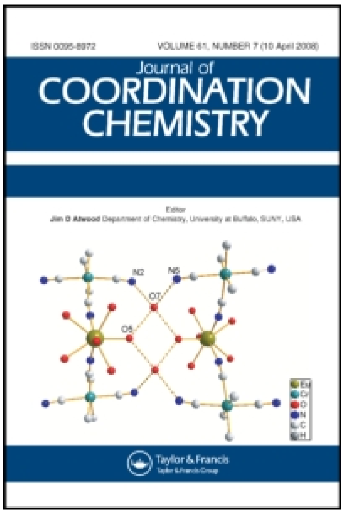

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REVIEW: HETEROMETALLIC SILVER COMPOUNDS; CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

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REVIEW

HETEROMETALLIC SILVER COMPOUNDS; CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

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This review summarizes the data for almost one hundred and forty crystallographic structures of silver coordination and organometallic compounds in which at least one other metal atom is present. The structures are classified in terms of the total number of metal atoms present, and discussed in terms of the coordination about the metal atoms, and the corresponding bond lengths and interbond angles.

KEYWORDS: silver, clusters, heterometallic, structures

CONTENTS

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ABBREVIATIONS

acac	acetylacetonate
Bu	butyl
Bu^i_2dtc	di-iso-butyl-dithiocarbamate
$C_3H_2O_6P$	tetrahydrothiophene
$C_4H_2O_6$	tartrate
C_4H_6NO	2-pyrrolidinone anion
C_6Cl_5	pentachlorophenyl
C_6F_5	pentafluorophenyl
$C_6H_6O_7$	citrate
$C_7H_4NS_2$	benzothiazole-2-thiolate
$C_8H_4O_4$	o-phthalate
$C_{37}H_{46}N_2O_2S$	Schiff base, from 2 equiv. of 2-amino-4,6-di-tert-butylphenol with 1 equiv. of 2-mercapto-5-methylisophthaladehyde
cod	cycloocta-1,5-diene
cp	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
dimen	1,8-diisocyanomethane
dmpe	bis(dimethylphosphino)ethane
dmso	dimethylsulphoxide
dppp	bis(diphenylphosphino)propane
dpam	bis(diphenylarsino)methane
dppm	bis(diphenylphosphino)methane
dtox	dithiooxalate
en	ethylenediamine
Et	ethyl
hcqd	camphorquinone dioximate
LX	ligand with donor atom X.
m	monoclinic
Me	methyl
Me_2am	dimethylaminomethyl
Meth	1-methylthyminate
mt	2-mercaptothiazoline
mtt	N,N′-methylparatolyltriazenide
OC_4H_8dtc	dialkyldithiocarbamate
or	orthorhombic
Pcy_3	tricyclohexylphosphine
Ph	phenyl
pp	bis(diphenylphosphinomethyl)benzo[c]penanthrene
pr	propyl
Pr^i_2dtc	di-iso-propyl-dithiocarbamate
pz	pyrazolate
tht	tetrahydrothiophene
tr	triclinic
trg	trigonal
tripod	$CH_3C(CH_2PPh_2)_3$
ttas	bis-(O-dimethylarsinophenyl)methylarsine

INTRODUCTION

Over the last twenty years studies on the reactivity of various metal derivatives with silver salts have been carried out by many research groups. Many of these studies have resulted in isolable compounds suitable for crystallographic structural studies. There have been several annual reviews of silver chemistry,[1] and we have recently completed a classification and review of the structures of silver compounds.[2] The present review covers the structures of compounds of silver which contain at least one other metal published prior to the end of 1991.

One of the aims of this review is to compare and contrast the structural behaviour of heteronuclear copper and silver compounds, and to clarify the factors which govern the stereochemical interactions around these metal atoms in such complexes. Nearly one hundred and forty heterometallic silver compounds have been surveyed, and the structures have been classified according to nuclearity. Within each subgroup, the derivatives are referenced in order of increasing silver-metal distance.

HETEROBINUCLEAR SILVER COMPOUNDS

There are nineteen heterobinuclear silver derivatives listed in Table 1. Four of these examples[3,4] have a PtC_3S or PtC_4 moiety combined with the AgP or AgS moiety through direct Pt-Ag bonding, unsupported by covalent bridges. The Pt-Ag bond distances range from 263.7(1) to 269.2(2) pm and the Pt-Ag-P or Pt-Ag-S angles range from 168.6(2) to 174.3(1)°. The distance of 275.8(2) pm, between the Ag(I) and Ir(III) atoms in a single hydride bridged derivative,[6] also indicates a direct metal-metal bond.

