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3. Silver

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CONTENTS

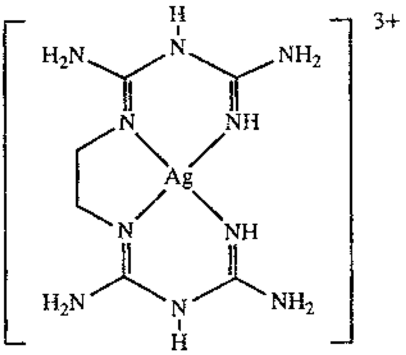
INTRODUCTION

This chapter surveys the coordination chemistry of silver reported during 1990 and includes some silver cluster chemistry. The format follows that of Chapter 2 (Gold) and the reader is directed to related compounds in the previous review. Section 3.3.2 is not comprehensive but, as in Chapter 2, reports clusters and their syntheses that may be of interest to the coordination chemist. The present survey is based upon a search of volumes 112, 113, and 114 (parts 1–10) of Chemical Abstracts; major inorganic chemistry journals have been searched separately for the period January to December 1990. I am particularly grateful to the Cambridge Crystallographic Data Base for allowing access to coordinates for many of the structural figures redrawn for this review.

3.1 SILVER (III) and SILVER (II)

The kinetics of the oxidation of hydrazine by the silver (III) complex cation (**1**) have been investigated. Over the pH range 2–3 and in the presence of a silver(I) catalyst, the rate follows equ. (i) with values of 10^4k = 2.22 ± 0.16, 4.10 ± 0.25, 7.17 ± 0.50 and 12.8 ± 0.8 at 15, 20, 25 and 30°C respectively. [1]

$$-d[(\mathbf{1})] / dt = 2k\,[Ag^+]^2[N_2H_5^+] / [H^+] \qquad \text{equ. (i)}$$



(1)

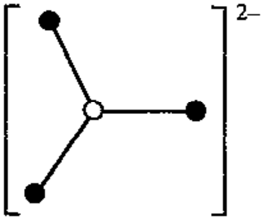
The preparation and characterisation of the silver(II) complex AgL where H_2L = tetraneopentoxyphthalocyanine has been reported. The complex is soluble in most organic solvents. Electrochemical studies show that oxidation to the stable $[AgL]^+$ occurs followed by further oxidation to the radical cation $[AgL]^{2+}$. Reduction to the anion $[AgL]^-$ leads to demetallation of the complex. [2] Fast atom bombardment mass spectrometry has been used to study porphyrins H_2P and their metal complexes; rates of demetallation and inter- and intramolecular electron transfer processes have been investigated. The one electron reduction of AgP occurs via an excited state intermediate and the rate of electron transfer from the porphyrin ring to Ag(II) is 2×10^{11} s^{-1}. [3] The magnetic properties of a polymer containing derivatised Ag(TPP)-side chains have been compared to those of a monomer model compound. Antiferromagnetic interactions between the side chains in, *e.g.* poly[5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphinatosilver(II)] have been assessed; results are consistent with superexchange interactions involving carbonyl groups between the Ag(II) ions. [4]

Silver(II) complexes of polyaza-macrocyclic ligands have been prepared and investigated electrochemically. The synthetic strategy has been the disproportionation of Ag(I) induced by the macrocycles themselves; complexes with [15]aneN_5 and [16]aneN_5 are stable in aqueous solutions but pure crystalline materials could not be isolated. The Ag(II) complexes undergo reversible 2-electron reductions at a dropping mercury electrode. [5]

3.2 SILVER (I)

3.2.1 Complexes with halide and pseudohalide ligands

Two papers have appeared detailing silver(I) polyhalide anions. An X-ray diffraction study (295 K) of $[Ph_3MeP]_2[AgI_3]$ confirms a trigonal planar geometry for the anion, (2); Ag-I distances are 2.742 (1), 2.746 (1) and 2.755 (1) Å and $\angle$IAgI are 115.90 (3), 119.38 (4) and 124.67 (3)°. [6] Syntheses of the anions $[Ag_2Cl_4]^{2-}$, $[Ag_2Br_4]^{2-}$, $[Ag_2Cl_5]^{3-}$, $[Ag_3I_4]^-$ and $[Ag_4I_8]^{4-}$ have been described. For example, the reaction of AgI with $[Ph_4P]I$ in refluxing MeCN leads to a mixture of $[Ph_4P][Ag_3I_4]$ and $[Ph_4P]_4[Ag_4I_8]$. Crystallographic results for salts containing the anions $[Ag_2Cl_4]^{2-}$, (3), $[Ag_2Br_4]^{2-}$ and $[Ag_4I_8]^{4-}$, (4), illustrate bridged chain structures. In (3), the bridges are asymmetrical with Ag-Cl = 2.809 (2) and 2.446 (2) Å. In (4), the central Ag(I) atoms are tetrahedrally coordinated; nonbonded Ag---Ag separations are 3.171 (2) and 3.256 (2) Å or 3.198 (1) and 3.306 (2) Å for the two independent molecules. [7]



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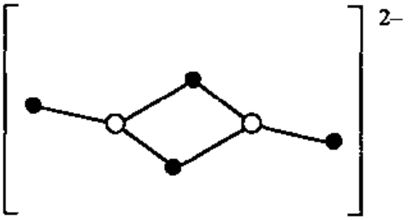

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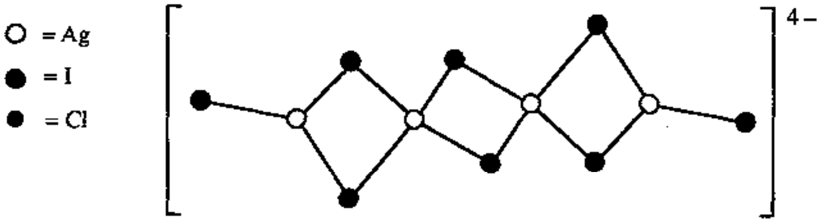
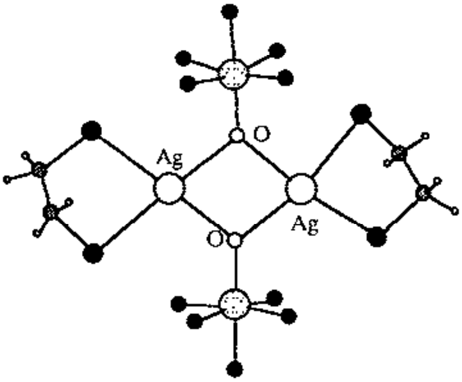


(4)

