared by methods which include the reaction of $RhCl_3.3H_2O$ and L in the presence in $AgNO_3$ in acetone. The complex $[AgL(ClO_4)]_2$, **(15)**, has been characterised by IR and ^1H NMR spectroscopy, and by X-ray crystallography. Ligand L acts as an approximate *trans*-chelate (∠ NAgN = 163.1 (2)°). The dimeric structure is supported by bridging perchlorate ligands; important distances are Ag-N = 2.187 (5) and 2.14 (1) Å and Ag-O = 2.89 (1), 2.732 (6), and 2.87 (1) Å, and the bridge angle is ∠Ag-O-Ag = 111.9 (2)°. The net result is that each silver(I) centre is in a highly distorted 5-coordinate environment with the ferrocene unit blocking the vacant coordination site

[31]. Silver(I) nitrate reacts with bpy and an excess of KSCN in aqueous acetone to give the complex Ag(bpy)(SCN).0.25bpy. A polymeric structure, supported by thiocyanate bridges, is confirmed by an X-ray diffraction study. The complex has also been characterised by IR spectroscopy and thermal decomposition studies [32].



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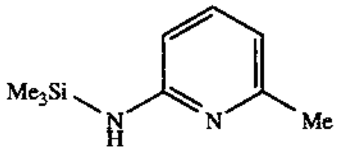

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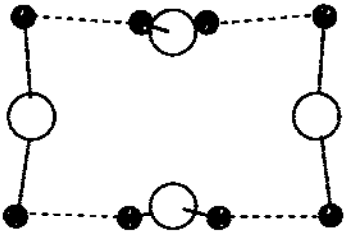
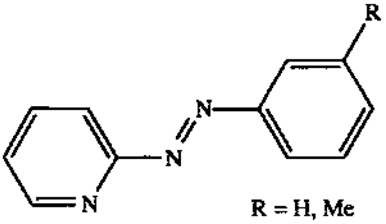


(18)

The molecular structure of Ag_2L_2, HL = **(16)**, has been reported; the complex is prepared by the reaction of HL with $AgBF_4$ and is characterised in its infrared spectrum (KBr disc) by an absorption at 1129 cm^{-1} assigned to the ν_{SO} mode. The Ag_2-unit is supported by the *N,N'*-donor set of each ligand; pertinent bond distances are Ag-Ag = 2.739 (1) Å, and Ag-N = 2.163 (3) and 2.149 (3) Å. Despite the relatively short Ag-Ag distances, the authors question whether there is indeed any silver-silver bonding [33]. The synthesis and structure of the tetrameric amido-complex Ag_4L_4, where HL = **(17)**, have been detailed. The ligands bridge the silver(I) centres in a "head-to-head" and "tail-to-tail" fashion to give a cyclic structure with non-bonding Ag---Ag separations in the range 3.006 (1) to 3.164 (1) Å; the Ag_4N_8-core is shown in structure **(18)**. The four silver atoms lie in a plane; Ag-N distances are 2.140 (3) and 2.169 (6) Å for the pyridyl *N*-donor atoms and 2.099 (3) and 2.097 (4) Å for the amido *N*-donors. The $N_{pyridyl}$-Ag-$N_{pyridyl}$ bond angles are 169.3 (2)° and 171.2 (2)°. Related copper(I) and zinc(II) complexes have also been reported [34].

The 1:1 reaction in methanol of $RuCl_3.3H_2O$ with $[AgL_2][ClO_4]$, where L = **(19)**, yields the green complex *trans,trans*-RuL_2Cl_2 as a green precipitate. After separation of this product by filtration, concentration of the filtrate and addition of water gives RuL_2Cl_2 as a mixture of the green *trans,trans*-, blue *trans,cis*- and blue-violet *cis,cis*-isomers. If $RuCl_3.3H_2O$ and $[AgL_2][ClO_4]$ are combined in a molar ratio 1:3 in methanol under reflux, the product is the brown complex, *mer*-$[RuL_3][ClO_4]_2.H_2O$. The reactions provide efficient methods of preparing the isomeric complexes via ligand transfer from silver(I) to ruthenium(II) [35].



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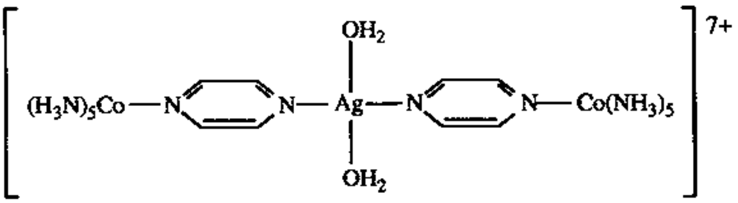
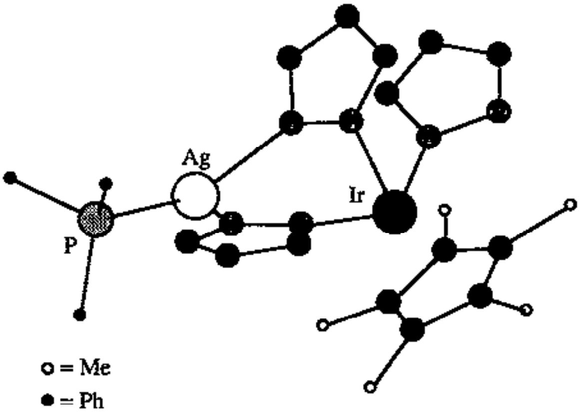
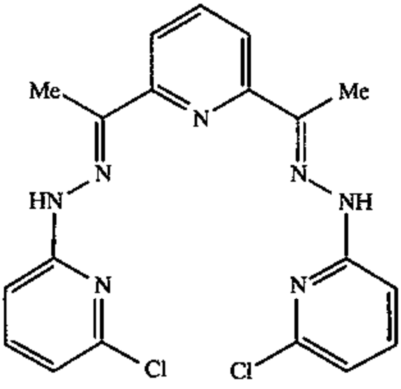


(20)

The crystal structure of the complex $[(\mathbf{20})][NO_3]_7.4H_2O$ has been determined. Cation **(20)** has C_{2h} symmetry with the silver(I) centre in a square planar environment and lying on a crystallographic centre of symmetry; distances around the silver ion are Ag-N = 2.320 (5) Å and Ag-O = 2.585 (5) Å [36]. The pyrazolato ligand, L^-, like pyrazine, is capable of linking together two metal centres. This is observed in the complex $Cp^*IrL_3AgPPh_3$, **(21)**, which is synthesised from Ph_3PAgCl and $Cp^*IrL_2(HL)$ with KOH present. Complex **(21)** is fluxional in solution, with the Ph_3PAg-unit exchanging between the three heterocyclic ligands. In the solid state, **(21)** exhibits an IrN_4Ag-ring in a boat conformation; the Ir---Ag separation is 3.8601 (2) Å. Bonding distances in the coordination sphere of the silver(I) centre are Ag-N = 2.211 (4) and 2.205 (3) Å and Ag-P = 2.341 (1) Å. Some reactions of the complex have been investigated [37]. A group of complexes containing heterocyclic ligands HL (HL = pyrazole), HL' (HL' = 1,2,4-triazole), or L'' (L'' = 8-aminoquinoline) has been prepared and characterised. Neutral ligands react with $AgNO_3$ in acidic aqueous solution. The complex $[Ag(HL)_2][NO_3]$ has been structurally characterised by single crystal X-ray diffraction; the cation is centrosymmetric with a linear silver(I) coordination environment. With HL' and L'', dinuclear complexes of formula $[Ag(HL')(NO_3)]_2$ and $[Ag(L'')(NO_3)]_2$ are produced. Structural data show that the dinuclear framework in each complex is supported by bridging *N*-donor ligands and there are short bonding contacts between the silver(I) and nitrate ions. The coordination geometry at each silver(I) centre is distorted tetrahedral [38].

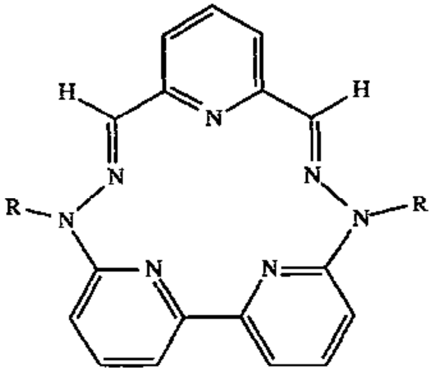


(21)



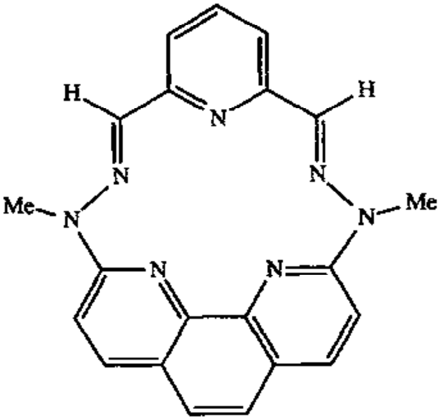
(22)

The area of supramolecular chemistry is producing some fascinating complexes. The structure of the dinuclear silver(I) complex $[Ag_2L_2][PF_6]_2$, where L = **(22)**, has been elucidated and the results confirm a double-helical array, stabilised by ligand-ligand π-stacking interactions. Each silver(I) ion resides in a distorted 4-coordinate environment with a weak interaction to the fifth *N*-donor atom. Each ligand presents two *N*-donors to *each* metal centre and within the primary coordination sphere of each silver(I) ion, distances are Ag-N = 2.428 (4), 2.371 (5), 2.324 (5) and 2.320 (5) Å. The silver---silver atom separation of 3.142 (1) Å is short [39]. Complex formation between the macrocyclic ligands **(23)** and **(24)** and silver(I) ions has been investigated. The complexes produced in the reactions of $[HL][BF_4]$ with $Ag[BF_4]$ have a 1:1 Ag^+:L stoichiometry and a crystallographic study of the product for L = (**23**) with R = CH_2CH_2OH confirms the dinuclear nature of the complexes. The cation $[Ag_2L_2]^{2+}$ (L = (**23**); R = CH_2CH_2OH) is shown in structure (**25**). Each silver(I) ion interacts with five *N*-donor atoms from one of the ligands, with the metal atom raised above the plane of the five nitrogen atoms. Each macrocyclic ligand is folded into a "dome" with the Ag^+ ion at the apex of the dome. The two silver centres are connected by a single bridging *N*-donor atom with Ag---Ag = 3.472 (1) Å. The unusual dimeric structure is attributed a mismatch between the size of the metal ion and the hole-size of the ligand [40].

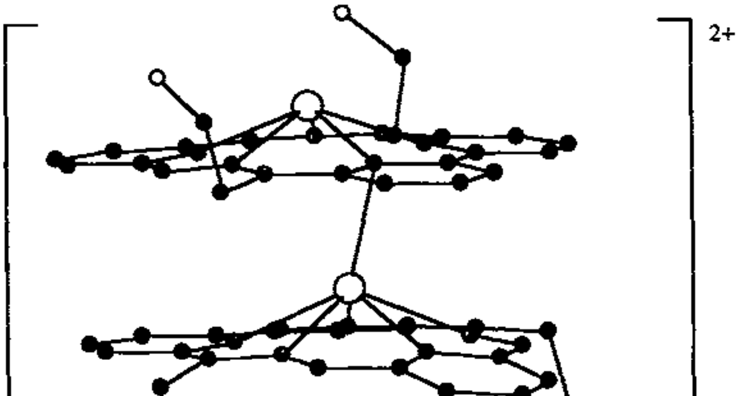


R = Me or CH_2CH_2OH

(23)

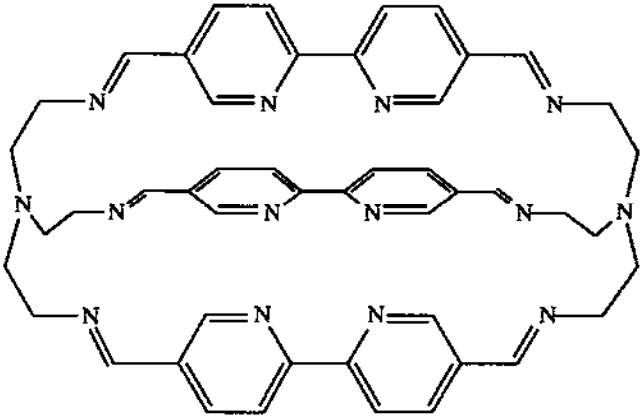


(24)



(25)

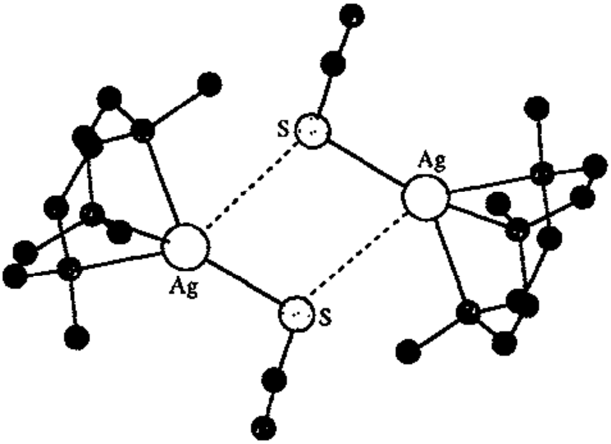
The preparation of the cryptand ligand **(26)** and its complexation with silver(I) ions has been described. A crystallographic study of **(26)** shows that the ligand has C_3 symmetry and the bpy units exhibit the expected *anti*-conformation which minimises *N*(lone pair)-*N*(lone pair) repulsion. The ligand reacts with three equivalents of $Ag[BF_4]$ to give the cryptate complex Ag_3L which has been structurally characterised. The conformation of **(26)** changes in going from free to the complexed ligand; the six bpy *N*-donors face into the cryptand cavity in Ag_3L. The three silver ions are separately coordinated within the macrocyclic cavity. Two Ag^+ ions are four coordinate in the upper and lower *N,N',N",N'"*-donor sets of ligand **(26)** with Ag-N bond lengths in the range 2.280 (8) and 2.446 (7) Å. The third silver(I) centre interacts with the three *N,N'*-bpy donor sets and is thus six-coordinate with Ag-N distances in the range 2.444 (6) to 2.506 (7) Å [41].