In two bimetallic complex anions,[7,8] $Pt(C_6X_5)_2Cl_2$ and $Ag(PPh_3)$ units are bonded by a direct Pt-Ag bond (278.2(1) pm[7] and 279.6(2) pm[8]). In addition one of the chlorine atoms of the Pt group bridges to the Ag atom (Ag-Cl = 266.7(3) pm[7] and 247.3(5) pm[8]). The Ag-Cl-Pt bridge angle is larger for the longer Ag-Pt bond distance (67.24(6)°[7] and 71.0(1)°[8]). In bimetallic dianions $[(CN)Ag^1(\mu\text{-}S)_2M^{VI}S_2]^{-2}$ (M = Mo or W),[10,12] the MS_4 group acts as a bidentate ligand to an essentially linear AgCN unit. The Ag^1-M^{VI} distances of 286.8(1) pm (Mo)[10] and 289.0(1) pm (W)[12] indicate that metal-metal bonding is occurring.

In the yellow compound $(PPh_3)(C_6Cl_5)ClPt^{II}(\mu\text{-}Cl)Ag^I(PPh_3)$[13] the moieties $Pt(C_6Cl_5)(PPh_3)Cl$ and $Ag((PPh_3)$ are bridged by a single chlorine atom. The Ag-Pt distance of 294.5(1) pm and Ag-Cl-Pt bridge angle of 74.6(1)° are both larger than those found in the above Ag/Pt complex anions, again showing the interdependence between Ag-Pt distances and Ag-Cl-Pt bridge angles.

In another Ag/Pt derivative,[14] two bidentate bis(diphenylphosphino)methane molecules act as tri-atom bridges between AgP_2I and PtC_2P_2 moieties. Here the Ag-Pt distance of 314.6(3) suggests that there is no significant metal-metal bonding. A complex Ag/Cu dianion $[Ag^ICu^IBr_4]^{-2}$[15] has two bromine bridges between the metal atoms, with a resulting Ag-Cu separation of 344.9(2) pm. Both metal atoms have a three-coordinate geometry (Table 1).

The structure of $[cp^*(pz)Ir(pz)_2Ag(PPh_3)]$[16] is shown in Figure 1. Two bridging pyrazolate groups are observed between the metal atoms. The silver atom completes its trigonal planar coordination with a PPh_3 group. The iridium atom coordinates an able 1 Crystallographic and structural data for heterobinuclear silver compounds[a]

OMPOUND	Crys. cl Sp.Grp Z	a, [ppm] b [pm] c [pm]	α [°] β [°] γ [°]	chromo- phore	M-L [pm]	Ag-M [pm] Ag-L-M [°]	L-M-L [°]
$\mathrm{C_6F_5)(tht)Pt^{II}\cdot}$ $\mathrm{g^{I}(PPh_3)}$	m $P2_1/n$ 4	1400.6(2) 1744.1(3) 1740.7(2)	110.74(1)	AgP^b $\mathrm{PtC_3S}$	P 235.8 (3) C 205(1,5) S 232.8(1)	263.7(1)	P,Pt[b] 174.3(1) C,C 87.4(5,7) C,S 72.4(3,2.0)
$\mathrm{Bu)[(C_6F_5)_4Pt^{II}\cdot}$ $\mathrm{g^{I}(tht)\cdot {}^1\!/_2C_6H_{14}}$	tr $P\bar{1}$ 2	1167.0(8) 1223.5(5) 2092(10)	103.87(3) 91.64(4) 116.95(2)	AgS $\mathrm{PtC_4}$	S 240.1(6) C 205.5(18,37)	264.1(1)	S,Pt 168.6(2) C,C 90.0(7,2.3)
$\mathrm{ht)(C_5Cl_5)\cdot}$ $\mathrm{_5F_5)_2Pt^{II}Ag^{I}(PPh_3)}$	m $P2_1/n$ 4	1435.0(3) 1775.0(5) 1773.3(4)	110.35(2)	AgP $\mathrm{PtC_3S}$	P 236.3(8) C 212.0(21) C 205.3(22,37) $\mathrm{S_{tht}}$ 234.5(7)	265.0(2)	P,Pt 173.0(2) C,C 87.5(9,1.2) C,S 92.2(6,3.0)
$\mathrm{tas)Ag^0Co^0(CO)_4}$	m $P2_1/n$ 4	1291 1691 1207	100.17	$\mathrm{AgS_3}$ $\mathrm{CoC_4}$	As 262(1,0) 272(1) OC 173(4,9)	266(1)	As,As 87.7(2,15.4) AsCo 125.4(2,8.0) C,C 109.0(2.3,10.7)
$\mathrm{Bu_4)[(C_6Cl_5)_2\cdot}$ $\mathrm{_6F_5)_2Pt^{II}Ag^{I}(tht)]}$	tr $P\bar{1}$ 2	1197.6(2) 1239.8(1) 1999.6(4)	94.81(1) 91.95(1) 116.01(1)	AgS $\mathrm{PtC_4}$	S 242.4(8) C 209.2(22,32) C 207.2(22,34)	269.2(2)	S,Pt 169.3(2) C,C 90.0(8,2.7)
$\mathrm{PPh_3)Ag^{I}(\mu\text{-}H)\cdot}$ $\mathrm{^{III}(H)_2(PPh_3)_3]\cdot}$ $\mathrm{F_3SO_3)}$	m Cc 4	1946.1(4) 1945.8(5) 2005.4(5)	96.16(2)	AgHP $\mathrm{IrH_3P_3}$	μH 180 (20) P 238.4(6) H 180(20,10) μH 140(20) P 232.7(5,35)	275.8(2) 118(8)	H,P not given P,Ir 160.1(2) H,H 81.172(9) P,P 100.9(2,3) 153.2(2) H,P 95(8,9) 172(4)
$\mathrm{Bu_4)[(C_6Cl_5)_2\cdot}$ $\mathrm{^{II}Cl_2Ag^{I}(PPh_3)]}$	m $P2_1/n$ 4	2007.6(6) 2850.7(5) 947.9(3)	97.17(3)	AgClP $\mathrm{PtC_2Cl_2}$	μCl 266.7(3) P 239.5(2) C 206.5(9,1) Cl 229.5(2) μCl 233.1(2)	278.2(1) 67.24(6)	Cl,P 118,74(9) Cl,Pt 50.60(5) P,Pt 163.42(8) C,C 177.3(3) Cl,Cl 176.7(1) C,Cl 90.0(2,3.2)