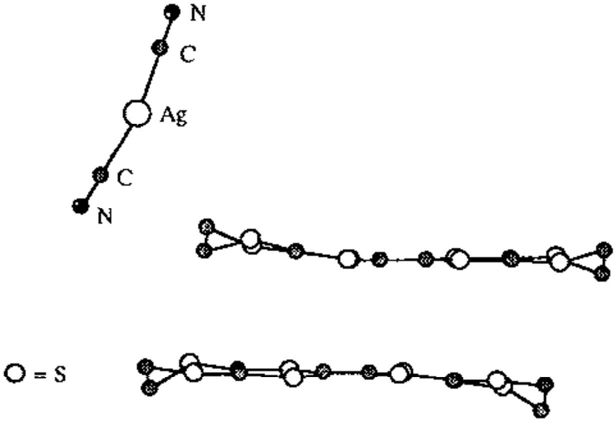
An interesting series of compounds (see also Section 3.2.4) includes $[Ag(CH_2Cl_2)(OTeF_5)]_2$ and the crystallographically characterised $[Ag(1,2\text{-}C_2H_4Cl_2)(\mu\text{-}OTeF_5)]_2$, (5), $Ag_2(CH_2Cl_2)_4Pd(\mu\text{-}OTeF_5)_4$, (24), and $Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(\mu\text{-}OTeF_5)_4$. The preparation and characterisation by solution conductimetry and IR, Raman, ^{13}C NMR, and ^{35}Cl NQR spectroscopy of these complexes have been reported. The structural data provide the first unambiguous evidence that simple chlorocarbons are able to coordinate to transition metal ions with CH_2Cl_2 and $1,2\text{-}C_2H_4Cl_2$ forming 4- or 5-membered chelate rings respectively; *e.g.* in (5), the Ag-Cl distances lie in the range 2.626 (3)–3.000 (3) Å. [8]

An orthorhombic modification of $Ag\{N(CN)_2\}$ has been described. Infinite $-\{Ag{-}N{\equiv}C{-}N{-}C{\equiv}N{-}Ag\}_n-$ chains run parallel to the crystallographic *a* axis. A comparison of the orthorhombic with the previously reported trigonal form of the complex shows that the two differ in that the 3_1 axis of the latter is replaced by a 2_1 axis in the new structure. [9]



(5)

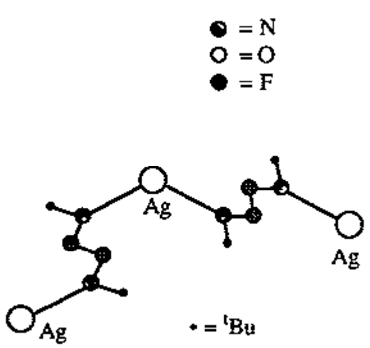
The complex *bis*(3,4,3',4'-*bis*(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium) dicyano silver(I) monohydrate, (**6**), has been structurally characterised. The organic units stack in columns and (**6**) is related to the organic superconductor, $(DMET)_2AuCl_2$, described in Section 2.4.1 of the previous chapter. [10] The liquid crystal behaviour of the silver(I) complexes $[AgL_2][X]$ (L = pyridyl derivatives of the general formula $(NC_4H_4)CH{=}N\text{-}C_6H_4OC_nH_{2n+1}$ or $(NC_4H_4)C(O)\text{-}O\text{-}C_6H_4OC_nH_{2n+1}$ and $X^- = BF_4^-$, $CF_3SO_3^-$, NO_3^- or PF_6^-) have been investigated by using DSC, optical microscopy and X-ray diffraction methods. $[AgL_2][X]$ species exhibit mesogenic behaviour and, dependent upon L and X, additional stable phases may occur between the low temperature solid phase and the liquid crystal phase. [11]



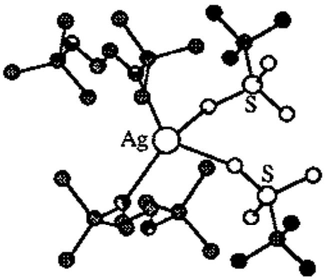
(6)

3.2.2 *Complexes with nitrogen donor ligands*

Bridging *bis*triazenido groups support a rhombus of silver(I) atoms in the complex that results from the reaction of $AgNO_3$ with $Na[PhN_3\text{-}C_6H_4\text{-}N_3(H)Ph]$, NaL, in thf. The brown complex Ag_4L_4 has been structurally characterised and Ag–Ag distances are in the range 2.799 to 3.103 Å. [12] Treatment of AgO_3SCF_3 with 1,4-di-^{t}butyldiazabut-1,3-diene (^{t}Bu-DAB) leads to the light sensitive coordination polymer (7). Each silver atom is in an N_2O_2-ligation shell and are linked by the ^{t}Bu-DAB ligands; the ∠NAgN is 123.9 (1)° and Ag-N distances are 2.330 (3) and 2.313 (4) Å. [13]



Linkage of Ag atoms via ^{t}Bu–DAB bridges; O_3SCF_3 groups omitted for clarity



Coordination sphere at a single Ag atom

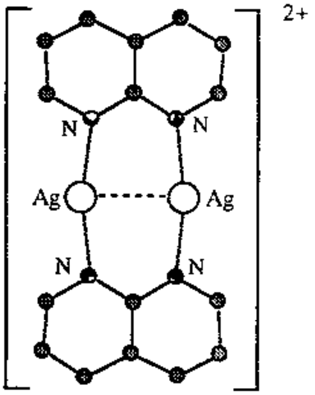
(7)

Reactions of $AgNO_3$ with the ligands L (L = 2-NC-py) or L' (L' = 3- or 4-NC-py and 2-, 3- or 4-$NC\text{-}C_6H_4\text{-}NH_2$) lead to $LAgNO_3$ and L'_2AgNO_3 which have been characterised by elemental analyses, conductance measurements and IR spectroscopy. The complexes are non-electrolytes in ethanol and 1:1 electrolytes in aqueous solutions. [14] For L = 2-arylazopyridines, the complexes $[AgL_2][ClO_4]$ (1:1 electrolytes in methanol) have been prepared. From free ligand to $[AgL_2]^+$, only a slight shift in $\nu_{N=N}$ is observed indicating that there is a negligible $d_{\pi\text{-}\pi^*}$ interaction upon ligand coordination. ^1H NMR spectroscopic data are also reported. [15]

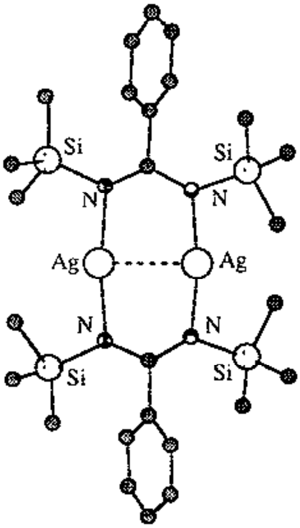
Complexes of silver(I) involving ligands L derived from the reactions of isonicotinoylhydrazide and 2-hydroxybenzaldehyde, 2-hydroxynaphthaldehyde or 2-hydroxyacetophenone have been described. Complexes AgL_2X (X = ClO_4 or NO_3) have been characterised by conductance measurements, IR spectroscopy and thermal decomposition studies. L coordinates via the pyridinium nitrogen atom. Other related complexes are also reported. [16]

The reaction of Ag^+ ions with 1,8-naphthyridine, L, leads to the dinuclear complex cation (8). A crystallographic study is complimented by discussion of ^1H NMR, IR and electronic spectroscopic data. Pertinent structural parameters for (8) are Ag-N = 2.211 (15) and 2.179 (15) Å, Ag--Ag = 2.748 Å and ∠NAgN = 167.82 (50)°. [17] A related framework to that found in (**8**) is also represented in complex (**9**), the product of the reaction of $PhC(NSiMe_3)\{N(SiMe_3)_2\}$ with AgO_2CMe in acetonitrile. The Ag-Ag separation of 2.655 (2) Å is shorter than that observed in (**8**); Ag-N distances average 2.124 (2) Å. [18] (See structure (**12**) in Section 2.4.2 of the previous chapter for gold(I) analogue of (**9**)).