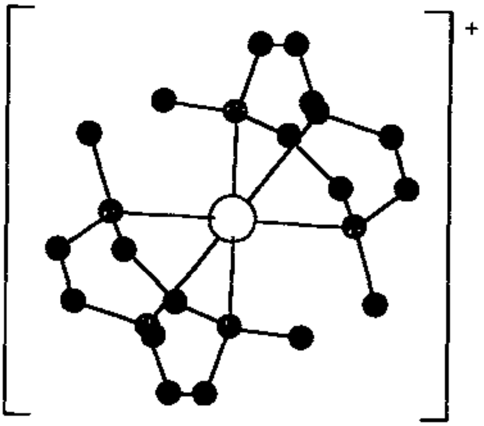
(26)

Complex formation between silver(I) ions and the macrocyclic ligand 1,4,7-triazacyclononane, L, and its tri-*N*-methylated derivative, L', has been investigated. Silver(I) hexafluorophosphate reacts with L in MeCN and, after the addition of $[Bu_4N]X$ (X = Cl, Br, I, or CN), the complexes AgL(X) precipitate from solution. The complexes AgL'(X) (X = CN or SCN) are formed in similar reactions using ligand L' in place of L. If the ratio of the reagents is changed to 2 L (or L') : 1 Ag^+, the cationic complexes produced are $[AgL_2]^+$ or $[AgL'_2]^+$. By treating a pyridine solution of $Ag[PF_6]$ and L (1:1) with sodium cyanide, the dinuclear complex $[LAg(\mu\text{-}CN)AgL][PF_6]$ can be isolated. The crystal structures of AgL'(SCN), **(27)**, and $[AgL'_2][PF_6]$, ($[AgL'_2]^+$ = **(28)**), have been determined. In **(27)**, the silver(I) centre is tetrahedrally coordinated within the primary coordination sphere and pairs of molecules interact in the solid state via weak Ag---S contacts of distance 3.948 (8) and 3.959 (8) Å. For each silver(I) ion, the macrocyclic ligand occupies three coordination sites (Ag-N = 2.413 (11), 2.399 (8) and 2.399 (8) Å for one molecule, and Ag-N = 2.431 (12), 2.350 (10) and 2.350 (10) Å for the second molecule). The direct thiocyanate to silver(I) contact is of length 2.360 (4) Å in one molecule and 2.368 (5) Å in the other. Cation **(28)** is an example of a fully characterised bis(1,4,7-trimethyl-1,4,7-triazacyclononane)metal complex; the Ag^+ ion is in a pseudo-octahedral environment and the Ag-N distances lie in the range

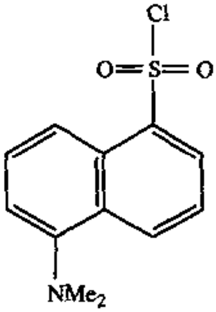
2.543 (1) to 2.607 (7) Å [42]. The preparation and characterisation of two novel macrocyclic polyamines with *N*-dansyl substituents have been reported (dansyl chloride = **(29)**). Quenching reactions between the ligands (for example, [14]aneN_4-{*N*-$CH_2CH_2CH_2NH$(dansyl)}$_4$) and silver(I) have been studied and the results show that such reactions can be used for the determination of the metal ion [43].



(27)



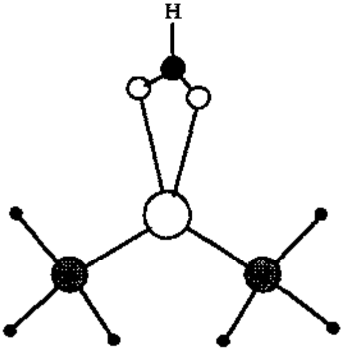
(28)



(29)

1.3.4 Complexes with phosphorus donor ligands

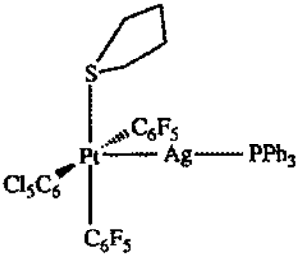
The complex $(Ph_3P)_2Ag(O_2CH)$, **(30)**, has been synthesised by the reaction of AgOAc with PPh_3 in acetone and methanol, followed by addition of HCO_2H and $K[BH_4]$. Complex **(30)** has been structurally characterised; the formate ion functions as a bidentate ligand and the silver(I) centre is in a distorted tetrahedral environment [44].



● = Ph

(30)

The $\{AgPPh_3\}$-unit has been incorporated into compounds in the series $L(C_6Cl_5)_{3-x}(C_6F_5)_xPtAg(PPh_3)$ (x = 0–2; L = tht, PPh_3 or py). The complexes result from stoichiometric reactions of $[Bu_4N][PtL(C_6Cl_5)_{3-x}(C_6F_5)_x]$ with $(Ph_3P)AgOClO_3$. Preparations of the complexes $[Bu_4N][(C_6F_5)_4PtAg(PPh_3)]$, $(Ph_3P)(C_6F_5)_3PtAg(PPh_3)$, and other related species have also been reported (see also Section 1.3.7). The structure of the complex $(tht)(C_6Cl_5)(C_6F_5)_2PtAg(PPh_3)$, **(31)**, has been determined. The complex exhibits a Pt→Ag interaction and the perhalogenated aryl substituents are oriented such as to provide X---Ag close contacts for the *ortho*-halogen atoms, X [45].



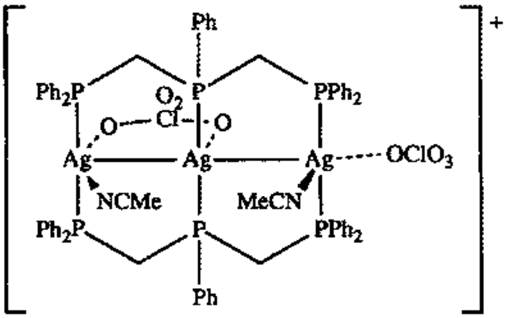
Ag-P = 2.363 (8) Å

Ag-Pt = 2.650 (2) Å

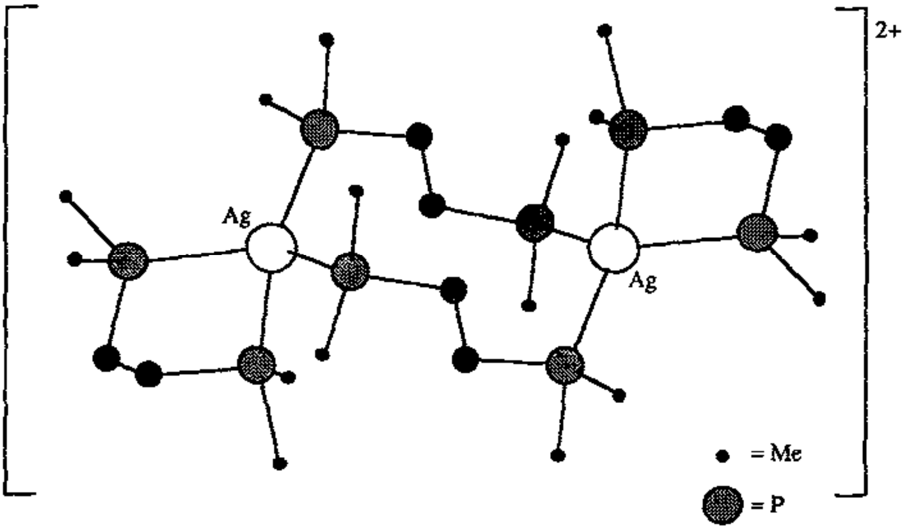
∠Pt-Ag-P = 173.0 (2)°

(31)

Several silver(I) complexes involving bis(phosphine) ligands have been reported. A series of reactions between gold(I) phosphines and 2-thiouracil, adenine, and 9-methyladenine have been complemented by studies with silver(I) ions where the phosphine ligand is dppe. The results indicate that, rather than associating directly with the nucleobases, silver(I) ions prefer to coordinate to the phosphorus donors of dppe and form $[Ag(dppe)_2]^+$ [46]. The crystal structure and spectroscopic and luminescent properties of the complex $[Ag_3(\mu\text{-}L)_2(MeCN)_2(ClO_4)_2]^+$, (32), (L = $Ph_2PCH_2P(Ph)CH_2PPh_2$) have been described. The complex is prepared as the perchlorate salt by treating $Ag(O_3SCF_3)$ with ligand L followed by metathesis with $LiClO_4$ and recrystallisation from Et_2O/MeCN. Structural data show that two of the three perchlorate ions interact with the trisilver framework although these interactions are regarded as being electrostatic in nature. The Ag_3-unit is near linear with ∠Ag-Ag-Ag = 175.33 (7)° and is supported by two doubly-bridging, tridentate *P,P',P"*-ligands which are related by a crystallographic mirror plane (Ag-P = 2.420 (3), 2.397 (3) and 2.447 (3) Å). The acetonitrile ligands are associated with the two terminal silver(I) centres. Cation (32) exhibits a $^1(d_{\sigma^*} \rightarrow p_\sigma)$ transition at 288 nm and photoluminescence in the solid state at 467 nm [47].

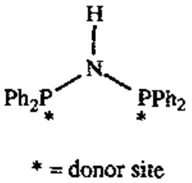


(32)

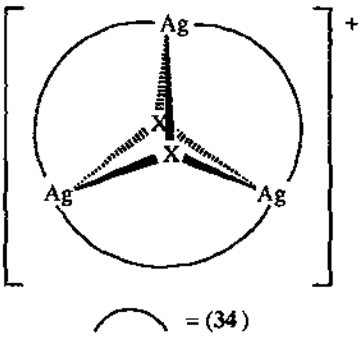


(33)

Reaction of $Ag(O_3SCF_3)$ with two equivalents of $Me_2PCH_2CH_2PMe_2$ (dmpe) in MeCN in the presence of sodium tetraphenylborate leads to $[Ag_2(dmpe)_4][BPh_4]_2$ which has been the subject of a crystal structure determination. In the cation $[Ag_2(dmpe)_4]^{2+}$, (33), the two silver(I) centres are bridged by two of the bis(phosphine) ligands and each silver(I) ion is also coordinated to a chelating dmpe ligand. The environment about each silver(I) centre is distorted tetrahedral with an angle of $\angle$P-Ag-P = 83.5 (2)° within the chelate. Important distances are Ag-$P_{chelate}$ = 2.491 (4) and 2.557 (6) Å, and Ag-P_{bridge} = 2.471 (4) and 2.465 (4) Å. In solution, ^1H and ^{31}P NMR spectral data are consistent with the retention of the solid state structure [48]. The heterometallic dinuclear complex $\{(c\text{-}C_6H_{11})_3P\}_2H_3Re(\mu\text{-}L)(\mu\text{-}H)_2AgI$, (L = $Ph_2PC(=CH_2)PPh_2$), has been prepared from AgI and $\{(c\text{-}C_6H_{11})_3P\}_2ReH_5L$; an analogous complex where L = dppm has been similarly prepared. The solution properties of the complexes have been studied in detail by using variable temperature ^1H and ^{31}P NMR spectroscopy [49].

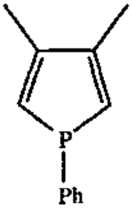


(34)



(35)

Treatment of AgX (X = Cl, Br or I) with the ligand L, (34), in methanol yields $[Ag_3X_2L_3]X$; metathesis with ammonium hexafluorophosphate gives the corresponding PF_6^- salts. The new complexes have been characterised by elemental analyses, conductivity measurements, ^{31}P and ^1H NMR, IR and Raman spectroscopies, and structure (35) is proposed; the spectroscopic properties are compared with those of $[Ag_3X_2(dppm)_3]X$. The Raman spectra of complexes (35) show characteristic absorptions at 135, 125, and 105 cm^{-1} for X = Cl, Br, and I, respectively, assigned to the mode $\nu_s(XAg_3X)$. These values are the same as those observed for $[Ag_3X_2(dppm)_3]X$ [50].