$(NBu_4)[(C_6F_5)_2Pt^{II}$ $Cl_2Ag^I(PPh_3)]$ $0.1CH_2Cl_2$	*tr* $P\bar{1}$ 2	1271.0(3) 1886.5(5) 1212.9(5)	103.10(3) 114.44(2) 77.07(2)	AgClP	μCl 247.3(5) P 235.0(6)	279.6(2) 71.0(1)	Cl,P 161.6(2) Cl,Pt 52.3(1) P,Pt 145.2(2)	8
				PtC_2Cl_2	C 208(2,3) Cl 229.6(5) μCl 233.9(5)		C,C 175(1) Cl,Cl 178.4(2) C,Cl 90.0(6,1.3)	
Os{(p-tolyl)C}$Ag^I\cdot$ $Cl_2(CO)$	*m* $P2_1/n$ 4	1302.1(2) 2371.4(2) 1299.9(2)	90.55(1)	AgCCl	C 217.0(5) Cl 231.1(2)	279.94(4)	C,Cl 162.5(2) C,Os 41.1(1) Cl,Os 150.36(6)	9
				OsC_2P_2Cl	C 184.2(6,3) P 241.0(1,0) Cl 248.8(1)		C,C 104.4(2) P,P 169.96(4)^c	
$(PPh^4)_2[(CN)Ag^I\cdot$ $(\mu\text{-}S)_2Mo^{VI}S_2]$	*m* $P2_1/N$ 4	2003.4(3) 1445.1(3) 1577.2(4)	92.30(2)	AgS_2C	NC 208.2(12) μS 249.1(3,16)	286.8(1) not given	not given C,Mo 169.1(3)	10
				MoS_4	S 216.0(3,1) μS 221.8(3,6)			
$(PPh_4)_2[(CN)Ag^I\cdot$ $(\mu\text{-}S)_2W^{VI}S_2]$	*m* $P2_1/n$ 4	2002.4(8) 1445.3(5) 1578.6(5)	92.35(3)					10
$[(CO)(PPh_3)_2Ir^I\cdot$ $Ag^I(Me_2CHCO_2)(mtt)]$ Me_2CHCO_2H	*m* $P2_1/n$ 4	1241.2(1) 2170.1(1) 1902.7(1)	97.22(2)	AgON	O 214.8(17) N 211.1(14)	287.4(2)	O,N 166.1(6) O,Ir 110.3(5) N,Ir 80.6(4)	11
				IrP_2CN	P 232.5(5,11) OC 186.4(25) N 208.6(13)		P,P 172.6(2) P, C 89.0(8,1.8) P,N 90.6(4,1.7) CN 174.4(9)	
$(NPr_4)_2[(CN)Ag^I\cdot$ $(\mu\text{-}S)_2W^{VI}S_2]$	*tr* $P\bar{1}$ 2	954.6(3) 1300.9(2) 1469.2(2)	75.62(1) 84.93(2) 80.57(2)	AgS_2C	NC 209.3(11) μS 247.9(3,3)	289.0(1) 75.6(1,1)	S,S 96.5(1) S,C 131.8(2,7) C,W 179.0(3)	12
				WS_4	S 215.6(3,3) μS 222.7(2,2)		S,S 109.5(1,2.8)	
$[(PPh_3)(C_6Cl_5)Cl\cdot$ $Pt^{II}(\mu\text{-}Cl)\cdot$ $Ag^I(PPhn^3)]$	*m* $P2_1/n$ 4	1427.0(2) 1466.3(2) 2002.4(2)	93.58(1)	AgClP	P 238.2(3) μCl 251.4(2)	294.5(1) 74.6(1)	Cl,P 162.8(1)	13
				$PtCl_2CP$	C 203.6(12) P 233.4(3) Cl 230.6(3) μCl 234.1(3)		Cl,Cl 172.9(1) Cl,C 86.5(3,3) Cl,P 93.4(1,1.7) C,P 172.6(3)	