An interesting complex is Ag_3NSeO_3, the red α-trisilver amidoselenate. Each selenium and nitrogen atom is tetrahedrally coordinated and each nitrogen atom is associated with three silver(I) ions. The N-Se distance is very short (1.70 (2) Å) and the Ag-N separations are 2.164 (8) Å. Each Ag_3NSeO_3 unit bridges to three other units via short Ag---O interactions (2.23 (1) Å) to generate a 3-dimensional network. The complex is insoluble in water but is soluble in aqueous ammonia or in acidic media. A discussion of the bonding in the system is included in the paper. [19]



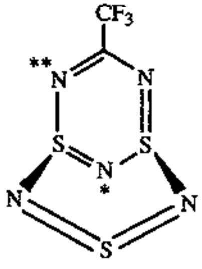
(**8**)



(**9**)

The coordination of $CF_3CN_5S_3$, (**10**), to silver(I) ions generates an interesting dinuclear species $[Ag_2\{CF_3CN_5S_3\}_4]^{2+}$ in addition to the monocation $[Ag\{CF_3CN_5S_3\}]^+$. In the dication, two ligands are terminally attached, one to each Ag^+ ion coordinated through N* shown in (**10**). The remaining two ligands bridge via N* and N** between the two metal centres. [20]

The products of the reaction of AgX ($X^- = NO_3^-$, ClO_4^- or BF_4^-) with *bis*(pyrazol-1-yl)alkanes such as $(pz)_2CMe_2$, (**11**), 3,5-dimethylpyrazole or 4-nitropyrazole are dependent upon X^-. For $X^- = NO_3^-$, 1:1 complexes are formed whereas for $X^- = ClO_4^-$ or BF_4^-, 2:1 complexes result. The molecular structure of $[AgL_2][ClO_4]$, L = (**11**), has been determined; each ligand is bidentate and the silver ion is sited within a distorted tetrahedral array of donor atoms. Important distances are Ag-N = 2.289 (4), 2.324 (4), 2.432 (4) and 2.247 (4) Å; ∠NAgN lie in the range 82.6 (1) to 145.1 (1)°. [21] There is evidence from the results of surface-enhanced Raman spectroscopic studies for Ag-N bond formation when 2,2'-bipyrimidine is adsorbed on a silver sol. There are similarities between the spectral data for the sol-complex and those observed for the 1:1 2,2'-bipyrimidine:$AgNO_3$ species. [22]



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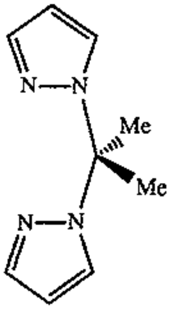

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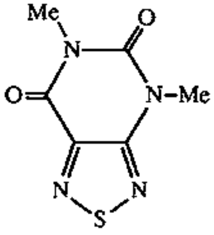
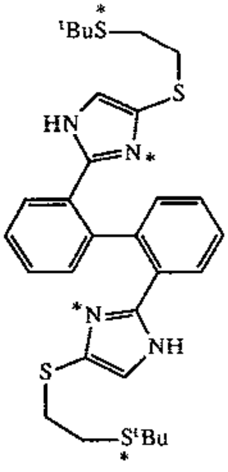


(12)

The complex $[AgL][NO_3]$ where L = **(12)** has been prepared and fully characterised by IR, ^1H and ^{13}C NMR spectroscopy and X-ray diffraction. Ligand **(12)** is coordinated via *N*- and *O*-donor atoms only with the silver(I) ion being tetrahedrally sited; Ag-N = 2.422 (3) and 2.356 (2) Å, Ag-O = 2.435 (4) and 2.518 (4) Å. The net structure is polymeric. [23]

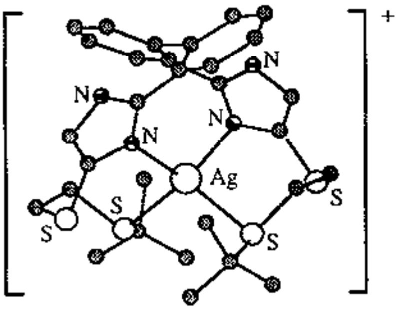
The ligation of *E*-1(4-ethoxyphenyl)-4-hydroxyiminoethylimidazole to transition metal ions has been studied and an assessment of the antimicrobial activity of the complexes has been made. Characterisation by IR, UV, ^1H and ^{13}C NMR spectroscopy and magnetic measurements has been described. Unlike the $N(3)_{imidazole}/N_{oxime}$ coordination mode exhibited to other metal ions, ligation to Ag^+ is monodentate through the imidazole-*N*(3) atom. [24] Stability constants have been determined for complexes AgL formed from the reaction of $AgNO_3$ with HL in ethanol/benzene solution in the presence of Et_3N where HL = 1-toluenesulfonamido-4-(4-tolyl)-2(1*H*)-pyramidinethione, 1-benzamido-4-(4-tolyl)-2(1*H*)-pyramidinethione or 1-amino-2-anilino-4-(4-tolyl)-2(1*H*)-pyramidinethione. [25]

Models for reduced blue copper sites are represented by copper(I) and silver(I) complexes of the ligand **(13)**, the synthesis of which has been described. Full structural characterisation of the complex cation **(14)** shows a distorted tetrahedral Ag^+ ion with two additional weak Ag-----S interactions; Ag-N = 2.292 (4) and 2.301 (5) Å, both Ag-S = 2.586 (2) Å, and Ag----S = 3.702 (2) and 3.746 (2) Å. [26] Note that ligand **(13)** adopts a twisted conformation in order to satisfy the coordination needs of the silver(I) ion. The ability for a multidentate ligand to twist is an essential prerequisite to the self-assembly of molecular helicates and the series of bipyridyl ligands **(15)** are designed to possess just this ability. Silver(I) ions react with **(15)** to give the helical cations $[Ag_mL_2]^{m+}$; an X-ray diffraction study for m = 3 confirms the beauty of the helical array. [27]



* = coordination site

(13)



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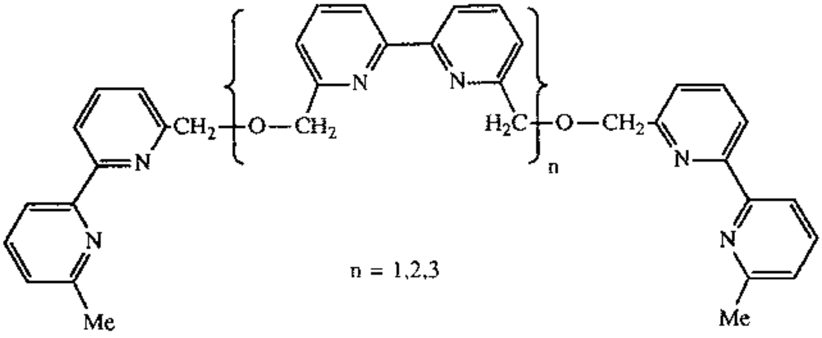


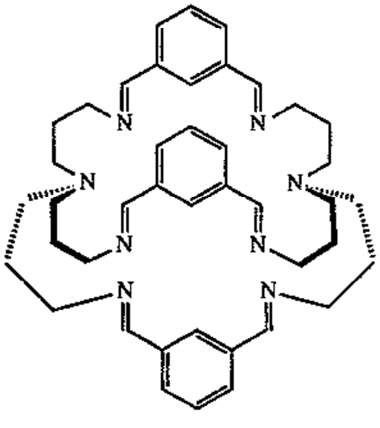
(15)