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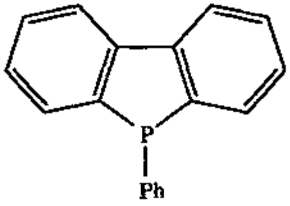
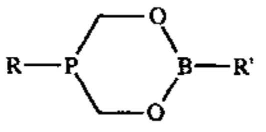
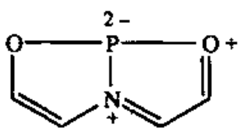


(37)

Complex formation between silver(I) ions and the phospholes (36) and (37) has been investigated. The products are of the general type $[L_nAgX]_m$ where X = Cl, Br, or I, and L = (36) and $n = 1, m = 4$, or $n = m = 2$, or L = (37) and $n = 3, m = 4$, or $n = m = 2$. The cation $[L_4Ag]^+$ with L = (37) has been isolated as the tetrafluoroborate salt. The structure of $[L_2AgCl]_2$ for L = (37) has been determined. It exhibits an Al_2Cl_6-like framework containing a crystallographic inversion centre; the phosphole ligands are in terminal sites (Ag-P = 2.504 (3) and 2.525 (4) Å) and the bridging chloride ligands (Ag-Cl = 2.643 (3) and 2.634 (4) Å) hold the silver(I) centres at a non-bonded separation (Ag---Ag = 3.750 (2) Å). Solid state CP/MAS and solution ^{31}P NMR spectroscopic data are presented for the new complexes [51]. Reactions of silver nitrate with 1,3,2,5-dioxaboraphosphorinanes (38), L, leads to the complexes $LAg(NO_3)$ and $L_3Ag(NO_3)$ in which ligands L are *O*-bonded. For R = R' = Ph, the complex $L_3Ag(NO_3)$ can also be prepared by assembling L *in situ*. This method begins with the reaction of $AgNO_3$ with $PhP(CH_2OH)_2$ to give $\{PhP(CH_2OH)_2\}_3Ag(NO_3)$ in which the ligand is *P*-bonded. The condensation of $\{PhP(CH_2OH)_2\}_3Ag(NO_3)$ with $PhB(OH)_2$ generates $L_3Ag(NO_3)$. Products have been spectroscopically characterised [52].



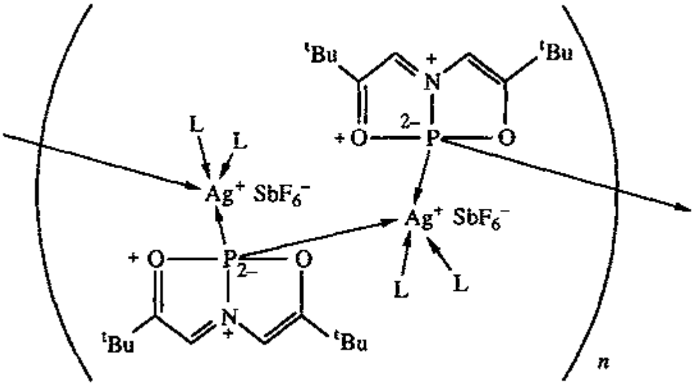
(38)



(39)

The bicyclic ligand (39) has been given the acronym ADPO; the ligand exhibits a 10-electron phosphorus centre. The reaction of four equivalents of ADPO with $[Ag(NCMe)_4][SbF_6]$

in CH_2Cl_2 yields the yellow complex $[Ag(ADPO)_4][SbF_6]$ which has been structurally characterised. The silver(I) ion resides in an unusual square planar environment with the ligands, each planar, forming a "paddle-wheel" arrangement around the metal centre (Ag-P = 2.612 (1) Å). The phosphorus atom of each coordinated ligand possesses a stereochemically active lone pair of electrons ($\angle$Ag-P-N = 113.3 (1)°). Solution NMR spectroscopic data are presented for $[Ag(ADPO)_4][SbF_6]$ [53]. The activity of the phosphorus lone pairs of electrons in $[Ag(ADPO)_4]^+$ is illustrated by the formation of the polymeric complex **(40)**. A crystallographic study of **(40)** shows that each phosphorus atom connects two silver(I) centres with $\angle$Ag-P-Ag = 131.5 (2)°; the Ag-P distances are 2.434 (5) and 2.574 (5) Å. Complex **(40)** is prepared by the 1:1 reaction of ADPO and $[Ag(NCMe)_4][SbF_6]$ [54].



L = NCMe

(40)

1.3.5 *Complexes with arsenic donor ligands*

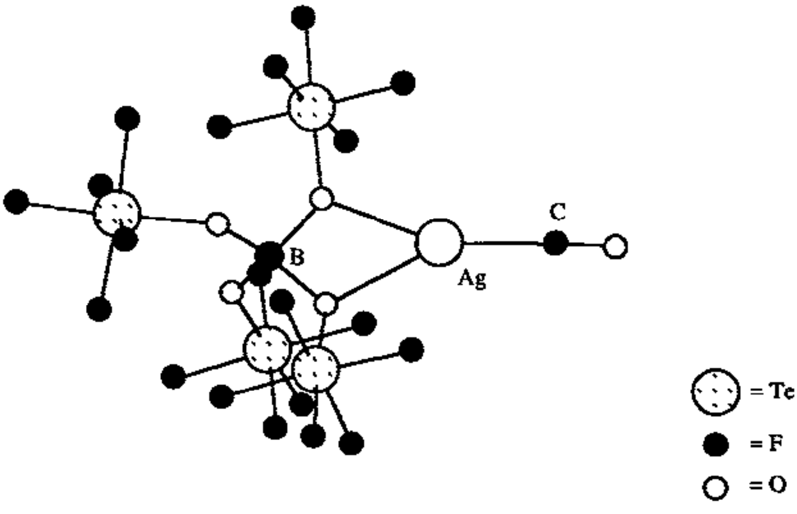
The new complex $[Ag(AsPh_3)_4]_2[Sn_2Ph_4(NO_3)_4(OH)_2].2MeCN$ has been synthesised by treating $SnPh_3(NO_3)$ with $Ag(AsPh_3)_2(NO_3)$ in a mixture of acetone and acetonitrile. A single crystal X-ray diffraction study of the product is of interest here with respect to the cationic portion of the compound. In $[Ag(AsPh_3)_4]^+$, the silver(I) centre is tetrahedrally sited with Ag-As bond distances of 2.648 (2), 2.698 (1), 2.665 (1) and 2.685 (1) Å [55].

1.3.6 *Complexes with oxygen donor ligands*

Coordination to silver(I) ions of the dioxaboraphosphorinanes **(38)** was described in Section 1.3.4.

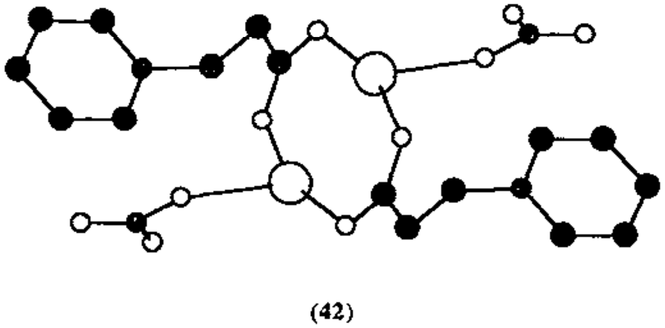
Two papers from the same researchers report the kinetics and mechanism of the silver(I) catalysed oxidation of $[Fe(phen)_3]^{2+}$ by $[P_2O_8]^{4-}$ ions. The rate of reaction depends upon the concentration of silver(I) ion; the catalytic role of the silver(I) ions is explained in terms of complex formation between $[P_2O_8]^{4-}$ and Ag^+ [56, 57]. It has been shown that during the titration of thiosulfate with silver(I) ions, three complexes are formed; these are $[Ag(S_2O_3)_2]^{3-}$, $[Ag(S_2O_3)]^-$ and $Ag_2S_2O_3$. However, in the reverse titration, the only complex produced is $Ag_2S_2O_3$. The $[Ag(S_2O_3)_2]^{3-}$ complex anion is preferentially formed when freshly precipitated silver(I) chloride or bromide is titrated with thiosulfate ions. An analysis of the results indicates that the relative concentrations of the silver(I) and thiosulfate ions in aqueous solution control the preferential complex formation [58]. The crystal structure of the commercially available complex $Ag(4\text{-}ClC_6H_4SO_3)$ has been determined [59].

The silver(I) complex $Ag(CO)\{B(OTeF_5)_4\}$, **(41)**, has been prepared and structurally characterised; this appears to be the first silver(I) carbonyl complex to be isolated but another feature of significant interest is the borate ligand. The complex $Ag(CO)_2\{B(OTeF_5)_4\}$ is formed by reacting $AgOTeF_5$ with the volatile compound $B(OTeF_5)_3$ under conditions of excess CO (25°C, 36 hr). Under vacuum, $Ag(CO)_2\{B(OTeF_5)_4\}$ loses one equivalent of CO to give **(41)**, which in turn, decomposes to the starting materials. Complex **(41)** is characterised in its IR spectrum by an absorption at 2204 cm^{-1} assigned to the mode ν_{CO}. This value compares with one of 2143 cm^{-1} for free carbon monoxide and 2165 cm^{-1} for the adduct $BH_3.CO$. Thus, it is concluded that the silver(I) centre is *not* back donating charge density to the CO π^* orbital. A crystallographic study of **(41)** shows that the silver(I) centre is in a trigonal planar environment with pertinent distances being Ag-C = 2.10 (1) Å, Ag-O = 2.324 (6) and 2.436 (7) Å, C-O = 1.077 (16) Å. The angle $\angle$Ag-C-O is 176 (1)°. There are two intra- and two inter-molecular close contacts between silver(I) and tellurium-associated fluorine atoms (Ag---F = 3.076 (8), 2.959 (6), 2.972 (6) and 3.028 (7) Å). The authors state that they will, in the future, be reporting the catalytic properties of new silver(I) carbonyl complexes [60].



(41)

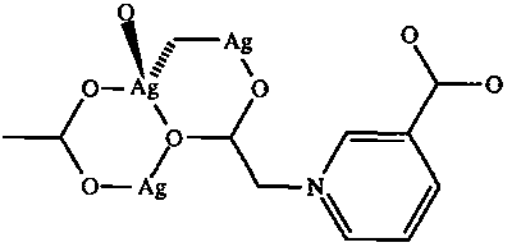
A series of papers deals with metal betaine interactions; five parts of this series have reported silver(I) coordination chemistry. Complexes involving the betaines $Me_3N^+CH_2CO_2^-$ (L) and $py^+CH_2CO_2^-$ (L') which have been prepared and fully characterised are $\{Ag_2L_2(H_2O)_2(NO_3)_2\}_n$ and $\{Ag_2L'_2(ClO_4)_2\}_n$. The two are structurally related; each is a centrosymmetric dimer, the disilver unit of which is supported by bridging carboxylate ligands (Ag-O bond distances lie in the range 2.21–2.41 Å). In the solid state, the dimeric units associate together via the carboxylate ligands (Ag-O bond lengths are in the range 2.47–2.50 Å) [61]. The structure of the complex $\{AgL'(NO_3)\}_n$ ($L' = py^+CH_2CO_2^-$) has also been reported; it is a one dimensional polymer. Each silver(I) centre is described as being distorted trigonal planar (i.e. an AgO_3-unit) and the Ag-O distances to the two different carboxylate ligands are 2.289 (1) and 2.334 (1) Å with the distance $Ag\text{-}O_{nitrato}$ being 2.434 (2) Å [62]. Coordination of the betaine ligand $Et_3N^+CH_2CO_2^-$, L, to silver(I) ions is observed in $Ag_2L_2(NO_3)_2$ and $[Ag_2L_2]_n[ClO_4]_{2n}$. These complexes possess structural features in common with the complexes described above; $Ag_2L_2(NO_3)_2$ and $[Ag_2L_2]_n[ClO_4]_{2n}$ both contain centrosymmetric Ag_2L_2-dimeric units with Ag-O bond lengths lying in the range 2.16 to 2.23 Å. For the coordinated nitrato ion in $Ag_2L_2(NO_3)_2$, Ag-O distances are 2.524 (3) and 2.619 (3) Å [63]. Further related polymeric complexes of formulae $[Ag_2L_2]_n[ClO_4]_{2n}$, $[Ag_2L_2(NO_3)_2]_n$, $[Ag_2L'_2(NO_3)_2]_n$, and $[Ag_2L'_2(H_2O)]_n[ClO_4]_{2n}.nH_2O$ involve the betaines $py^+CH_2CH_2CO_2^-$, L, and $Me_3N^+CH_2CH_2CO_2^-$, L'. Crystallographic data have been reported; one example is $[Ag_2(py^+CH_2CH_2CO_2^-)_2(NO_3)_2]_n$, (42) [64]. The structure of the polymeric complex $[AgL]_n.nH_2O$ where $HL = (HO_2C)C_5H_4N^+CH_2CO_2^-$ has been determined. A 2-dimensional network is present in the solid; part of the structure is shown in (43). Each silver(I) centre is in a distorted tetrahedral environment with distances Ag-O = 2.374 (5), 2.284 (5), 2.358 (5) and 2.570 (5) Å. One acetato group is tridentate and bridges a pair of silver(I) centers thereby contributing to the formation of unusual 6-membered chelate rings. The coordination sphere of the silver(I) ion is completed by a monodentate carboxylate group [65].



(42)

The structure of the complex formed between silver(I) ions and antimony(III) (+)-tartrate has been determined by X-ray diffraction analysis at 163 K. Although elemental analyses of the complex are consistent with an empirical formula of $AgSb(C_4H_2O_6)(H_2O)$, the X-ray data confirm a repeating tetrameric unit in a complex polymeric network. There are four distinct silver(I) sites;

one environment is 5-coordinate, one is 6-coordinate and two are 4-coordinate. The Ag-O distances lie in the range 2.156 to 2.666 Å. Both carboxylate and water groups are involved in some bridging interactions [66]. The preparation and crystal structure of $Sb_2Ag_2(HL)_4$, (H_3L = citric acid, **(44)**) have been reported. Centrosymmetric dimeric units, $Sb_2Ag_2(HL)_4$, are present in the crystal lattice with the silver(I) ions bridging between two antimony(III) citrate complexes. Each silver(I) centre is 3-coordinate, being surrounded by three *O*-donor atoms in a trigonal planar environment with distances of Ag-O = 2.314 (2), 2.661 (2) and 2.323 (2) Å [67].