Table 1 Continued

COMPOUND	Crys. cl Sp.Grp Z	a, [ppm] b [pm] c [pm]	α [°] β [°] γ [°]	chromo-phore	M-L [pm]	Ag-M [pm] Ag-L-M [°]	L-M-L [°]
$(PhC{\equiv}C)_2Pt^{II}\cdot$ $(dppm)_2Ag^{I}I$	m C2/m 4	2223.9(4) 1572.7(4) 2080.8(3)	 116.82(2)	AgP_2I PtC_2P_2	P 250.4(7,0) I ;279.6(4) C 200(4,0) P 230.0(6,0)	314.6(3)	P,P 126.4(1) P,I 114.9(2) C,P 90.2(2,1.7)
$(PPh_4)_2[Ag^{I}Cu^{I}Br_4]$	m P2₁/n 2	1441.6(7) 795.1(5) 1983.4(10)	 102.58(4)	MBr_3	Br 240.1(2) μBr 254.3(2) 268.8(2)	344.9(2) not given	μBr,μBr 97.55(5) Br,μBr 131.2(1,7.9)
$[cp^*Ir^{III}\cdot$ $(pz)_3Ag^{I}(PPh_3)]$	m P2₁/n 4	961.71(4) 1421.15(7) 2622.9(2)	 91.90(1)	AgN_2P IrC_5N_3	N 220.8(4,3) P 234.1(1) N 207.7(3,6) C 217.9(5,16)	386.01(2)	N,N 95.0(1) N,P 132.5(1,4.3) N,N 86.6(1,3.8) N,cp* 127.6(1,2.9)
$cp(C_5H_4CH_2NMe_3FeAg$							
$AgEu(fod)_4$							
$[^1/_3Ag_I{}^2/_3Au_I(PPh_3)_3]NO_3$	tr $P\bar{1}$ 2	1335.1(2) 1389.9(3) 1436.1(2)	64.23(2) 88.52(2) 75.52(2)				

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is th and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these c

[c] C-Os-P = 91.8(2,4.1)°; C-Os-Cl = 107.6(2) and 148.1(2)°; P-Os-Cl = 85.8(1,1)°.

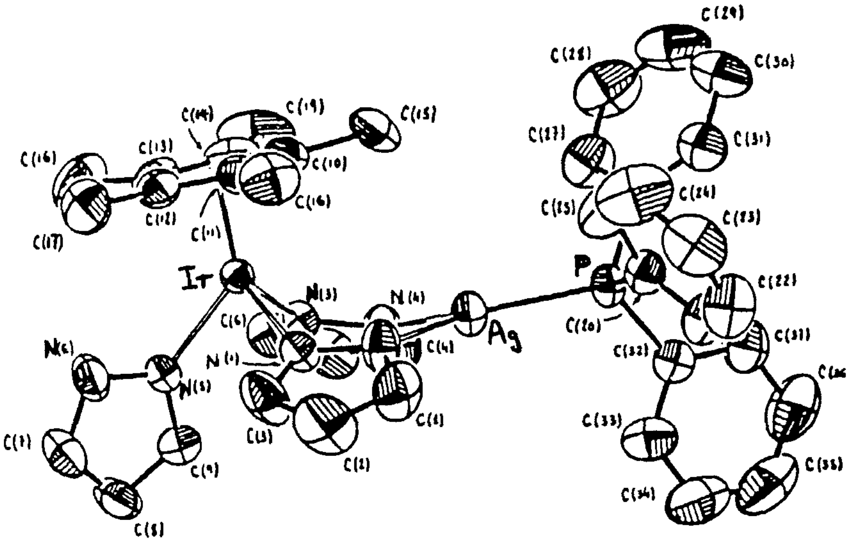

Figure 1 Structure of $[cp^*Ir^{III}(pz)_3Ag^I(PPh_3)]$.[16]

additional terminal pyrazolate ligand and an η^5-pentamethylcyclopentadienyl ring. The Ag-Ir distance of 386.01(2) pm excludes any significant metal-metal interaction.