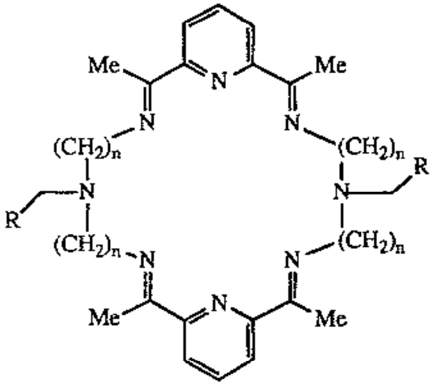
Potentiometric and calorimetric measurements at 25°C have been made for the complex formation between silver(I) ions and the tetramine ligands trien (L), tren (L') and 1,5,8,12-tetraazadodecane (L"). All three ligands function in a tetradentate manner and form stable 1:1 complexes although L' and L" form additional species; some stability constant data are given in Table 1. [28]

Table 1 Stability constant data for complexation of tetramines L, L' and L'' (defined in text) with silver(I) ions

Speciation			**log β**
$Ag^+ + L$	=	$[AgL]^+$	10.32 (1)
$Ag^+ + L'$	=	$[AgL']^+$	9.49 (3)
$Ag^+ + 2L'$	=	$[AgL'_2]^+$	11.1 (3)
$2Ag^+ + L'$	=	$[Ag_2L']^+$	11.51 (7)
$Ag^+ + L''$	=	$[AgL'']^+$	7.93 (3)
$Ag^+ + 2L''$	=	$[AgL''_2]^+$	9.72 (22)
$2Ag^+ + L''$	=	$[Ag_2L'']^+$	11.20 (8)
$2Ag^+ + 2L''$	=	$[Ag_2L''_2]^+$	17.66 (11)
$3Ag^+ + 2L''$	=	$[Ag_3L''_2]^+$	22.90 (6)

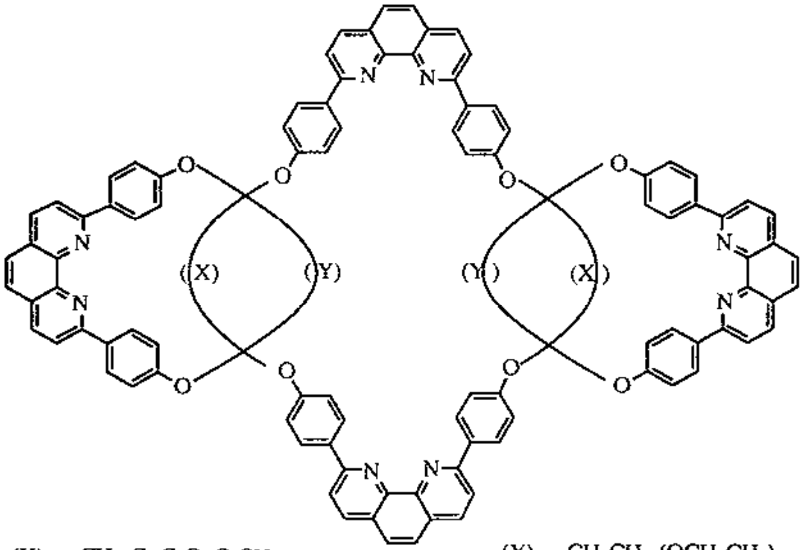
The template synthesis of (**16**) involves the condensation of *tris*(3-aminopropyl)amine with 1,3-benzenedicarboxaldehyde in the presence of $AgNO_3$ giving first a dinuclear silver(I) complex which transmetallates in the presence of $[Cu(NCMe)_4][ClO_4]$ or $CuClO_4.6H_2O$. The dicopper complex of (**16**) is produced in the final step and has been structurally characterised. [29] Related work is described in a study of the series of ligands (**17**). Complexation with Ag^+ ions leads to the dinuclear dications $[Ag_2L]^{2+}$ for each of the four macrocycles and structural determinations have been carried out for all complexes. [30]





L' R = py n = 2
L'' R = py n = 3
L''' R = CH_2OMe n = 3
L'''' R = 2-MeO-C_6H_4 n = 3

(**16**) (**17**)

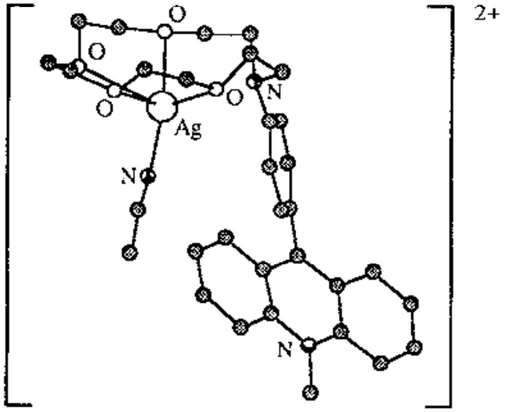


(X) = -CH$_2$-C≡C-C≡C-CH$_2$-

(Y) = -CH$_2$CH$_2$-(OCH$_2$CH$_2$)$_4$-

(18)

As a member of a series of related complexes, the silver(I) [3]-catenate of the beautiful ligand **(18)** has been synthesised as colourless crystals of the BF_4^- salt in 99% yield and characterised by elemental analysis, FAB mass spectroscopy and ^{1}H NMR spectroscopy. The latter is particularly informative as regards the molecular topology of the complex $[Ag_2(\mathbf{18})]^{2+}$. Electrochemical studies indicate that, unlike the copper(I) analogue, $[Ag_2(\mathbf{18})]^{2+}$ shows no oxidation wave before there is irreversible oxidation of **(18)** ($E > 1.5$ V vs. SCE). [31]



(19)

The silver(I) complex (**19**), along with Na^+ and Ba^{2+} analogues, has been described. The ligand and complexes exhibit chromoionophoric behaviour in solution and the Ag^+ ion induces a significant spectral shift upon coordination to the acridinium ligand. [32] The cationic ligand itself is nonfluorescing but on coordination to Ag^+, fluorescent behaviour is observed. [33] The molecular structure of (**19**) has been reported [32,34] and the Ag^+ ion is bound within the macrocycle with an axial acetonitrile group. Pertinent distances are $Ag\text{-}N_{MeCN}$ = 2.21 (1) Å, $Ag\text{-}N_{macrocycle}$ = 2.72 (1) Å, Ag-O = 2.499 (8) to 2.56 (1) Å.

For a discussion of the triazene-bridged tetrasilver cluster, see Section 3.3.1.