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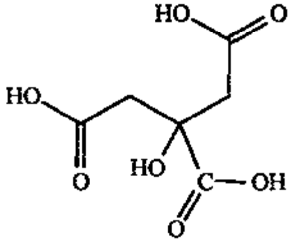

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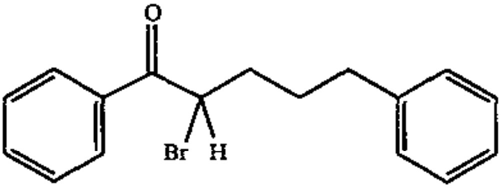
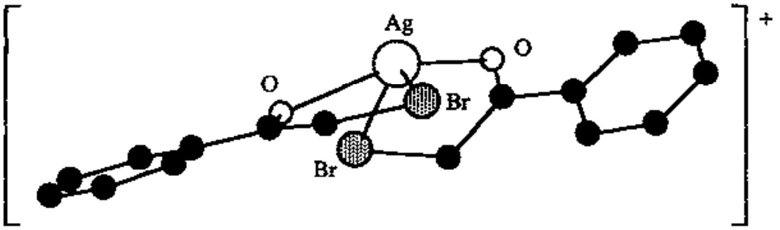


(45)

A study which provides structural information concerning the regioselective activation of α-bromoketones has been detailed. The α-bromoketones are activated through complexation with hard and soft Lewis acids and included are data for the complex $L.AgSbF_6$ where L = **(45)**. Ligand **(45)** was prepared by a previously reported method. The addition of L to $AgSbF_6$ leads to the formation of $L.AgSbF_6$ which has been structurally characterised. The silver ion interacts with the ketonic *O*-donor (Ag-O = 2.378 (4) Å) and with the bromo-group (Ag-Br = 2.738 (1) Å). A related complex in which the ligand, L', is $C_6H_5C(O)CH_2Br$ has been incorporated into the complex $L'_2.AgSbF_6$. The structure of this complex has also been determined and part of the structure is shown in **(46)**; the open face of the silver(I) ion interacts with the aromatic ring of another ligand in an η^6-mode. Important distances are Ag-O = 2.46 (1) and 2.39 (1) Å, Ag-Br = 2.740 (3) and 2.794 (4) Å, and Ag---F = 3.27 (1) Å [68].



(46)

A study of the extraction of the complex $K[Ag(CN)_2]$ and its gold(I) analogue by dicyclohexane-18-crown-6 in various media has been reported [18]. Complex formation between the cyclic ether dibenzo-30-crown-10 with metal(I) ions including silver(I) has been investigated by a conductometric method in the solvents 1,2-$C_2Cl_2H_4$, $MeNO_2$, MeCN and Me_2CO at 298 K. Stability constants (Table 2) have been determined [69].

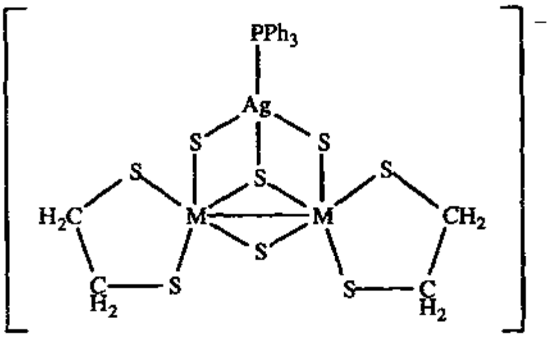
Table 2 Stability constants for complex formation between dibenzo-30-crown-10 and silver(I) ions in various solvents.

Solvent	1,2-$C_2Cl_2H_4$	$MeNO_2$	MeCN	Me_2CO
lg *K*	5.27	4.79	4.22	3.88

1.3.7 Complexes with sulfur donor ligands

Crystal structure data for thiolate complexes AgSR (R = $(CH_2)_2Me$, $(CH_2)_3Me$, $(CH_2)_5Me$, $(CH_2)_7Me$, Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-MeC_6H_4 and 4-$MeOC_6H_4$) have been obtained by using X-ray powder diffraction analysis; single crystals of the complexes could not be obtained. The solid state structure of each complex exhibits $^{2}_{\infty}\{AgSR\}$ layers in which the substituents are oriented at right angles to the layer of silver and sulfur atoms. If the steric requirements of R are too great, the layer structure is not feasible (e.g. R = CMe_3, 2-Cl-C_6H_4, 2-Me-C_6H_4 or 4-$Me_2C(CH_2Me)$-C_6H_4) [70].

The compounds $[Et_4N][(M_2AgS_4)(S_2C_2H_4)_2(PPh_3)].CH_2Cl_2$ (M = Mo or W) have been synthesised and structurally characterised. The preparative route involves the reactions of $[Et_4N]_2[(Mo_2S_4)(S_2C_2H_4)_2]$ or $[Et_4N]_2[(W_2S_4)(S_2C_2H_4)_2]$ with $Ag(PPh_3)(NO_3)$. In the anions $[(M_2AgS_4)(S_2C_2H_4)_2(PPh_3)]^-$, **(47)**, the silver(I) centre is coordinated to three sulfide ligands and to the triphenylphosphine donor. The Ag-S distances in **(47)** for M = Mo are 2.55 (1), 2.587 (9) and 2.71 (1) Å and for M = W, are 2.568 (4), 2.720 (5) and 2.573 (4) Å. The Mo-Mo and W-W distances are 2.881 (4) and 2.874 (1) Å, respectively but the Mo---Ag and W---Ag separations are are all > 3Å and are considered to be non-bonding [71].

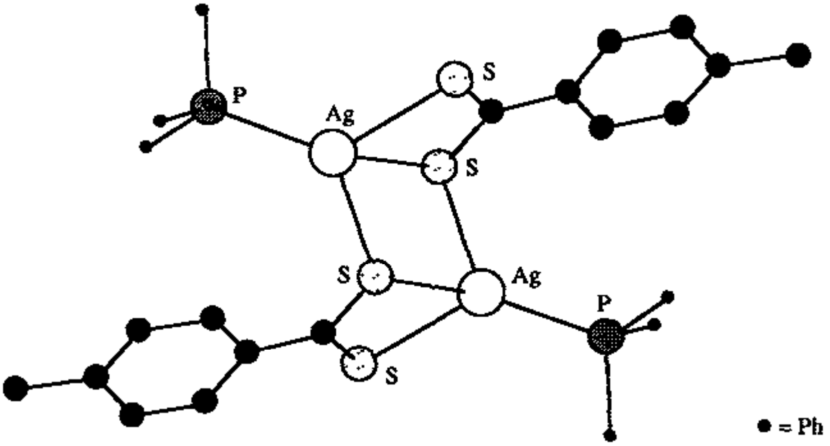


M = Mo or W

(47)

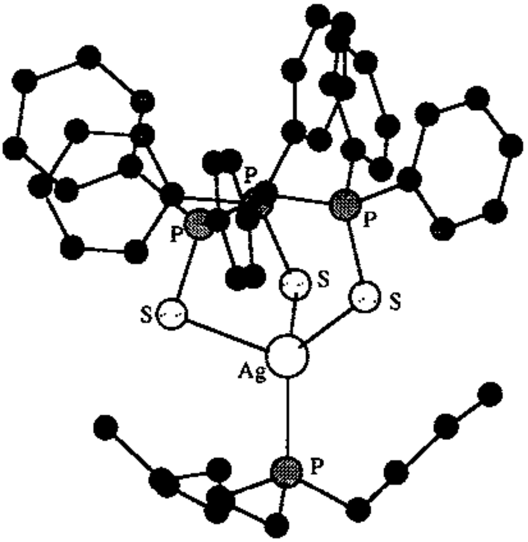
The molecular structure of the complex $3AgNO_3.2L$, in which L is the thioether **(48)**, has been elucidated. Each silver(I) ion is associated with five donor atoms but the coordination polyhedra are different. Atom Ag(2) is in a trigonal bipyramidal environment, atom Ag(3) is in a tetragonal pyramidal site, and the environment of atom Ag(1) is between those of Ag(2) and Ag(3). The nitrate ions are involved in direct bonding to the silver(I) ions. Ligand **(48)** coordinates to silver(I) ions in two modes to give a chair conformation with C_i symmetry and a gauche conformation [72].

(48)



(49)

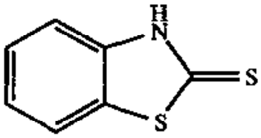
The solution dissociation and dynamic behaviour of the complexes $Ag(S_2CAr)L_2$ (Ar = Ph, 2-Me-C_6H_4 or 4-Me-C_6H_4; L = PPh_3) have been investigated by use of ^1H, ^{31}P and ^{13}C NMR spectroscopy. There is no evidence for any stable species in solution in which there are more than two PPh_3 ligands coordinated to one silver(I) centre. Monophosphine complexes of type $[Ag(S_2CAr)L]_2$ (L = phosphine) have also been prepared and the crystal structure of $[Ag(S_2C\text{-}C_6H_4\text{-}4\text{-}Me)(PPh_3)]_2$, **(49)**, has been determined. The dimeric structure is quite unusual and pertinent distances are Ag-S = 2.631 (2), 2.657 (2) and 2.692 (3) Å and Ag-P = 2.392 (2) Å [73]. Silver(I) complexes incorporating coordinated Me_2S ligands have been prepared. The complexes, $Ag(SMe_2)(NO_3)$ and $[Ag(SMe_2)_2][PF_6]$, have been characterised by using IR and ^1H NMR spectroscopies; a Raman spectroscopic analysis of $Ag(SMe_2)(NO_3)$ has also been carried out. $[Ag(SMe_2)_2][PF_6]$ is a photosensitive complex. The complex $[AgL_2][NO_3]$, where L = thiourea, has also been prepared [74]. The synthesis, and NMR spectroscopic and X-ray diffraction analyses of the silver(I) complex $^nBu_3PAgL$, **(50)**, where HL = $HC\{P(S)Ph_2\}_3$, have been described. The complex is prepared by reacting $AgNO_3$ with $^nBu_3P$ and $[^nBu_4N][L]$. The anion L^- functions as tripodal ligand and the Ag-S distances are 2.639 (3), 2.585 (2) and 2.670 (2) Å [75].



(50)

Members of the series of complexes $L(C_6Cl_5)_{3-x}(C_6F_5)_xPtAg(PPh_3)$ (x = 0–2; L = tht, PPh_3 or py) were described in Section 1.3.4. Other related complexes in which Ag-S bonds are a feature are $[Bu_4N][(C_6F_5)_4PtAg(tht)]$ and $[Bu_4N][\textit{cis}\text{-}(C_6F_5)_2(C_6Cl_5)_2PtAg(tht)]$. These salts are obtained by the stoichiometric reactions of $Ag(OClO_3)(tht)$ with $[Bu_4N]_2[Pt(C_6F_5)_4]$ or $[Bu_4N]_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C_6Cl_5)_2]$, respectively. Both new complexes have been structurally characterised. In $[(C_6F_5)_4PtAg(tht)]^-$, the Pt-Ag-S bond angle is 168.6 (2)° while in $[\textit{cis}\text{-}(C_6F_5)_2(C_6Cl_5)_2PtAg(tht)]^-$, the corresponding angle is 169.3 (2)°. The Ag-S distances are 2.401 (6) and 2.424 (8) Å, respectively [45].

The heterometallic complexes $(Ph_3P)_2(CO)_2Rh_2(\mu_3\text{-}L)_2Ag_2(OClO_3)_2$, $(cod)_2Rh_2(\mu_3\text{-}L)_2Ag(O_2ClO_2)$, $(cod)_2Ir_2(\mu_3\text{-}L)_2Ag(O_2ClO_2)$, $(cod)_2Rh_2(\mu_3\text{-}L)_2AgCl$, $(cod)_2Rh_2(\mu_3\text{-}L)_2Ag(O_2NO)$, $(cod)_2Rh_2(\mu_3\text{-}L)_2Ag(F_2BF_2)$, $(cod)_2Ir_2(\mu_3\text{-}L)_2AgCl$, $[(cod)_2Rh_2(\mu_3\text{-}L)_2Ag(PPh_3)]^+$, $[(cod)_2Ir_2(\mu_3\text{-}L)_2Ag(PPh_3)]^+$, and $[(cod)_2Rh_2(\mu_3\text{-}L)_2Ag(py)]^+$ in which HL = **(51)** have been prepared and characterised. The crystal structure of $(cod)_2Rh_2(\mu_3\text{-}L)_2Ag(O_2ClO_2)$ has been determined. Each ligand, L^-, is bonded to the silver(I) centre *via* a thiolato *S*-donor and to the rhodium atom via the *N*-donor giving a bridging mode for the ligand overall. The perchlorate ion also coordinates to the silver(I) centre. Important distances are Ag-O = 2.532 (17) Å, Ag-S = 2.609 (4) Å, and Ag-Rh = 2.796 (3) Å and angles are ∠O-Ag-O = 52.2 (5)° and ∠S-Ag-S = 104.1 (1)° [76].