The data in Table 1 indicate the occurrence of only two crystal classes, monoclinic and triclinic. Except for one example of zero oxidation state for silver,[5] the silver atom is found only in its +1 oxidation state. Silver is found in a digonal environment, one of the ligand sites being occupied by a Pt atom in two cases.[3,4] The mean Ag-L bond distances in the digonal examples increase in the order: 211.1 pm (LN) < 214.8 pm (LO) < 231.1 pm (Cl) < 237.2 pm (PPh_3) < 241.3 pm (LS). The mean Ag-L(bridge) distances are: 180 pm (H) < 255.1 pm (Cl). Silver is also found in a trigonal-planar environment, with bond distances for unidentate ligands of; 208.8 pm (CN) < 234.1 pm (PPh_3) < 240.1 pm (Br) < 279.6 pm (I). For bidentate ligands the values are; 220.8 pm (LN) < 250 pm (LP); and for bridging ligands; 248.5 pm (S) < 261.6 pm (Br).

There are some 38 examples of heterobinuclear copper(I) compounds,[20] with the copper(I) atom in digonal, trigonal and tetrahedral arrangements. In general, the Cu(I)-L distances are shorter than the corresponding Ag(I)-L distances (Table 8).

The most common heterometallic atom in the silver derivatives is platinum, with intermetallic distances ranging from 263.7(1) pm to 314.6(3) pm. The former is the shortest observed value in Table 1 and indicates a firm M-M bond, while the latter excludes any such bonding. The mean Ag(I)-M distances (excluding those over 300 pm) increase in the sequence: 273.5 pm (Pt) < 279.9 pm (Os) < 281.6 pm (Ir) < 286.8 pm (Mo) < 289.0 pm (W). This order closely follows the covalent radia of the respective heterometallic atoms. By contrast, the most common heterometals in the Cu(I) heterobinuclear derivatives are Co and Mo. There is only one Ag/Co example, and in this derivative both the silver and the cobalt have oxidation numbers of zero, with a Ag-Co distance of 266(5) pm. In general, the mean Cu-M distances are shorter than the corresponding Ag-M values, as might be anticipated, the mean

Cu-M versus Ag-M values being: 241.8 *vs* 266 pm (M = Co), 262.3 *vs* 286.8 pm (M = Mo) and 275.0 *vs* 289.0 pm (M = W).

HETEROTRINUCLEAR SILVER COMPOUNDS

Structural information for heterotrinuclear silver compounds are summarized in Table 2. The structures are listed in order of decreasing number of silver atoms and increasing Ag-M distance. There are eleven examples containing two silver atoms plus a heterometal atom. In three of these[21,22] the silver atoms are located above and below the NiS_4 planes in a "chair" configuration, and are in close proximity to a triad of atoms defined by two sulphur atoms and the nickel(II) atom, which is actually the "central" atom. Both the nickel(II) and the silver(I) atoms are four-coordinated, but with different types of geometry, square planar and tetrahedral, respectively. The Ag-Ni distances range from 290.7(3) to 301.0(1) pm. The mean M-S(bridge) distance is about 62 pm longer for Ag than Ni, which reflects the respective covalent radii of 153 and 120 pm. There is a relationship between the mean Ag-P and Ag-S distances in a given compound. As the former decreases; 248.5 pm > 248.0 pm > 244.9 pm, the latter increases; 278.0 pm < 279.8 pm < 285.5 pm. The P-Ag-P angle opens in the same order; 118.5° < 119.5° < 128.0°. This concomitant opening of the P-Ag-P angle and shortening of the Ag-P bond distance, optimizes the steric contact between the phosphine and sulphur ligands and reflects the decreased steric hindrance of an ethyl group relative to a phenyl group.

In another three examples,[10,23,24] the MS_4 or MSe_4 group acts as a double bidentate ligand, binding a $Ag(PPh_3)$ unit on one side and a $Ag(PPh_3)_2$ unit on the other. The mean Ag-Mo and Ag-W bond distances of 294.5 and 298.0 pm, respectively, indicate a metal-metal bond. The mean Ag-L and M-L distances increase with increasing coordination number and/or increasing covalent radius of the metal atom (Table 2).

The molecule $Ag_2Rh(C_6F_5CC)_5(PPh_3)_3$[25] has three metal atoms, $Ag\cdot\cdot Rh\cdot\cdot Ag$ in a bent configuration with an angle of 110.55(2)°. The central rhodium atom is essentially in a regular octahedral environment with one PPh_3 ligand and five σ-acetylide ligands. Each silver atom is in tetrahedral environment, bonded to one PPh_3 ligand and in an asymmetric fashion to three acetylenic π-bonds. The coordination arrangement and the mean Ag-Rh distance of 309.5 pm suggest a zwitterionic association between $[(PPh_3)Rh^{III}(C_6H_5CC)_5]^{-2}$ anion and $[Ag(PPh_3)]^+$ cations, held together by silver-acetylene π-bonding.