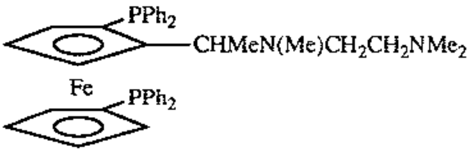
3.2.3 Complexes with phosphorus and arsenic donor ligands

A series of eighteen salts of formula $[M(PR_2R')_3]X$ (M = Ag or Au; X = BF_4, ClO_4; R ≠ R' = Ph, $c\text{-}C_6H_{11}$, $c\text{-}C_5H_9$, $c\text{-}C_7H_{13}$) have been isolated and characterised; IR spectroscopic data are presented. The coordination number of 3 in the cation is observed only when steric factors mitigate against the coordination of 2 or 4 ligands. For example, $[M(PPh_3)_4]^+$ (cone angle = 145°) and $[M\{P(c\text{-}C_6H_{11})_3\}_2]^+$ (cone angle = 170°) are preferred but mixing the two ligands produces steric requirements that favour tricoordinate silver(I) or gold(I). Results of an X-ray diffraction study of $[Ag\{PPh_2(c\text{-}C_5H_9)\}_3[BF_4]$ are reported; there is some deviation from planarity for the AgP_3-unit with ∠PAgP = 117.4 (1)° and Ag-P = 2.543 (3) Å. [35]

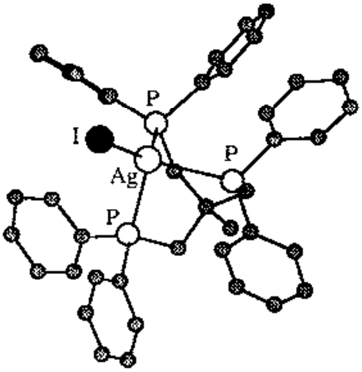
Reactions of $\{Ag(PPh_3)Cl\}_4$ with ligands L produce mononuclear complexes of the type $Ag(PPh_3)_2(L)Cl$ (*e.g.* L = py-2-thione, py-2-thione, pyrimidine-2-thione, 1,3-thiazolidine-2-thione, 1-methyl-1,3-imidazoline-2-thione, benz-1,3-thiazolidine-2-thione). A molecular structure determination of the complex for L = py-2-thione shows a *trans*-arrangement of the two phosphine ligands; Ag-P = 2.482 (1) and 2.476 (1) Å, Ag-S = 2.625 (1) Å, Ag-Cl = 2.595 (1) Å, bond angles at the silver atom vary from 100.8° to 123.0°. [36]

The stability of compounds in the series $(R_3P)_nAgSiR'_3$ (n = 1-3; R and R' = aryl, alkyl), $(dppm)(AgSiR'_3)_2$ and $(dppe)(AgSiR'_3)_2$ increases in going from monodentate to bidentate phosphine ligands and for the monodentate examples, complex stability increases with n. Spectroscopic data are presented for the complexes. [37] Thermodynamic parameters (log β, ΔG°, ΔH° and ΔS°) have been determined by potentiometric and calorimetric methods in dmso at 25°C for the complex formation of Ag^+ ions with the bidentate ligands dppm, dppe, dppp, *bis*{2-diphenylphosphine-ethyl}phenylphosphine and *tris*{2-diphenyl phosphine-ethyl}phosphine. [38]

Structural data for the $[Ag(dppe)_2]^+$ cation (nitrate salt) have been reported. The silver(I) ion is in a distorted tetrahedral environment with intra-ligand ∠PAgP = 84.5 (1)° and 83.8 (1)°. [39] The dppf ligand reacts with $AgClO_4$ to give a complex proposed as "$[Ag(dppf)][ClO_4]$". The coordination of the phosphine to Ag^+ is supported by a shift to lower field of the ^{31}P and ^1H NMR spectral resonances compared to the free ligand. [40] The formulation of the $[Ag(dppf)]^+$ cation appears to be odd since the bite angle of this ligand is not large enough to allow anything approaching linear coordination at the metal centre; $[Ag(dppf)_2]^+$ or $[Ag_2(dppf)_2]^{2+}$ would appear to be more realistic. A derivative of the dppf ligand is (**20**); this reacts with AgO_3SCF_3 with an excess of MeO_2CCH_2NC in CD_2Cl_2 to give a tetracoordinated silver(I) complex. In solution, the results of $^{1}H\{^{1}H\}$ NOE experiments show that the terminal Me_2N group in coordinated **(20)** lies close to the active hydrogen atoms of the coordinated isocyanoacetate. There is interest in the reaction in connection with the catalysis of the aldol reaction. [41]



(20)



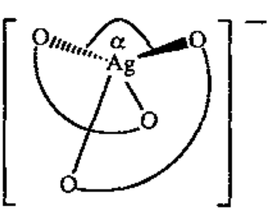
(21)

The complex cation $[Ag\{Ph_2PCH{=}CHPPh_2\}_2]^+$ is of interest with respect to antimicrobial and antitumour activity. The cation has a tetrahedral AgP_4-core for which ^{109}Ag NMR spectral data have been obtained by using a retro-INEPT 2D $^{31}P\{^{109}Ag\}$ pulse sequence. [42] A structural determination of the air stable dinuclear complex $[Ag(dppp)(NO_3)]_2$ shows that the Ag_2-unit is supported by the two dppp ligands. The molecule is centrosymmetric and each silver ion is also coordinated to a chelating nitrate ion; Ag-P = 2.403 (1) and 2.426 (1) Å, Ag-O = 2.581 (3) and 2.674 (3) Å, ∠PAgP = 152.2 (1)° and ∠OAgO = 46.9 (1)°. [43] Tetrahedrally coordinated Ag^+ is confirmed in Ag(triphos)X for X = I, **(21)**, and the complex exhibits the longest M-P distances (2.527 (6), 2.555 (5) and 2.510 (5)Å) and smallest PMP angles (88.9 (2)°, 90.3 (2)° and 87.8 (2)°) observed to that date in a triphos complex. In solution, the dynamics of the complex molecule depend upon X; for X = Cl, I and $MeCO_2$, the molecule is still fluxional at 193 K but this is not so for X = NO_3 and ClO_4. [44]

The *bis*(arsine) complexes $[Ag\{ER_2R'\}_2]X$ (E = P or As; R ≠ R' or R = R' = Ph, *c*-C_5H_9, *c*-C_6H_{11}; X = BF_4 or ClO_4) have been synthesised and characterised by IR spectroscopic studies and X-ray diffraction investigations on $[Ag\{PPh_2(c\text{-}C_5H_9)\}_2][ClO_4]$ and $[Ag\{As(c\text{-}C_5H_9)_3\}_2][ClO_4]$. Both cations are nonlinear; for the former, ∠PAgP = 145.1 (1)° and 153.0 (1)° for 2 independent molecules and for the latter, ∠AsAgAs = 151.2 (1)°. Pertinent distances are Ag-P = 2.432 (2) and 2.415 (2) Å or 2.419 (2) and 2.397 (2) Å for the 2 molecules of $[Ag\{PPh_2(c\text{-}C_5H_9)\}_2]^+$ and Ag-As = 2.480 (2) and 2.482 (2) Å in $[Ag\{As(c\text{-}C_5H_9)_3\}_2][ClO_4]$. Related gold(I) complexes have also been described (see Section 2.4.3 in the previous chapter). [45]

3.2.4 Complexes with oxygen donor ligands

In 1935, Poulenc proposed the formulation *trans*-$[Rh(py)_4Cl_2]NO_3.AgNO_3$ for this mixed metal complex. An X-ray diffraction study of the compound has now shown that it contains the dinitroargentate(I) ion. There are 2 independent anions in the unit cell and each Ag^+ ion is in a significantly distorted tetrahedral environment as shown in (**22**); values of angle α are 169.3 (2)° and 150.7 (1)° for the two independent molecules. [46] A related environment is observed in $[Ag(dppp)(NO_3)]_2$ [43] and in (nitrato-*N,N'*)*bis*(4-nitropyridine-*N*-oxide-*O*)silver(I), (**23**); within the chelate ring, Ag-O = 2.453 (5) and 2.573 (6) Å, $Ag\text{-}O_{N\text{-oxide}}$ = 2.364 (3) and 2.318 (3) Å, $\angle OAgO_{\text{chelate ring}}$ = 48.1 (2)° and $\angle O_{N\text{-oxide}}AgO_{N\text{-oxide}}$ = 117.7 (1)°. [47]