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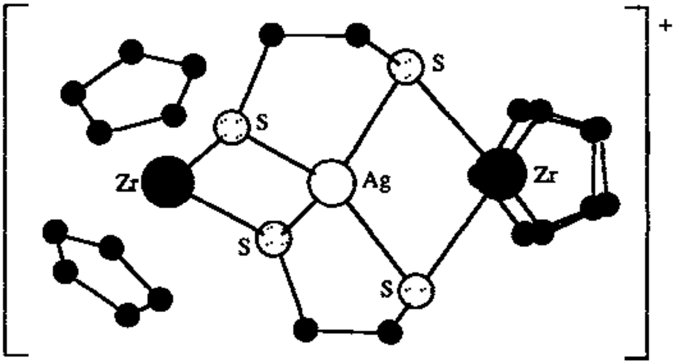
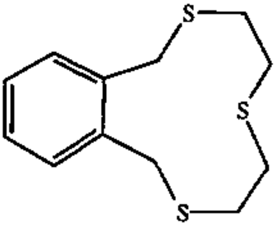


(52)

The reaction of Cp_2ZrMe_2 with propane-1,3-dithiol gives the dinuclear complex $Cp_2Zr(\mu\text{-}S(CH_2)_3S)_2ZrCp_2$ which acts as a macrocyclic ligand, L, reacting with $AgBPh_4$ to give yellow crystals of $[AgL][BPh_4]$ [77]. The preparations of further zirconocene dithiolates have been reported in a full paper [78]; $Cp_2Zr(\mu\text{-}S(CH_2)_2S)_2ZrCp_2$ also acts as a macrocyclic ligand and forms a 1:1 complex with silver(I) ions. The crystal structures of $[AgL]^+$ for L = $Cp_2Zr(\mu\text{-}S(CH_2)_nS)_2ZrCp_2$, $n = 2$ or 3, have been elucidated. For $n = 2$, the Ag-S distances in $[AgL]^+$, **(52)**, are 2.514 (5), 2.489 (5), 2.479 (5) and 2.497 (5) Å. For $n = 3$, the coordination sphere of the silver(I) ion is a flattened tetrahedron with bond lengths of Ag-S = 2.590 (5), 2.657 (5), 2.658 (5) and 2.599 (5) Å. The structure of $Cp_2Zr(\mu\text{-}S(CH_2)_3S)_2ZrCp_2$ has also been determined [77, 78].

The synthesis of the macrocyclic ligand **(53)**, L, and its reaction with $AgClO_4$ in the presence of PPh_3 have been detailed. The complex $[LAg(PPh_3)][ClO_4]$ has been structurally characterised; the silver(I) ion is tetrahedrally coordinated with three sites occupied by the three *S*-donor atoms of the macrocycle (Ag-S = 2.600 (1), 2.565 (1) and 2.554 (2) Å) [79]. The silver(I) complex $[AgL][ClO_4]$ where L = **(54)** has been prepared from $AgClO_4$ and L, and structurally characterised. In the solid state, the coordination geometry is distorted tetrahedral (Ag-S = 2.557 (3), 2.537 (3), 2.564 (3) and 2.540 (3) Å). The ^1H NMR spectrum of $[AgL][ClO_4]$ in acetonitrile exhibits a sharp resonance at δ +3.80 (assigned to S-CH_2-S protons) and a multiplet at δ +3.05 (assigned to S-CH_2CH_2-S protons). Changes in the spectrum as a function of temperature are intepreted in terms of a fluxional process in which all six sulfur donor atoms are involved in coordination to the silver(I) ion, four at any one instant [80].



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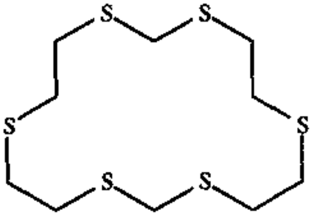

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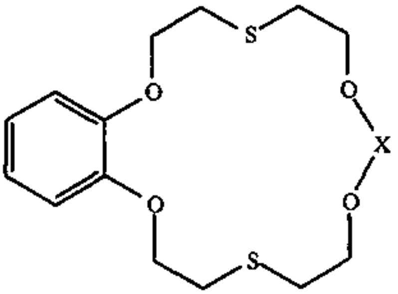
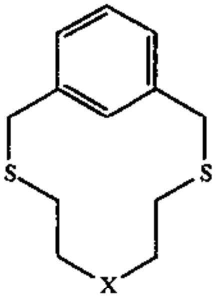


X = MeP(O), S(O), MeP(S)

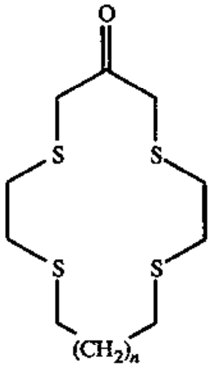
(55)



X = CH_2, O or S

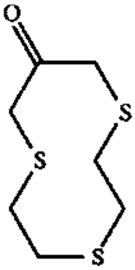
(56)

Members of the family of crown ethers **(55)**, L, can be prepared by reacting 1,2-$(HOCH_2CH_2SCH_2CH_2O)_2C_6H_4$ with XCl_2. Ligands L react with silver(I) ions to give complexes in which **(55)** coordinates via the sulfur atoms. When X = MeP(S), the thiophosphoryl *S*-atom also functions as a donor [81]. The cyclic ligands **(56)** have been synthesised and their use as sensors in solid state electrodes has been assessed. All the electrodes are highly selective with respect to silver(I) ions. It is proposed that in the complexes $[AgL]^+$, where L = **(56)**, the aliphatic chain is folded over the aromatic ring and thus the ligand encapsulates the silver(I) ion [82]. Synthetic routes to members of series of macrocyclic ligands which include **(57)**-**(59)** have been described. Each ligand is a crown thioether with a 2-oxopropane-1,3-diyl unit present in the ring. Conformational changes are observed on complex formation with silver(I) ions. For example, ligand L, **(57)**, for n = 1, reacts with $AgClO_4$ to give a dimeric complex $[Ag_2L_2][ClO_4]_2$; the cation $[Ag_2L_2]^{2+}$ is shown in structure **(60)**. Each silver(I) ion is coordinated by three sulfur atoms, two from one ligand and one from the second (Ag-S = 2.616 (2), 2.510 (1) and 2.457 (1) Å). The ketonic oxygen atom is also involved in the coordination sphere with the distance Ag-O being 2.612 (3) Å [83].



$n = 0$ or 1

(57)



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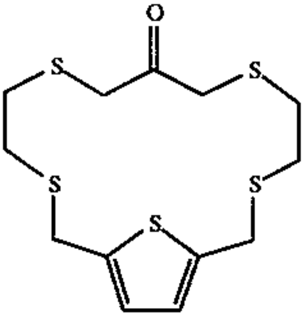

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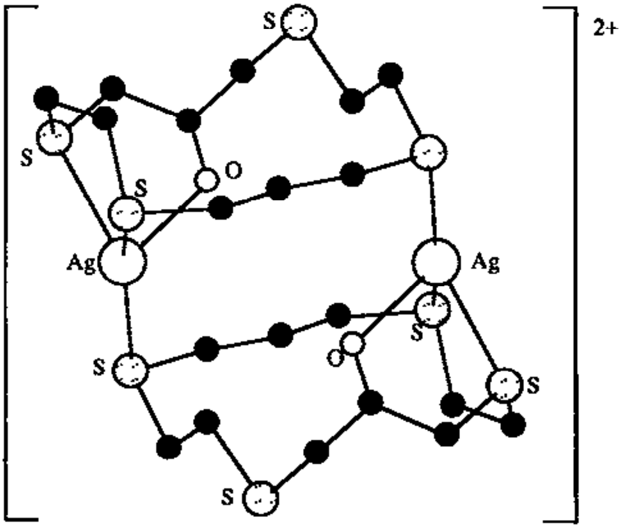

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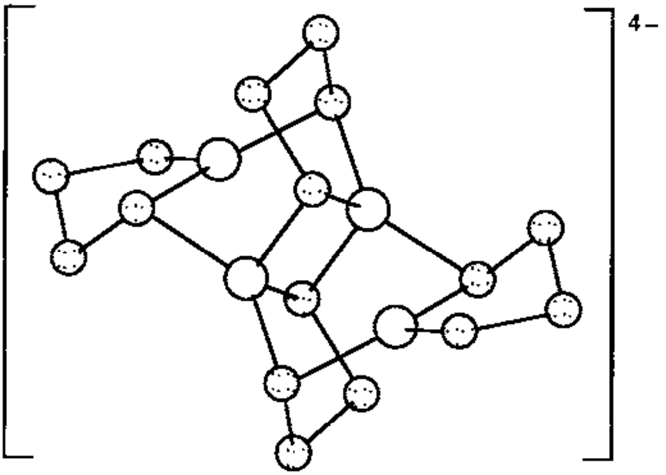

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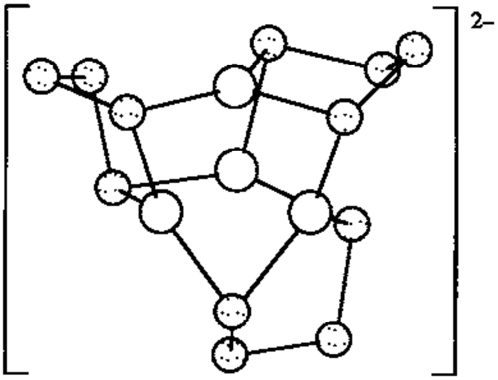
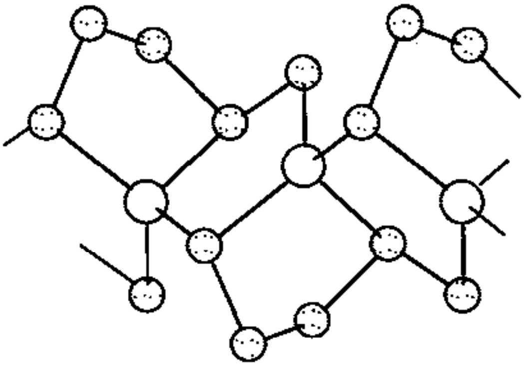


(62)

1.3.8 Complexes with selenium donor ligands

New silver(I) polyselenide complexes have been reported. A range of products arises as a function of the cation added to the reaction mixture of Na_2Se_5 and $AgNO_3$ in dmf. Products isolated and structurally characterised are $\{[Ph_4P][Ag(Se_4)]\}_n$, $\{[Me_4N][Ag(Se_5)]\}_n$, $\{[Et_4N][Ag(Se_4)]\}_4$ and $[Pr_4N]_2[Ag_4(Se_4)_3]$. Inspection of the structures reveals that both trigonal planar and tetrahedral environments are exhibited by the silver(I) ions in these complexes. The complex $\{[Et_4N][Ag(Se_4)]\}_4$ contains the discrete anion $[Ag(Se_4)]_4^{4-}$, **(61)**. This anion exhibits five-membered $AgSe_4$-chelate rings and pairs of silver(I) ions are bridged by one selenium atom; the mean Ag-Se distance is 2.67 (4) Å. The central unit of the dianionic complex $[Ag_4(Se_4)_3]^{2-}$, **(62)**, consists of four silver(I) ions arranged in a tetrahedral array with the Ag-Ag distances lying in the range 2.990 (1) and 3.193 (1) Å. Three Se_4^{2-} ligands support the tetrasilver core; the mean Ag-Se and Se-Se distances are 2.604 (15) Å and 2.345 (16) Å, respectively. In the solid state, the complex $\{[Me_4N][Ag(Se_5)]\}_n$ forms an infinite one-dimensional structure. The anions $[Ag(Se_5)]_n^{n-}$, **(63)**, are non-centrosymmetric and the chains run parallel to the crystallographic c-axis. The mean Ag-Se distance in **(63)** is 2.677 (3) Å and the Ag---Ag separations are 3.786 (4) Å [84]. The selenide Ag_2Se is discussed in Section 1.5.



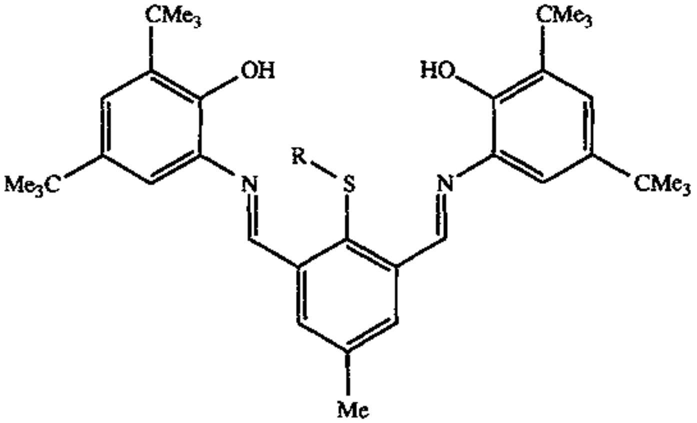
$n\ [AgSe_5]^-$

(63)

1.3.9 Complexes with mixed donor-atom ligands

Titration calorimetry has been used to determine the enthalpies of protonation and transition metal complex formation of the *N*-acylureas $Et_2NC(X)NHC(O)Ph$ (X = O, S or Se), (HL). The metals used in the study include silver(I) ions [85]. Anions derived from the Schiff base **(64)** (R = H) are potential dinucleating ligands. A convenient source of the ligand is as an *S*-protected ligand, i.e. **(64)** with R = $C(O)NMe_2$. The reaction of $Pd(MeCO_2)_2$ with the *S*-protected ligand gives $LPd_2(MeCO_2)$; during the reaction, deprotection occurs and the ligand is thus the di-Schiff base, L^{3-}. When $LPd_2(MeCO_2)$ reacts with PPh_3, the complex produced is $L'Pd(PPh_3)$ in which H_2L' = **(65)**; ligand rearrangement has occurred to give a benzoxazole. Silver(I) perchlorate reacts with $L'Pd(PPh_3)$ to give $[L'Pd(PPh_3)Ag]_2[ClO_4]_2$, the structure of which has been determined. The sulfur donor atoms of the ligand bridge between the two silver(I) centres to give a central Ag_2S_2-core in the complex cation $[L'Pd(PPh_3)Ag]_2^{2+}$ and each ligand functions as an *N,S*-chelate to one silver(I) ion. The *O,N,S*-donor set of the Schiff base ligand occupies three of the four sites of the square planar palladium(II) centre with the phosphine ligand completing the coordination shell.