The molecule $(C_6Cl_5)_2PtCl_2Ag_2(PPh_2Me)_2$[7] has a crystallographic centre of symmetry. The Pt(II) atom occupies a square planar site with two chlorine atoms and two C_6Cl_5 groups in exactly *trans* positions at 180°. The chlorine atoms act as bridges between the metal atoms (Table 2). The Ag-Pt distance of 313.1(1) pm does not support the existence of a metal-metal bond.

Two other examples[26,27] provide the first unambiguous evidence that simple chlorinated hydrocarbons can coordinate to metal atoms. Two symmetry related $Ag(CH_2Cl_2)^+$ or $Ag(ClCH_2CH_2Cl)^+$ moieties are bridged by the centrosymmetric $Pd(OTeF_5)_4^{-2}$ core, which contains a planar PdO_4 array. Each silver(I) atom contains a pseudo-octahedral $AgCl_4O_2$ array.

There is one example[28] which consists of two trigonal planar AgO_2P moieties triply bridged by $\{PPh_2(cp)\}Fe$ plus two benzoato fragments (Table 2).

able 2 Crystallographic and structural data for heterotrinuclear silver compounds[a]

OMPOUND	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	M-L [pm]	Ag-M [pm] Ag-L-M [°] M-M [pm] M-L-M [°]	L-M-L [°]
$PPh_3)_4Ag^I{}_2 \cdot Ni^{II}$	m	2653.4(12)		AgS_2P_2	P^b 248.0(5,39)	293.7(3,30)	S,S^b 75.0(1,6)
$-S_2CC(CN)_2\}_2]$	$P2_1/a$	1267.1(7)	105.03(1)		μS 279.8(5,118)	71.9(2,1.9)	P,P 118.5(1)
	4	2288.7(10)					S,P 112.7(2,22.9)
				NiS_4	μS 279.8(5,118)		S,S 90.0(1,10.5)
$PPh_2Et)_4Ag^I{}_2 \cdot$	or	1842.7(9)		AgS_2P_2	P 244.9(2,10)	298.6(1)	S,S 63.61(4)
$_2CC(CN)_2\}_2Ni^{II}]$	$Pbca$	2689.4(10)			μS 285.5(2,77)	not given	P,P 128.00(6)
	4	1314.9(9)					S,P 110.0(5,17.2)
				NiS_4	μS 217.7(2,1)		S,S 90.0(1,2.5)
$PPh_3)_4Ag^I{}_2 \cdot$	m	2258.1(28)		AgS_2P_2	P 248.5(4,20)	301.0(1)	S,S 66.1(1)
$_2CC(CN)_2\}_2Ni^{II}]$	$P2_1/a$	1301.5(12)	119.51(1)		μS 278.0(3,20)	73.6(1,4)	P,P 118.5(1)
	2	1435.2(14)					S,P 114.3(1,20.2)
				NiS_4	μS 218.2(3,11)		S,S 90.0(1,1.9)
$PPh_3)_3Ag^1{}_2 \cdot$	m	1815.4(4)		AgS_2P	P 238.0(4)	294.5(2,85)	S,S 97.0(2)
$-S)_2Mo^{VI}S_2] \cdot$	$P2_1/c$	1732.2(3)	95.11(2)		μS 245.9(5,2)	76.9(2,1.7)	S,P 131.6(2,1.1)
$8CH_2Cl_2$	4	1779.0(3)		AgS_2P_2	P 247.1(4,1)		S,S 90.4(2)
					μS 257.2(5,1)		P,P 120.6(2)
							S,P 110.5(2,5.4)
				MoS_4	μS 220.5(5,11)		S,S 109.5(2,3.1)
$Ph_3)_3Ag^1{}_2 \cdot$	m	1811.1(2)		AgS_2P	P 236.2(5)	297.1(2,85)	S,S 96.2(2)
$-S)_2W^{VI}S_2 \cdot$	$P2_1/c$	1735.6(2)	95.02(1)		μS 247.6(6,1)	not given	S,P 131.9(2,9)
	4	1779.7(2)		AgS_2P_2	P 246.0(6,13)		S,S 89.7(2)
					μS 257.9(6,1)		S,P 110.4(2,5.8)
				WS_4	μ 220.7(6,17)		S,S 109.5(2,2.9)
$PPh_3)_3Ag^1{}_2 \cdot$	m	1817.3(8)		$AgSe_2P$	P 236.6(7)	299.0(2,79)	not given
$-Se)_2W^{VI}Se_2] \cdot$	$P2_1/c$	1743.4(7)	95.72(3)		μSe 254.6(4,6)	not given	
$8CH_2Cl_2$	4	1790.7(6)		$AgSe_2P_2$	P 246.9(7,15)		
					μSe 263.7(4,4)		
				WSe_4	μSe 232.8(3,18)		
$g^I{}_2Rh^{III} \cdot$	m	1590.2(2)		AgC_3P	P 238.9(2,1)	309.5(1,8)	C,P 98.6–164.5(2)
$_5F_5CC)_5(PPh_3)_3$	$P2_1/n$	2149.7(2)	102.00(1)		C 268.3(7,434)	–	
	4	2504.1(3)		RhC_5P	P 234.3(2)		C,C 89.6(6,4.7)
					C 202.2(7,18)		C,P 91.0(2,4.3)