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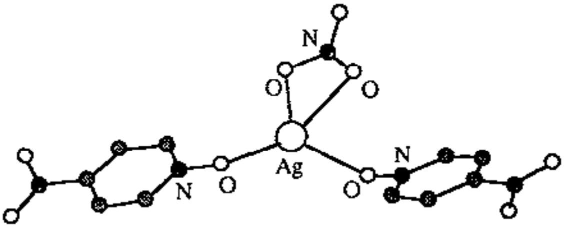


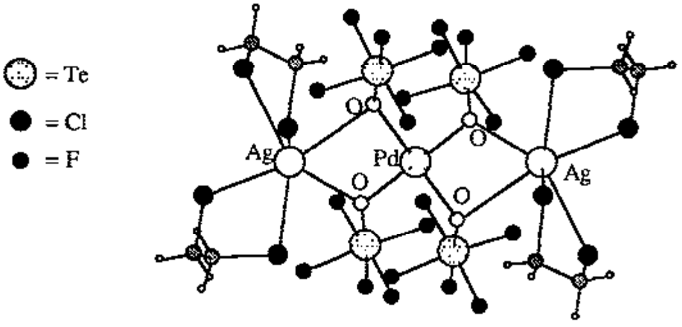
(23)

For HL = salicylic acid, the preparation of $\{AgL\}_2$ from NaL and $AgNO_3$ has been described. Structural characterisation of the complex shows that the two metal ions, each 3-coordinate, are bridged by the carboxylate ligands in a *syn,syn*-configuration; the Ag---Ag separation is 2.855 (1) Å. [48] Carboxylate bridges have also been confirmed crystallographically in $[Ag(PhOCH_2CO_2)_2]_n$ (bridged Ag---Ag = 2.866 (2) Å) and $[Ag_2(4\text{-}F\text{-}C_6H_4OCH_2CO_2)_2(H_2O)_2]_2$ (bridged Ag---Ag = 2.836 (2) Å). The former complex is polymeric whereas the latter is a discrete centrosymmetric tetranuclear species. [49]

The coordination of a $\{O_4N\}$-macrocycle containing acridinium ligand to Ag^+, (**19**), has been described in Section 3.2.2. [32-34]

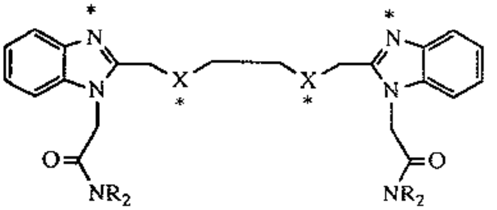
An interesting complex involves $CpCo\{P(O)R_2\}_3$ (R = OMe, OEt, O^iPr) as a ligand that forms a *tris*-chelate upon coordination via the phosphorus oxide O-atoms to Ag^+. The dimeric complex $[CpCo\{P(O)R_2\}_3Ag]_2$ reacts with ^tBuNC or CO (1 atm) to give $CpCo\{P(O)R_2\}_3AgL$ (L = ^tBuNC or CO). The carbonyl complex is characterised in its IR spectrum by ν_{CO} = 2147 cm^{-1}. [50]

A series of complexes (already mentioned in Section 3.2.1 for the interest in the coordinated chlorocarbon molecules) includes $\{Ag(1,2\text{-}C_2H_4Cl_2)(\mu\text{-}OTeF_5)\}_2$, (**5**), $Ag_2(CH_2Cl_2)_4Pd(\mu\text{-}OTeF_5)_4$, (**24**), and $Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(\mu\text{-}OTeF_5)_4$ (for all of which crystallographic data are available) and $[Ag(CH_2Cl_2)(OTeF_5)]_2$. Each complex exhibits $[OTeF_5]^-$ anions bridging either between two silver(I) ions or between silver(I) and Pd(II) centres. [8]



(24)

Bis(benzimidazole) ligands L, (**25**), containing ether or thioether chains between the imidazole groups have been used in an investigation of the selectivity in transition metal ion transport. Silver(I) ions form complexes with all the ligands; the results of molecular modelling with COSMIC force field calculations assuming a tetrahedral Ag(I) ion indicate that L^4 coordinates via an *N,N',S,S'*-donor set. Selective complexation has been observed for the following pairs of ions: Ag^+ and Pb^{2+}, Ag^+ and Cu^{2+}, Ag^+ and Zn^{2+}, Ag^+ and Cd^{2+}. [51]



L^1 X = O R = ^{n}butyl
L^2 X = S R = ^{n}butyl
L^3 X = O R = ^{n}hexyl
L^4 X = S R = ^{n}hexyl

* = coordination site

(25)

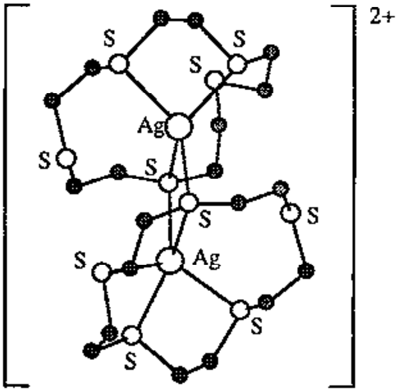
3.2.5 *Complexes with sulphur donor ligands*

The yellow silver(I) thiolates Ag_2S_2L ($H_2L = 1,n\text{-}C_nH_{2\text{-}n}(SH)_2$, n = 2-6; $1,2\text{-}C_3H_6(SH)_2$; $2,3\text{-}C_4H_8(SH)_2$) have been synthesised electrochemically in MeCN solution in cells $Pt_{(-)}|R(SH)_2$ + $MeCN|Ag_{(+)}$ in which the reaction may be represented by the half equations (ii) and (iii). Yields of the complexes are high (90-95%) and the structure of a related copper(I) complex has been reported. [52]

At cathode: $R(SH)_2 + 2e = H_2\,(g) + [RS_2]^{2-}$ equ. (ii)
At anode: $[RS_2]^{2-} + 2M = M_2S_2R + 2e$ equ. (iii)

The reaction of $AgNO_3$ with HL (HL = 2-(SH)-6-($SiMe_2Ph$)-py) produces the complex $[AgL]_6$ in addition to $[Ag_8L_6][Ag(NO_3)_2]_2.2MeOH.CH_2Cl_2$. In the latter, the cluster dication is closely associated with the two anions. The former exhibits a "paddle-wheel" structure with a pseudo-C_3 axis. [53] Cluster formation is also a result of the reaction of $AgNO_3$ with 4-mercapto-1-methylpiperidine, HL, carried out in aqueous solution in the presence of $NaClO_4$ at pH 8.5 (a critical feature); the product cation, $[Ag_{13}L_{16}]^{13+}$, consists of a central $\{Ag_6S_6\}$-core with two 8-membered rings of alternating silver and sulphur atoms. [54] Complexation of silver(I) ions with ligands 3-(dimethylamino)propane-1-thiol and 3-aminopropane-1-thiol has been studied as a function of pH [55] and the results have been compared with those obtained for the ligand 4-mercapto-1-methylpiperidine. [56] The species formed in solution at strongly acidic pH is independent of the aliphatic chain in the ligand. At higher pH values, complexes produced in solution depend on the identity of the γ-mercaptoamine. A series of mixed ligand complexes $Ag(Ph_3P)_2LCl$ involving a variety of thiones, L, have been described in Section 3.2.3. [36]