Pertinent bond distances associated with the silver(I) ion in $[L'Pd(PPh_3)Ag]_2^{2+}$ are Ag-S = 2.867 (6) and 2.506 (6) Å and Ag-N = 2.16 (2) Å [86].



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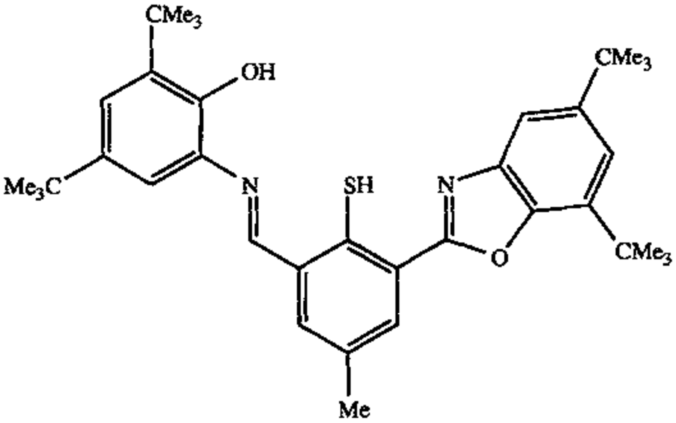
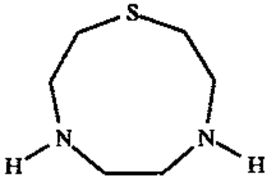


(65)

A variety of complexes contining *N,S*-donor ligands has been reported. Complex formation between the macrocyclic ligand L, **(66)**, and silver(I) ions has been studied and the tetrameric complex, $[Ag_4L_4][CF_3SO_3]_4$ has been structurally characterised. The complex cation, $[Ag_4L_4]^{4+}$, is schematically represented in structure **(67)**. The four $[AgL]^+$-units are connected together *via* sulfur donor bridges to yield a centrosymmetric tetramer. The Ag-S bond distances are 2.332 (8), 2.369 (9), 2.306 (8) and 2.339 (9) Å and Ag-N distances are 2.403 (2), 2.705 (2), 2.635 (2) and 2.415 (2) Å [87].



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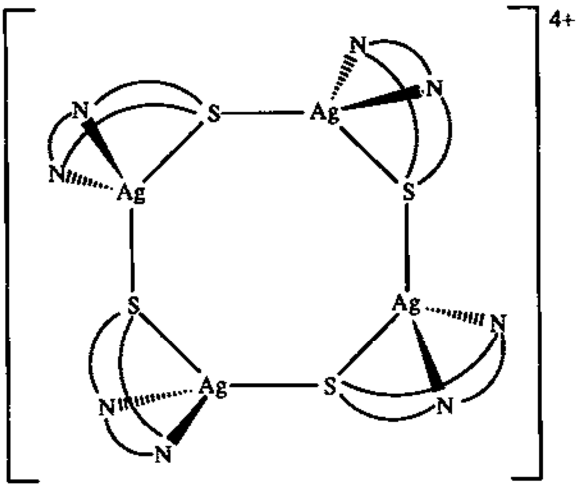

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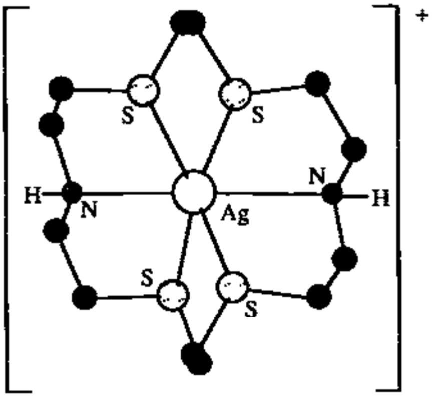
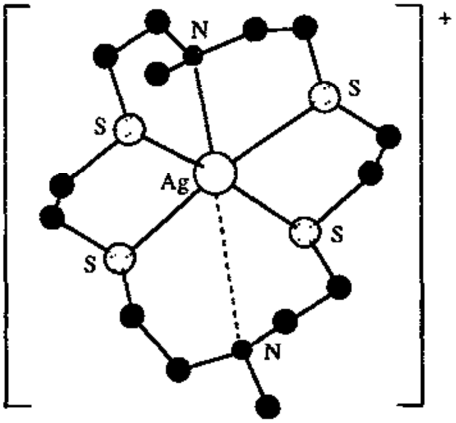


(68)

The reactions of silver(I) nitrate with the two cyclic ligands 1,4,10,13-tetrathia-7,16-diazacyclooctadecane, L, and *N,N'*-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane, L', yield the silver(I) complex cations $[AgL]^+$, **(68)**, and $[AgL']^+$, **(69)**. These have been structurally characterised as the $[PF_6]^-$ and $[BPh_4]^-$ salts, resepectively. The cation **(68)** exhibits a *rac*-configuration, and the silver(I) ion is in a distorted octahedral environment with Ag-S = 2.630 (4), 2.664 (4), 2.719 (4) and 2.774 (4) Å and Ag-N = 2.533 (10) and 2.817 (15) Å. The crystal structure of **(69)** suffers from a disorder and the cation exhibits two configurations, which differ in the orientations of the donor atoms. The silver(I) ion is 5-coordinate. In the dominant component of the disordered structure, the bond lengths around the silver(I) centre are Ag-S = 2.583 (4), 2.819 (3), 2.663 (4) and 2.673 (4) Å and Ag-N = 2.517 (11) Å; the remote *N*-donor is 3.684 (11) Å distant from the silver(I) ion [88]. Complex formation between the pentadentate macrocyclic ligand 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dithiacycloheptadecane, L, and silver(I) ions has been investigated. The ligand reacts with $AgClO_4$ to yield white crystals of $[AgL][ClO_4]$. The structure of the new complex has been determined and in the cation, **(70)**, the data confirm that L functions as an N_3S_2-donor set. The coordination geometry is highly distorted; the silver(I) ion lies 0.29 Å out of the plane containing two of the nitrogen and one of the sulfur donor atoms (Ag-N = 2.367 (5) and 2.392 (6) Å and Ag-S = 2.652 (3) Å). The remaining two donor atoms subtend an angle of 145.0 (1)° at the silver(I) centre and the distances are Ag-S = 2.713 (2) Å and Ag-N = 2.522 (6) Å [89].



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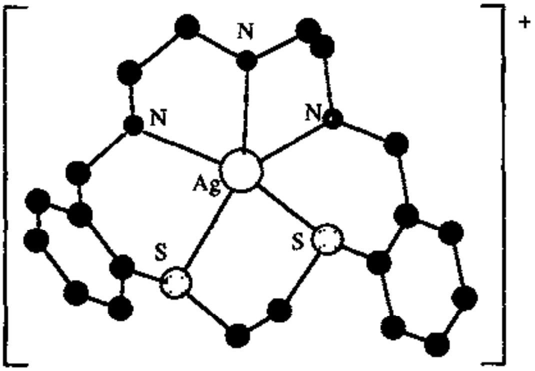

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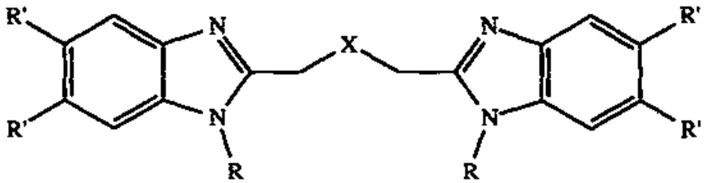


X = S, CH_2SCH_2, $S(CH_2)_nS$ (n = 1-3), $CH_2SCH_2SCH_2$

R = H, C_8H_{17}, $C_{12}H_{25}$ R' = H, Me

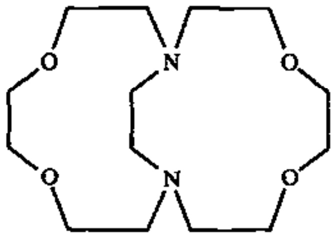
(71)

A series of ligands of type (71) has been synthesised; some of the ligands are new. The aim of the study is to assess metal ion selectivity in single and multiple phases and to identify a ligand that is able to transport silver ions selectively through a liquid membrane. Fast atom bombardment mass spectrometry and ^1H NMR spectroscopy are used for the single-phase studies. The results of molecular mechanics calculations (which assumed that both the tertiary nitrogen atoms and the sulfur atoms were involved in coordination to a tetrahedrally sited silver(I) ion) are discussed [90].

Ligand (72), L, is flexible and is able to wrap around a metal ion in a "clam-like" manner. Stability constant data for the complex cation $[AgL]^+$ have been determined at 298.2 K in various solvents (Table 3). The work reported includes a study of related lithium complexes and the use of ^7Li NMR spectroscopy to investigate the solution thermodynamics of the system [91].

Table 3 Stability constants for complex formation between ligand (72) and silver(I) ions in various solvents.

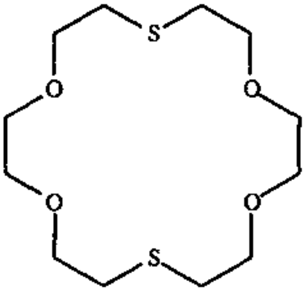
Solvent	MeCN	Me_2CO	H_2O	MeOH	py	dmf	Et_2NCHO
lg *K*	9.4	13.1	6.0	10.2	5.0	9.4	8.2



(72)

Complex formation between silver(I) ions and the crown thioethers, each containing a propan-2-one unit, was described in Section 1.3.7; the ligands include **(57)**, **(58)** and **(59)**. Ligand **(57)** with $n = 1$ reacts with $AgClO_4$ to yield the complex $[Ag_2L_2][ClO_4]_2$; the cation $[Ag_2L_2]^{2+}$ is shown in structure **(60)** [83].

Potentiometric and calorimetric methods have been used to determine stability constants (Table 4) and values of ΔH and ΔS for complexes between silver(I), mercury(II) and lead(II) ions and crown thioethers including **(73)** and **(74)**. ^{13}C NMR spectroscopic shift data and spin-lattice relaxation times have been recorded for the ligand **(74)**, in the presence and absence of the metal ions; these results, taken along with the thermodynamic data, provide detailed information about the metal ion-ligand interactions. The silver(I) ion interacts strongly (more strongly than does the mercury(II) ion) with the *S*-donor atom of **(74)**. One conclusion of the study is that the complexation between the ligands and the metal ions is driven by enthalpy changes [92].



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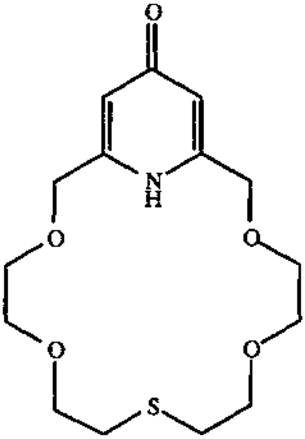


(74)

Table 4 Stability constants for complex formation between ligands **(73)**, **(74)** and $[(\mathbf{74})]^-$ with silver(I) ions in aqueous solution (298 K).

Ligand	(73)	(74)	$[(74)]^-$
lg *K*	5.27 (5)	5.36 (1)	9.44 (1)

1.4 CLUSTERS

This section of the review highlights selected silver-containing cluster molecules; the emphasis is on homonuclear clusters or clusters in which silver atoms predominate in the metal core. Transition metal (M) clusters in which one or two silver-centred fragments bridge M_2-edges or cap M_3-faces are not generally included.

Silver clusters, Ag_n, which are produced by a gas aggregation method, have been studied by mass spectroscopy. Results show anomalies in the relative abundances of singly and multiply charged species [93]. The cocondensation of silver atoms and silver(I) halides leads to non-stoichiometric clusters of formula Ag_nX_m where $0 \leq m \leq n$ and X = F and Br. Methods of controlling the degree of halogenation are described. Mass spectral data for the clusters are used to probe their stability. The results support the presence of a metallic core in each halide cluster [94]. Further work by the same authors investigates the fluoride clusters Ag_nX_m where $0 \leq m \leq n$ and $n \geq 2$. The clusters are formed by evaporating silver metal into an argon atmosphere enriched with SF_6 [95]. When isotopically (^{107}Ag) enriched silver foil is sputtered in the source of a double-focusing mass spectrometer in the presence of methyl iodide, clusters of the general formula $[Ag_nI_m]^k$ (k is either a positive or negative charge) are produced in addition to Ag_n clusters [96].

Crystal structures of dehydrated silver(I)- and calcium(II)-exchanged zeolites treated at 250°C with 0.1 torr of gaseous rubidium have been determined. The number of silver(I) ions per unit cell in each structure is 2.2, 2.4 and 4.8, respectively. The silver ions form Ag_6-clusters which reside at the centres of significant cavities in the crystal lattice. Each Ag_6-cluster is stabilised by interactions with up to thirteen rubidium ions [97].