able 2 Continued

OMPOUND	Crys.cl Sp.Grp *Z*	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore	M-L [pm]	Ag-M [pm] Ag-L-M [°] M-M [pm] M-L-M [°]	L-M-L [°]
$C_6Cl_5)_2Pt^{II}\cdot$ -Cl)$_2$Ag$^{I}_2$ Ph$_2$Me)$_2$	*tr* $P\overline{1}$ 1	1082.1(3) 1246.2(3) 926.8(2)	109.23(2) 99.87(2) 70.85(2)	AgClP	P 237.0(2) μCl 241.8(2)	313.1(1) 82.63(5)	Cl,P 163.1(1)
				PtC_4Cl_2	C 205.2(4,0) μCl 232.3(1,0)		C,C 90.0(1,8) Cl,Cl 180.0
g$^{I}_2$(CH$_2$Cl$_2$)$_4\cdot$ d^{II}(OTef$_5$)$_4$: 143K	*tr* PT 1	892.3(2) 995.3(3) 998.5(2)	114.23(2) 100.54(2) 91.42(2)	$AgCl_4O_2$	Cl 283.2(2,57) μO 246.8(5,64)	not given 123.9(3,1.7)	Cl,Cl 60.6–138.4(1) O,O 67.0(2) Cl,O 80.9–159.4(1)
				PdO_4	μO 201.2(5,3)		O,O 85.3(2)
g$^{I}_2$(ClCH$_2$CH$_2$Cl)$_4$ d^{II}(OTeF$_5$)$_4$ 146K	*tr* $P\overline{1}$ 1	957.1(2) 1031.4(3) 1039.9(2)	106.37(2) 91.98(2) 112.21(2)	$AgCl_4O_2$	Cl 274.2(1,186) μO 237.2(3) 277.7(2)	not given 96.1(1,6.2)	Cl,Cl 63.8–139.6(1) O,O 63.8(1) Cl,O 79.9–151.0(1)
				PdO_4	O 200.2(3,5)		O,O 86.6(1)
g$^{I}_2$(PhCO$_2$)$_2\cdot$ PPh$_2$(cp)}Fe]	*or* *Pbca* 8	1053.2(2) 1885.1(8) 4174(2)		AgO_2P	P 235.2(5,12) O 220.1(9,19) 243.9(5,39)	not given – *c*	O,O 103.7(4,3.0) O,P 103.0(3,4.9) 151.6(2,7)
				FeC_{10}	cpC 205(2)		
g^{I}Ir$^{I}_2$(dimen)$_4\cdot$ Ph$_3$)$_2$](PF$_6$)$_3$ 193K	*m* *C*2/*c* 4	2660(10) 1467(1) 2749(6)	117.8(3)			264.2(1) –	Ir,Ir 180
				IrC_4P	P 239(3) C not given		P,Ag 174(1)
g^{I}Ir$^{I}_2$(dimen)$_4\cdot$ mso)$_2$](PF$_6$)$_3$	*or* *Immm* 2	1442(7) 2450(4) 1172(8)	117,8(3)			264.2(1)	Ir,Ir 180 –
				IrC_4S	not given	528.4	
g^{I}{Rh(CO)$\cdot$ Ph$_3$)(cp)}$_2$]$\cdot$ F$_6$)$\cdot$PhMe	*m* $P2_1/c$ 4	1107.8(1) 2437.5(3) 1860.4(3)	92.90(1)			264.4(1,8)	Rh,Rh 171.0
				RhC_6P	P 227.2(2,6) OC 184.9(7,4) cpC 224.3(8,47)		C,C 102.9–166.6(3) C,P 91.9–158.0(2)
g^{I}{Ir(CO)$_2\cdot$ p*)}$_2$](BF$_4$)	*m* $P2_1/c$ 4	1235.5(2) 1371.3(2) 1667.2(3)	97.70(1)			265.9(1,0)	Ir,Ir 173.7(1)
				IrC_7	OC 184.8(15,30) cpC 224.7(12.36)		C,C 88.9(7,1.1) C,cp 134(–,1)