Stability constants have been measured for complexes of Ag^+ with diethylsulphide, ethyl(2-chloroethyl)sulphide and *bis*(2-chloroethyl)sulphide in acetone, methanol, dmf and dmso solutions. The 2-chloro-substituent causes a reduction in the stability of the silver(I) complex. [57] Coordination of the thioether 2,2'-*bis*{2-[4(5)-(2-^{t}butylthio)ethanethioimidazolyl]}biphenyl, **(13)**, to Ag^+ was described in Section 3.2.2. Complex **(14)** exhibits an $\{N_2S_2\}$-coordination shell with two additional long distance Ag---S interactions. [26]



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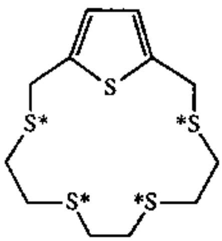
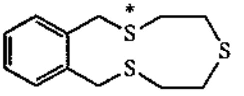


* = coordination site

(27)

The coordination of cyclic thioethers to silver(I) ions is exemplified in three independent pieces of work. 1,4,7,10,13-pentathiacyclopentadecane reacts with $AgNO_3$ in refluxing aqueous methanol to produce the dinuclear complex dication, **(26)**. Crystallographic results show that the one silver(I) ion is 4-coordinate although one interaction, to a bridging sulphur atom, is weak (Ag-S = 2.529 (3), 2.608 (4), 2.537 (3) and 2.907 (3) Å); the other metal ion is 5-coordinate, again with one long Ag-μ(S) interaction (Ag-S = 2.486 (3), 2.558 (4), 2.623 (5), 2.716 (5) and 3.131 (3) Å. [58] The macrocyclic thiophenophane **(27)** also complexes with silver(I) ions to give a dinuclear species which has been characterised by ^{1}H and ^{13}C NMR and IR spectroscopy as well as by an X-ray diffraction study. Here, each Ag atom is 5-coordinate and the two are bridged by sulphur donors; pertinent distances are Ag-S$_{\mathrm{nonbridging}}$ = 2.567 (2), 2.750 (3) and 2.564 (2) Å and Ag-S$_{\mathrm{bridging}}$ = 2.600 (2) and 2.995 (2) Å. [59] The product (87% yield of white crystals) of the reaction of ligand L, (**28**), with AgO_3SCF_3 provides the first example of a complex that contains both a monodentate ligand with the *exo*-conformation of free (**28**) and a tridentate L with the *endo*-conformation that is typical of a crown thioether. In $[AgL_2]^+$, Ag-S$_{\mathrm{monodentate\ L}}$ = 2.476 (3) Å and Ag-S$_{\mathrm{tridentate\ L}}$ = 2.600 (4), 2.590 (3) and 2.570 (3) Å. [60]

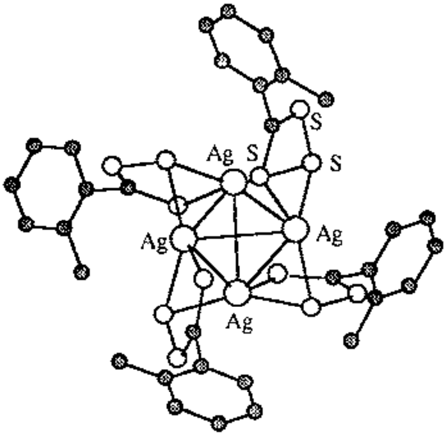
Stability constants for members of a series of silver(I) complexes incorporating dmso and thiourea, L, ligands have been measured potentiometrically in 0-100% aqueous dmso at 25°C. The ions $[Ag(dmso)]^+$, $[Ag(dmso)_2]^+$, $[Ag(dmso)(SCN)_2]^-$, $[Ag(dmso)(SCN)_3]^{2-}$, $[Ag(dmso)L_2]^+$, $[Ag(dmso)L_3]^+$, $[Ag(dmso)_2L_2]^+$, $[Ag(SCN)_n]^{1-n}$ (n = 2-4) and $[AgL_n]^+$ form in solutions with 25-60 wt. % dmso. [61]



* = coordination site
for monodentate ligand

(28)

The reaction of $AgNO_3$ with $Li[CH_2P(S)Ph_2]$ in thf at –78°C yields $[AgCH_2P(S)Ph_2]_2$ in which the ylide ligand bridges the two silver(I) atoms. In the solid state, a one dimensional chain structure is present with an intramolecular Ag'----Ag separation of 2.990 (2) Å and intermolecular separation (Ag---Ag") of 3.227 (2) Å. The chain is a "zig-zag" with ∠Ag'AgAg" = 155.7 (1)°. [62] Related gold complexes are described in Chapter 2.



(29)

A novel reaction involving the insertion of CS_2 into an Ag-S bond takes place. When $[^tBuSAg]_n$ and PPh_3 are dissolved in CS_2, orange crystals of $(Ph_3P)_2Ag(S_2CS^tBu)$ are produced. The insertion is reversible with CS_2 loss occurring at 120-130°C. The molecular structure of $(Ph_3P)_2Ag(S_2CS^tBu)$ has been determined; the silver atom is in a pseudo-tetrahedral $\{S_2P_2\}$-site and the CS_3-group is approximately planar. [63]

The preparation and structural characterisation of the silver(I) perthiocarboxylate $[Ag(S_3C\text{-}C_6H_4\text{-}2\text{-}Me)]_4$, (**29**), have been reported. Four edges of the Ag_4-core are bridged by one S atom of the ligand; Ag-$Ag_{bridged}$ = 3.026 (2) and 3.183 (2) Å, Ag-$Ag_{unbridged}$ = 3.327 (2) and 3.281 (2) Å. [64]

3.2.6 *Complexes with tellurium donor ligands*

The reaction of $Ag[AsF_6]$ with elemental tellurium or Ph_2Te_2 in liquid SO_2 yields $[AgTe_3][AsF_6]$ or $[Ag_2(Ph_2Te_2)_4][AsF_6]$ respectively. Products have been characterised by elemental analysis and IR, Raman and ^1H NMR spectroscopy. It is proposed that the $[AgTe_3]^+$ cation contains a cyclotritellurium unit. [65]

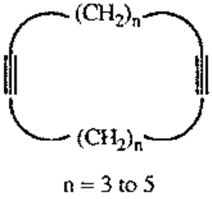
The 2-tellurothiophene anion has been isolated and structurally characterised as its tetraphenylphosphonium salt. Reaction with $AgNO_3$ in dmf yields $[Ph_4P]_2[Ag_4(TeSC_4H_3)_6]$. The solid state structure of the dication consists of a fully edge bridged Ag_4-cluster with Ag-Ag distances averaging 3.13 (9) Å. The Ag-Te distances lie in the range 2.727 (5) to 2.807 (5) Å and the average value of ∠AgTeAg is 69 (2)°. [66]