The mixed silver-gold cluster cation $[(Ph_3P)_{10}Au_{13}Ag_{12}Br_8]^+$ has been isolated as the hexafluoroantimonate salt and has been structurally characterised. The metal core has an exact staggered-eclipsed-staggered configuration. The structure provides evidence for icosahedral units as building blocks in large cluster structures [98]. Amongst a series of gold-platinum clusters is $[Pt(CO)Ag_2(AuPPh_3)_7][NO_3]_3$. This compound has been prepared by treating either $[Pt(CO)(AuPPh_3)_8][NO_3]_2$ or $[Pt(CO)Ag(AuPPh_3)_8][NO_3]_3$ with $Ag(PPh_3)(NO_3)$. The compound $[Pt(CO)(AgCl)_2(AuPPh_3)_7][NO_3]$ has also been prepared. Although crystallographic data are not available for these silver-containing clusters, a related copper(I) derivative has been structurally characterised [99]. The synthesis, ^{31}P NMR spectroscopic data and molecular structure of $Pt_3Ag(OSO_2CF_3)(\mu\text{-}CO)_3\{P(c\text{-}C_6H_{11})_3\}_2(dppp)$ have been reported. The $\{Ag(OSO_2CF_3)\}$-unit caps the Pt_3-framework (Ag-Pt = 2.927 (3), 2.919 (4) and 2.690 (3) Å). Within the $\{Ag(OSO_2CF_3)\}$-fragment, there is one short Ag-O bond length (2.30 (3) Å) and one long separation (Ag----O = 2.95 (4) Å) [100].

1.5 SOLID STATE COMPOUNDS

The thermal decomposition of silver(I) carbonate under CO_2 (1 to 40 atmos) has been studied by differential thermal analysis. Three endothermic peaks are observed. The first peak ($T \approx 200°C$) is assigned to a phase transition from the normal to high temperature form of Ag_2CO_3. The second peak occurs between 200° and 400°C, the variation being a function of carbon dioxide pressure. This peak is assigned to surface decarbonation ($Ag_2CO_3 \rightarrow Ag_2O$). The final peak is at 400°C and this is assigned to the bulk sample undergoing decarbonation and the simultaneous reduction of Ag_2O to silver metal [101]. Related work has been reported separately [102]. The thermal decomposition of $Ag_2C_2O_4$ under isothermal conditions under atmospheres of nitrogen, air, oxygen or carbon dioxide or under vacuum has been investigated. Mechanistic details of the decomposition process have been described [103].

Silver(II) oxide is a strong oxidising agent and a new process for its production in yields of up to 98% has been outlined. The method involves the oxidation of aqueous, alkaline silver(I) nitrate by SO_2 and O_2, or by sulfite ion and O_2 [104]. A new silver oxide has been observed in a cyclic voltammetric study; the anodic oxidation of silver(I) ions in aqueous solution yields the oxide which, X-ray powder diffraction data reveal, is an intergrowth of Ag_2O_3 and Ag_3O_4 [105].

The layered structure of the thiolate AgSR (R = various) was described in Section 1.3.7 [70]. The selenide Ag_2Se has been prepared by a melt-growth technique and coprecipitation. The results of X-ray diffraction and differential thermal analyses have been reported [106].

The results of an electrochemical study of powdered silver(I) chromate have been reported. Voltammetric curves have been recorded in acetic and formic acids; a partially reversible cathodic process is observed [107].

The new compound AgPbOBr has been synthesised from PbO and AgBr; the lattice of AgPbOBr represents a new structure-type, falling between the Sillén- and Aurivillius-phases. Pertinent distances around the silver(I) centres are Ag-Br = 2.81 (2) and 2.880 (5) Å [108]. Silver(I) germanate sulfate, $Ag_6(GeO_4)(SO_4)$, is prepared from Ag_2O, GeO_2 and Ag_2SO_4 in a silver(I) nitrate flux at 430°C under oxygen at a pressure of 2 kbar. The compound $Ag_6(GeO_4)(SO_4)$ is isostructural with the corresponding silicate and exhibits "folded bands" of silver(I) ions [109]. The preparation of $BaAg_2Hg_2O_4$ has been reported. An X-ray crystallographic study of this compound shows that it possesses tetragonal symmetry; each of the silver(I) and mercury(II) ions exhibits a "dumb-bell" like oxygen-coordination sphere [110].

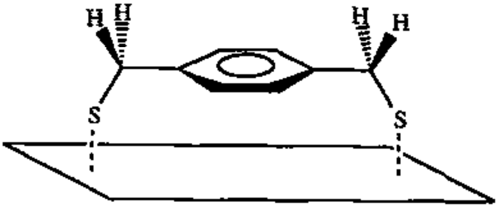
Several solid state silver(I) phosphate complexes have been detailed. The high and low temperature forms of the phosphate $AgZnPO_4$ have been investigated; a phase transition occurs at 666°C. The high temperature form possesses a beryllonite structure, whilst the low temperature form exhibits a lattice related to that of tridymite. Solid state ^{31}P NMR spectroscopic data have been recorded for both forms of $AgZnPO_4$ [111]. The crystal structure of the cyclohexaphosphate $Ag_3(NH_4)_3P_6O_{18}.H_2O$ has been determined. Trigonal symmetry is exhibited by the compound; the silver(I) ion is 5-coordinate with Ag-O distances lying in the range 2.360-2.652 Å [112]. The structure of $Ag_4Li_2P_6O_{18}.2H_2O$ has also been elucidated; it crystallises in the space group $P\bar{1}$. The $[P_6O_{18}]^{6-}$ rings are centrosymmetric. Each lithium ion is tetrahedrally sited at the centre of an O_4-donor set, three *O*-donor atoms are associated from the phosphate ion and one *O*-donor atom is provided by a water molecule. Pairs of lithium and silver(I) ions are linked via an oxygen bridge, the *O*-atom belonging to a $[P_6O_{18}]^{6-}$ unit; the silver(I) ions reside between $[Li_2P_6O_{18}]_n$-layers. There are two silver(I) environments present in the lattice; one is 5-coordinate and the other 6-coordinate [113].

The silicate Ag_2SiO_3 has been synthesised both as a powder and single crystals from Ag_2O and SiO_2 under hydrothermal conditions. X-ray diffraction analysis shows that the solid state lattice exhibits a single chain catena-polysilicate; the Ag-O distances lie in the range 2.147 (8)-2.404 (8) Å [114]. The Ag_2O-SiO_2 system has been studied for a Ag:Si ratio of 3:1. The compound $Ag_6Si_2O_7$ forms under an oxygen pressure of 0.2 GPa and at a temperature of 560–580°C. At $T < 470°C$, red crystals of $(Ag_4SiO_4)_2.(Ag_{10}Si_4O_{13})$ have been isolated. This transforms to $Ag_6Si_2O_7$ at $T = 495$

± 10°C. $(Ag_4SiO_4)_2.(Ag_{10}Si_4O_{13})$ has been structurally characterised; the lattice is composed of orthosilicate and catena-tetrasilicate anions. There is some degree of silver-silver bonding with the shortest contact being 2.821 Å [115].

1.6 SURFACES

This section includes reports of papers relating to surface studies in which coordination modes of silver atoms are discussed. Adsorption of the ligand $Me_2NC(S)Me$ on to the surface of silver electrodes has been studied by SERS. An analysis of the spectra is made by comparing the results to Raman spectroscopic data for the ligand and infrared spectra for various metal complexes incorporating $Me_2NC(S)Me$. The authors conclude that $Me_2NC(S)Me$ coordinates to the silver surface via the *S*-donor atom [116].



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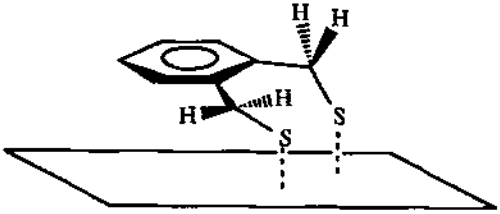

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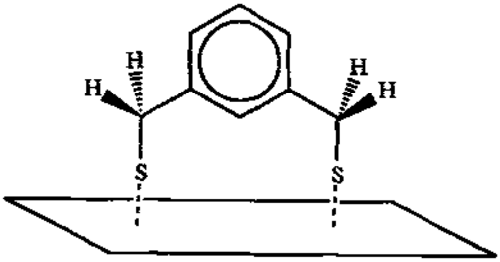

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The technique of SERS has also been used to investigate the interactions of pentamethylene sulfide, 1,4-dithiane and 1,3,5-trithiane with silver surfaces; the results are consistent with Ag-S bonding. One observation is that adsorption does not cause C-S ring-bond cleavage and a chair conformation for the rings is retained. The carbon-sulfur rings lie parallel to the silver surface [117]. In a related investigation by the same research group, SERS has been applied to probe the adsorption of 1,2-, 1,3- and 1,4-$(HSCH_2)_2C_6H_4$ on silver surfaces. Each ligand (as the dithiolate) binds to the surface via the *S*-donor atoms but the orientation of the aromatic ring depends on the relative positions of the two thiolate groups. The proposed surface structures are **(75)** for 1,4-$(HSCH_2)_2C_6H_4$, **(76)** for 1,2-$(HSCH_2)_2C_6H_4$, and **(77)** for the 1,3-isomer. In **(75)** and **(76)**, the aromatic ring lies parallel (or approximately so) to the silver surface, whereas in **(77)**, a perpendicular mode of attachment is suggested by the data [118]. The interaction between an evaporated-silver surface and poly(*p*-phenylene sulfide) has been studied by XPS. Molecular orbital calculations, (carried out at the Hartree-Fock level), and molecular mechanics calculations compliment the spectroscopic investigation. The geometries used for the sulfur donor bonded to a silver atom are trigonal pyramidal and trigonal planar [119].

The adsorption of porphyrins with silver, silver halide and silver(I) oxide colloids and the formation of silver(II) porphyrin complexes was detailed in Section 1.2 [10-12].

REFERENCES

1. C.E. Housecroft, *Coord. Chem. Rev.*, 115 (1992) 141.
2. J.L. Ennis and E.S. Shanley, *J. Chem. Ed.*, 68 (1991) A6.
3. J.A. Murphy, A.H. Ackerman and J.K. Heeren, *J. Chem. Ed.*, 68 (1991) 602.
4. B. Zemva, K. Lutar, A. Jesih, W.J. Casteel, A.P. Wilkinson, D.E. Cox, R.B. Vondreele, H. Borrmann and N. Bartlett, *J. Am. Chem. Soc.*, 113 (1991) 4192.
5. L.J. Kirschbaum and Y.F. Sun, *Inorg. Chem.*, 30 (1991) 2360.
6. Y.F. Sun, L.J. Kirschbaum and I. Kouadio, *J. Chem. Soc., Dalton Trans.*, (1991) 2311.
7. H.N. Po, E. Brinkman and R.J. Doedens, *Acta Crystallogr., Sect. C*, 47 (1991) 2310.
8. M.A.S. Goher and A.E.H. Abdou, *Acta Chim. Hung.*, 128 (1991) 219; *Chem. Abstr.* 115, (1991) 125631f.
9. H.C. Tung, P. Chooto and D.T. Sawyer, *Langmuir*, 7 (1991) 1635.
10. B. Vlčková, P. Matejka, P. Pančoška, V. Baumruk and V. Král, *Inorg. Chem.*, 30 (1991) 4103.
11. C.B. Mou, D.M. Chen, X.Y. Wang, B.Z. Zhang, T.J. He, H.W. Xin and F.C. Liu, *Chem. Phys. Lett.*, 179 (1991) 237.
12. C.B. Mou, D.M. Chen, X.Y. Wang, B.Z. Zhang, T.J. He, H.W. Xin and F.C. Liu, *Spectrochim. Acta, Part A*, 47 (1991) 1575.
13. A. Kajiwara, M. Kamachi and H. Maeda, *Polym. J. (Tokyo)*, 23 (1991) 343; *Chem. Abstr.* 114, (1991) 229749w.
14. E. Apra, E. Stefanovich, R. Dovesi and C. Roetti, *Chem. Phys. Lett.*, 186 (1991) 329.
15. G. Helgesson and S. Jagner, *Inorg. Chem.*, 30 (1991) 2574.
16. H. Reuter, *Angew. Chem., Int. Ed., Engl.*, 30 (1991) 1482.
17. R. Usón, J. Forniés, M. Tomás and I. Ara, *Inorg. Chim. Acta*, 186 (1991) 67.
18. M. Tromp, M. Burgard and A. Elbachiri, *Analusis*, 19 (1991) 97; *Chem. Abstr.* 114 (1991) 235867z.
19. K. Gyoryova and V. Balek, *Thermochim. Acta*, 179 (1991) 109.
20. J.-L. Wang, M. Sun, F.-M. Miao, S.-Y. Wu, F.-S. Gong and X.-H. Duan, *Acta Crystallogr., Sect. C*, 47 (1991) 2203.
21. D. Britton, *Acta Crystallogr., Sect. C*, 46 (1990) 2297.
22. J. Vincente, M.-T. Chicote, M.C. Lagunas and P.G. Jones, *J. Chem. Soc., Dalton Trans.*, (1991) 2579.
23. Y. Marcus, *J. Chem. Soc., Dalton Trans.*, (1991) 2265.