3.2.7 *Complexes with gold–carbon bonds*

This section highlights some of those complexes containing Ag-C interactions that should be of interest to the coordination chemist. Already mentioned in Section 3.2.5 is the polymeric ylide complex $[AgCH_2P(S)Ph_2]_2$. [62]

Silver(I) peroxyacetylides, $RO_2CMe_2C{\equiv}CAg$, are formed by reactions of $RO_2CMe_2C{\equiv}CH$ ($R = Me(CH_2)_4CMe_2$, $PhCMe_2$, $Me_3CO_2CMe_2C{\equiv}CCMe_2$) with $[Ag(NH_3)_2][NO_3]$. The acetylides react with acid chlorides, $(SCN)_2$ and I_2 to generate peroxyalkynyl esters, peroxyalkynyl thiocyanates and peroxyalkynyl iodides respectively. [67] Ligands L, (**30**), react with silver(I) triflate to give colourless crystals of $[L.AgO_3SCF_3]_n$ and spectroscopic data indicate the presence of a weak $C{\equiv}C \rightarrow Ag^+$ π-interaction. An X-ray diffraction study of $[C_{10}H_{12}.AgO_3SCF_3]_n$ shows that the structure is composed of a 2-dimensional network with each diyne ligand adopting a chair conformation and the diynes coupled (via alkyne→Ag^+) by $\{Ag(O_3SCF_3)Ag\}$-units; C-C_{alkyne} = 1.211 Å and Ag-C = 2.410 Å. Two other structures are also presented. [68]

With the stilbene (**31**), AgO_3SCF_3 forms a complex in which the silver(I) ion resides partially within the cavity formed by the two phenyl substituents. The distance from the silver(I) ion to the *para*-carbon atom of one phenyl ring is 2.579 (4) Å. The second phenyl group interacts with the Ag atom in a μ_2-mode (Ag-C_{para} = 2.583 (5) Å and Ag-C_{meta} = 2.510 (5) Å). The triflate ion is fully coordinated to the silver(I) ion with Ag-O = 2.356 (3) Å. Association between adjacent $LAgO_3SCF_3$ units leads to a polymeric chain. [69]



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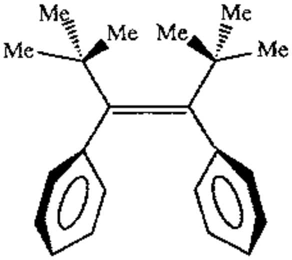


(31)

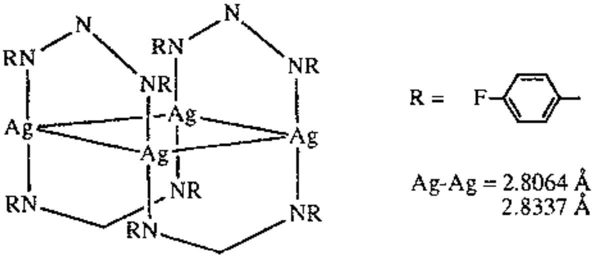
The 1:6 silver(I) acetylide: silver(I)nitrate complex has been crystallographically determined and consists of $[Ag_3C_2]^{6+}$ and NO_3^- ions. The C_2^{2-}ion resides in a rhombohedral Ag_8-cage and these are linked via nitrate ions to give a 3-dimensional lattice. [70]

An example of $\{Ag_4Pt_2\}$-cluster bound C≡CR (R = Ph, ^tBu) [71] has been described (see Section 3.3.2).

3.3 CLUSTERS CONTAINING SILVER

3.3.1 *Homometallic clusters*

An interesting tetrasilver cluster $[Ag\{4\text{-}F\text{-}C_6H_4\text{-}N_3\text{-}C_6H_4\text{-}4\text{-}F\}]_4$ has been prepared by the reaction of sodium(1,3-*bis*(4-fluorophenyl)triazenide) with $AgNO_3$ in acetonitrile. A molecular structure determination of the complex (**32**) confirms the presence of a planar Ag_4-rhombus with bridging RNNNR ligands. In the IR spectrum, (**32**) is characterised by absorptions at 1371 cm^{-1} ($\nu_{N=N\,asym}$) and 1194 and 663 cm^{-1} ($\nu_{N=N\,sym}$). [72]



(32)

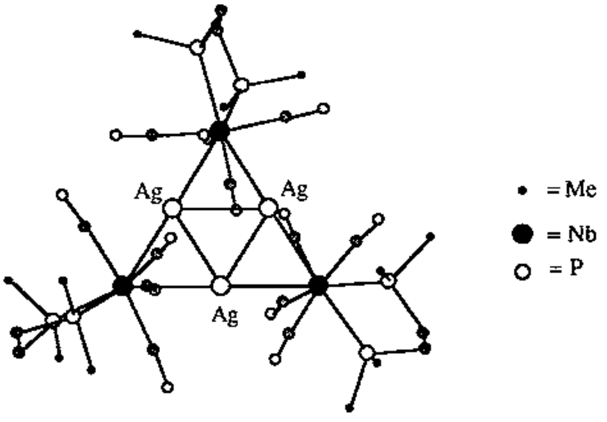
Several other Ag_x-clusters with supporting ligands have been discussed in previous Sections: $Ag_4[PhN_3\text{-}C_6H_4\text{-}N_3(H)Ph]_4$ [12], the complex cation (**14**) [26], $[AgL]_6$ and $[Ag_8L_6][Ag(NO_3)_2]_2.2MeOH.CH_2Cl_2$ for HL = 2-(SH)-6-($SiMe_2Ph$)-py) [53], the cation $[Ag_{13}L_{16}]^{13+}$ with HL = 4-mercapto-1-methylpiperidine [54], $[Ag(S_3C\text{-}C_6H_4\text{-}2\text{-}Me)]_4$ [64] and $[Ag_4(TeSC_4H_3)_6]^{2+}$. [66] In $[Ag_3C_2]^{6+}$ a lattice containing rhombohedral Ag_8-cages is present. [70]

3.3.1 Heterometallic clusters

Several mixed silver-gold clusters have been described in the previous chapter in Section 2.5.2.

$Ag(C{\equiv}CR)_n$ (R = Ph, ${}^tBu$) reacts with $PtCl_2(tht)_2$ to give $Pt_2Ag_4(C{\equiv}CR)_8$ for which a crystallographic study when R = ${}^tBu$ reveals an octahedral metal core with a *trans*-arrangement of platinum atoms. An alternative route to the cluster species involves the reaction of $[Pt(C{\equiv}CR)_4]^{2-}$ with $AgClO_4$. Related gold(I) compounds have also been prepared. [71]

Two raft-compounds, $Ag_3M_3(CO)_{12}(dmpe)$ (M = Nb or Ta), have been synthesised by the oxidation of $[M(CO)_4(dmpe)]^-$ with $AgNO_2$ or $AgBF_4$. Both clusters have been characterised by X-ray crystallography and the niobium complex is shown in (33). (Compare with the related raft $(\mu\text{-}H)_6(\eta^5\text{-}C_5H_4SiMe_3)_3Nb_3Au_3$ which is described in Section 2.5.2 in Chapter 2). The three silver atoms form a central equilateral triangular frame for the cluster. Both the niobium and tantalum derivatives are degraded by HI to generate $MI(CO)_4(dmpe)$. [73]



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