24. Z. Žák, A. Růžicka and T. Głowiak, *Can. J. Chem.*, 69 (1991) 1080.
25. S. Hamada, Y. Kudo and S. Ichikawa, *Colloid Polym. Sci.*, 269 (1991) 187; *Chem. Abstr.* 114 (1991) 189643y.
26. J.F. Modder, J.-M. Ernsting, K. Vrieze, M. Dewit, C.H. Stam and G. van Koten, *Inorg. Chem.*, 30 (1991) 1208.
27. Effendy, L.M. Engelhardt, P.C. Healy, B.W. Skelton and A.H. White, *Aust. J. Chem.*, 44 (1991) 1585.
28. F. Iwasaki, M. Hirota, N. Yamazaki and M. Yasui, *Acta Crystallogr., Sect. C*, 47 (1991) 2406.
29. V.P. Shram and N.R. Molchanova, *Ukr. Khim. Zh. (Russ. Ed.)*, 57 (1991) 124; *Chem. Abstr.*, 115 (1991) 58297m.
30. S. Kitagawa, S. Matsuyama, M. Munakata and T. Emori, *J. Chem. Soc., Dalton Trans.*, (1991) 2869.
31. K. Tani, T. Mihana, T. Yamagata and T. Saito, *Chem. Lett.*, (1991) 2047.
32. V.V. Davydov, V.I. Sokol, M.A. Poraikoshits, B.E. Zaitsev, V.A. Belonosov and E.V. Balebanova, *Koord. Khim.*, 17 (1991) 976.
33. C.-F. Lee and S.-M. Peng, *J. Chin. Chem. Soc. (Taipei)*, 559 (1991) 38; *Chem. Abstr.*, 116 (1992) 165041r.
34. L.M. Engelhardt, G.E. Jacobsen, W.C. Patalinghug, B.W. Skelton, C.L. Raston and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1991) 2859.
35. A.K. Deb, M. Kakoti and S. Goswami, *J. Chem. Soc., Dalton Trans.*, (1991) 3249.
36. B. Xu, D. Chen, W.X. Tang, K.B. Yu and Z.Y. Zhou, *Acta Crystallogr., Sect. C*, 47 (1991) 1805.
37. D. Carmona, F.J. Lahoz, L.A. Oro, M.P. Lamata and S. Buzarra, *Organometallics*, 10 (1991) 3123.
38. H. Schmidbaur, A. Mair, G. Muller, J. Lachmann and S. Gamper, *Z. Naturforsch, Sect. B*, 46 (1991) 912.
39. E.C. Constable, J.M. Holmes and P.R. Raithby, *Polyhedron*, 10 (1991) 127.
40. E.C. Constable, M.S. Khan, M.C. Liptrot, J. Lewis and P.R. Raithby, *Inorg. Chim. Acta*, 179 (1991) 239.
41. J. de Mendoza, E. Mesa, J.-C. Rodriguez-Ubis, P. Vazquez, F. Vogtle, P.-M. Windschief, K. Rissanen, J.-M. Lehn, D. Lilienbaum and R. Ziessel, *Angew. Chem., Int. Ed., Engl.*, 30 (1991) 1331.
42. C. Stockheim, K. Weighardt, B. Nuber, J. Weiss, U. Flörke and H.-J. Haupt, *J. Chem. Soc., Dalton Trans.*, (1991) 1487.
43. M. Fujiwara, H. Wakita, T. Matsushita and T. Shono, *Anal. Sci.*, 7 (1991) 483.
44. L.-S. Zheng, H.-H. Yang and Q.-E. Zhang, *J. Struct. Chem. (Jiegou Huaxue)*, 10 (1991) 97.
45. R. Usón, J. Forniés, M. Tomás, I. Ara, J.M. Casas and A. Martín, *J. Chem. Soc., Dalton Trans.*, (1991) 2253.
46. C.S.W. Harker, E.R.T. Tiekink and M.W. Whitehouse, *Inorg. Chim. Acta*, 181 (1991) 23.
47. C.M. Che, H.K. Yip, D. Li, S.M. Peng, G.H. Lee, Y.M. Wang and S.T. Liu, *J. Chem. Soc., Chem. Commun.*, (1991) 1615.
48. V. Saboonchian, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *Polyhedron*, 10 (1991) 737.
49. S.W. Carr, X.L.R. Fontaine and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1991) 1025.
50. J. Ellermann and K.J. Meier, *Z. Anorg. Allg. Chem.*, 603 (1991) 77.
51. S. Attar, N.W. Alcock, G.A. Bowmaker, J.S. Frye, W.H. Bearden and J.H. Nelson, *Inorg. Chem.*, 30 (1991) 4166.
52. B.A. Arbuzov, G.N. Nikonov, A.A. Karasik and K.M. Enikeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1991) 906; *Chem. Abstr.*, 115 (1991) 148912n.
53. A.J. Arduengo, H.V.R. Dias and J.C. Calabrese, *J. Am. Chem. Soc.*, 113 (1991) 7071.
54. A.J. Arduengo, H.V.R. Dias and J.C. Calabrese, *Inorg. Chem.*, 30 (1991) 4880.
55. A. Bonardi, A. Cantoni, C. Pelizzi, G. Pelizzi and P. Tarasconi, *J. Organomet. Chem.*, 402 (1991) 281.
56. P. Parasher, D.K. Misher and P.D. Sharma, *Transition Metal Chem. (London)*, 16 (1991) 571.
57. P. Parasher, J. Hussain and P.D. Sharma, *Int. J. Chem. Kinet.*, 23 (1991) 473.
58. G. Bernardinelli, E.A.C. Lucken and M. Costines, *Z. Kristallogr.*, 195 (1991) 145.
59. J.O. Hill and S. Lim, *Thermochim. Acta*, 188 (1991) 255.
60. P.K. Hurlburt, O.P. Anderson and S.H. Strauss, *J. Am. Chem. Soc.*, 113 (1991) 6277.
61. X.-M. Chen and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1991) 1219.
62. X.-M. Chen and T.C.W. Mak, *Polyhedron*, 10 (1991) 1723.
63. W.-Y. Huang, L. Lu, X.-M. Chen and T.C.W. Mak, *Polyhedron*, 10 (1991) 2687.
64. X.-M. Chen and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1991) 3253.

65. X.-M. Chen and T.C.W. Mak, *Aust. J. Chem.*, 44 (1991) 1783.
66. D.S. Sagatys, G. Smith, D.E. Lynch and C.H.L. Kennard, *J. Chem. Soc., Dalton Trans.*, (1991) 361.
67. D.W. Hartley, G. Smith, D.S. Sagatys and C.H.L. Kennard, *J. Chem. Soc., Dalton Trans.*, (1991) 2735.
68. T. Laube, A. Weidenhaupt and R. Hunziker, *J. Am. Chem. Soc.*, 113 (1991) 2561.
69. M.K. Amini and M. Shamsipur, *Inorg. Chim. Acta*, 183 (1991) 65.
70. I.G. Dance, K.J. Fisher, R.M.H. Banda and M.L. Scudder, *Inorg. Chem.*, 30 (1991) 183.
71. Z. Nianyong, W. Xintao and L. Jiaxi, *J. Chem. Soc., Chem. Commun.*, (1991) 235.
72. P.-X. Shao, X.-K. Yao, H.G. Wang, R.-J. Wang, L.-W. Luo, W.-H. Wang, W.-Z. Wang, Z.-T. Wang, *Acta Chim. Sinica (Huaxue Xuebao)*, 49 (1991) 677; *Chem. Abstr.*, 115 (1991) 219484n.
73. A.M.M. Lanfredi, F. Ugozzoli, F. Asaro, G. Pellizer, N. Marisich and A. Camus, *Inorg. Chim. Acta*, 190 (1991) 71.
74. M.M. El-Etri and W.M. Scovell, *Inorg. Chim. Acta*, 187 (1991) 201.
75. S.O. Grim, S.A. Sangokoya, A.L. Rheingold, W. McFarlane, I.J. Colquhoun and R.D. Gillard, *Inorg. Chem.*, 30 (1991) 2519.
76. M.A. Ciriano, J.J. Pereztorrente, L.A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, (1991) 255.
77. D.W. Stephan, *J. Chem. Soc., Chem. Commun.*, (1991) 129.
78. D.W. Stephan, *Organometallics*, 10 (1991) 2037.
79. B. de Groot, G.R. Giesbrecht, S.J. Loeb and G.K.H. Shimizu, *Inorg. Chem.*, 30 (1991) 177.
80. B. de Groot and S.J. Loeb, *Inorg. Chem.*, 30 (1991) 3103.
81. G.G. Talanova, A.V. Podgornyi, V.A. Zasorina and K.B. Yatsimirskii, *Dokl. Akad. Nauk SSSR, (Russ)*, 318 (1991) 347; *Chem. Abstr.*, 115 (1991) 159261a.
82. J. Casabó, L. Mestres, L. Esriche, F. Teixidor and C. Pérez-Jiménez, *J. Chem. Soc., Dalton Trans.*, (1991) 1969.
83. J. Buter, R.M. Kellogg and F. van Bolhuis, *J. Chem. Soc., Chem. Commun.*, (1991) 910.
84. S.P. Huang and M.G. Kanatzidis, *Inorg. Chem.*, 30 (1991) 1455.
85. F. Dietze, J. Lerchner, S. Schmidt, L. Beyer and R. Kohler, *Z. Anorg. Allg. Chem.*, 600 (1991) 37.
86. B.F. Hoskins, R. Robson, G.A. Williams and J.C. Wilson, *Inorg. Chem.*, 30 (1991) 4160.
87. U. Heinzel and R. Mattes, *Polyhedron*, 10 (1991) 19.
88. A.J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, (1991) 615.
89. U. Kallert and R. Mattes, *Inorg. Chim. Acta*, 180 (1991) 263.
90. J.C. Lockhart and D.J. Rushton, *J. Chem. Soc., Dalton Trans.*, (1991) 2633.
91. A. Abouhamdan and S.F. Lincoln, *Inorg. Chem.*, 30 (1991) 462.
92. G. Wu, W. Jiang, J.D. Lamb, J.S. Bradshaw and R.M. Izatt, *J. Am. Chem. Soc.*, 113 (1991) 6538.
93. I. Rabin, C. Jackschath and W. Schulze, *Z. Phys. D: At., Mol. Clusters*, 19 (1991) 153.
94. I. Rabin, C. Jackschath, W. Schulze and F.W. Froben, *Z. Phys. D: At., Mol. Clusters*, 19 (1991) 401.
95. I. Rabin, W. Schulze and G. Ertl, *Z. Phys. Chem. (Munich)*, 169 (1990) 85.
96. C.K. Fagerquist, D.K. Sensharma and M.A. El Sayed, *J. Phys. Chem.*, 95 (1991) 9169.
97. S.H. Song, Y. Kim and K. Seff, *J. Phys. Chem.*, 95 (1991) 9919.
98. B.K. Teo, X. Shi and H. Zhang, *J. Am. Chem. Soc.*, 113 (1991) 4329.
99. M.F.J. Schoondergang, J.J. Bour, P.P.J. Schlebos, A.W.P. Vermeer, W.P. Bosman, J.M.M. Smits, P.T. Beurskens and J.J. Steggerda, *Inorg. Chem.*, 30 (1991) 4704.
100. A.D. Burrows, J.G. Jeffrey, J.C. Machell and D.M.P. Mingos, *J. Organomet. Chem.*, 406 (1991) 399.
101. Y. Sawada, N. Kanou and N. Miztani, *Thermochim. Acta*, 183 (1991) 279.
102. D. Dollimore and T.A. Evans, *Thermochim. Acta*, 179 (1991) 49.
103. D. Dollimore and T.A. Evans, *Thermochim. Acta*, 179 (1991) 263.
104. S. Kielhorn, D.H. Buss, O. Glemser, R. Gerner and G. Jeske, *Angew. Chem., Int. Ed., Engl.*, 30 (1991) 1017.
105. P. Fischer and M. Jansen, *Acta Chem. Scand.*, 45 (1991) 816.
106. H. Miki, *Jpn. J. Appl. Phys., Part I*, 30 (1991) 1765; *Chem. Abstr.*, 115 (1991) 171329m.
107. A. Bennouna, B. Durand and O. Vittori, *Electrochim. Acta*, 36 (1991) 1505.
108. H.J. Riebe and H.L. Keller, *Z. Anorg. Allg. Chem.*, 597 (1991) 151.
109. M. Jansen and K. Heidebrecht, *Z. Kristallogr.*, 196 (1991) 294.
110. M. Soll and H. Muller-Buschbaum, *Monatsh. Chem.*, 122 (1991) 915.
111. M. Andratschke, *Z. Anorg. Allg. Chem.*, 601 (1991) 103.

112. M.T. Averbuch-Pouchot, *Acta Crystallogr., Sect. C*, 47 (1991) 930.
113. M.T. Averbuch-Pouchot and A. Durif, *Acta Crystallogr., Sect. C*, 47 (1991) 1150.
114. M. Jansen, K. Heidebrecht, R. Matthes and W. Eysel, *Z. Anorg. Allg. Chem.*, 601 (1991) 5.
115. K. Heidebrecht and M. Jansen, *Z. Anorg. Allg. Chem.*, 597 (1991) 79.
116. B.H. Loo, Y.G. Lee and T. Kato, *Bull. Chem. Soc. Jpn.*, 64 (1991) 3126.
117. S.T. Oh, K. Kim and M.S. Kim, *J. Mol. Struct.*, 243 (1991) 307.
118. T.G. Lee, K. Kim and M.S. Kim, *J. Phys. Chem.*, 95 (1991) 9950.
119. L.J. Gerenser, K.E. Goppert-Berarducci, R.C. Baetzold and J.M. Pochan, *J. Chem. Phys.*, 95 (1991) 4641.