$\{(NH_3)_2Pt^{II}\cdot$ $C_6H_7N_2O_2)_2Ag^I\cdot$ $NO_3)]\cdot 5H_2O$	*tr* $P\bar{1}$ 2	1412.2(11) 1342.2(23) 1174.7(12)	101.6(1) 100.01(8) 95.94(11)	AgO_4	O 245.3(12,110)	268.7(1,18)	Pt,Pt 145.11(5) O.O 82.8(4,3.6) 155.9(4,3.8)
				PtN_4	N 205.0(12,370		N,N 89.5(5,1.7) 178.0(5)
$Ag^I\{CHC(Ph)N(H)$ $Me\{Fe_2(CO)_6\cdot$ $PPh_2)](ClO_4\cdot$ $_6H_6\cdot PhMe$	*tr* $P\bar{1}$ 2	1410.1(3) 1065.4(4) 1577.7(4)	93.68(4) 114.27(2) 95.03(3)	AgC_2	C 251(1,1)	269.4(1,9)	not given
				FeC_4P	not given		
$Ag^I(MeCO_2)Rh_2$ $CO)(dppm)(cp)_2]$	*or* *Pnma* 4	1513.3(2) 1817.6(3) 1265.6(1)		AgO_2	O 252.2(9,0)	271.9(1)	Rh,Rh 61.4(1) O,O 48.6(6)
				RhC_6P	P 223.6(10 μOC 198.6(7,O) cpC 225.7(9,29)	277.6(1) 88.7(1)	C,P 89.7(1)
$Ag^I(MeCO_2)Rh_2\cdot$ $CO)(dppm)(cp)_2]$	*or* *Pnma* 4	1442.6(1) 1813.4(2) 1261.4(1)		AgO_2	O 243.2(7)	273.0(1)	Rh,Rh 60.5(2) O,O 51.0(3)
				RhC_6	P 221.7(2) μOC 197.0(8) cpC 224.6(7,42)	275.1(1) 88.7(5)	C,P 88.8(3)
$NBu_4)_2[Et_2O)Ag^I\cdot$ $t_2^{II}(\mu\text{-}Cl)_2\cdot$ $C_6F_5)_4]$	*m* $P2_1/n$ 4	1257.4(2) 1474.9(2) 2798.3(3)	92.73(1)	AgO	O 229.9(10)	277.1(1,12)	Pt,Pt 72.15(3) Pt,O 140.0(3,4.7)
				PtC_2Cl_2	C 197.O(14,17) μCl 240.6(3,8)	326.3(1) 85.4(1,2)	C,C 89.1(5,3) Cl,Cl 84.4(1,1)
$ClO_4)Ag^I\cdot$ $C_7H_4NS_2)_2Rh_2\cdot$ $cod)_2]$	*or* *Pbcn* 4	763.5(5) 2756.4(11) 1556.4(8)		AgO_2S_2	O 253(2,0) μS 260.9(3,0)	279.6(3) 68.3(1)	Rh,Rh 110.5(1) O,O 52.2(5) S,S 104.1(1) O,S 101.9,154.0(4)
				RhC_4NS	N 208.0(9) C 213.4(14,32) μS 235.8(3)		S,N 93.7(3)
$NBu_4)\{(Et_2O)Ag^I$ $t_2^{II}(C_6F_5)_4\cdot$ $_2\cdot C_6H_{14}$	*m* $P2_1/c$ 4	1127.8(6) 2564.3(8) 2235.9(7)	94.92(3)	AgO	O 225.9(1)	281.0(2,6)	Pt,Pt 57.13(3) Pt,O 150.8(3,9)
				PtC_4	C 203(2,3) μC 224(2,5)	268.7(1) 73.9(6,2)	C,C 89.9(7,11.3) 170.7(7,2.7)
$Re^{VII}(H)_7\cdot$ $PPhPr_2)_2\}_2Ag^I]\cdot$ $PF_6)$	*tr* $P\bar{1}$ 2	1318.8(6) 1601.4(6) 1482.7(6)	112.47(3) 101.03(3) 90.65(3)			287.3(2,128)	Re,Re 169.1(1,3.4)
				ReH_7P_2	H not given P 248.5(4,175)		P.P 134.2(1,9.2)

able 2 Continued

OMPOUND	Crys.cl Sp.Grp *Z*	*a* [pm] *b* [pm] *c* [pm]	*α* [°] *β* [°] *γ* [°]	Chromo- phore	M-L [pm]	Ag-M [pm] Ag-L-M [°] M-M [pm] M-L-M [°]	L-M-L [°]
$\mathrm{Mn_2\{\mu\text{-}Ag^I(ClO_4)}$ $\mathrm{PPh_3)\}(H)_2(CO)_6}$ ppm)]	*tr* $P\bar{1}$ 2	1330.8(2) 1466.0(1) 1473.8(1)	113.90(1) 91.19(4) 109.08(1)	AgHOP	μ_3H 187(4) O 254.2(9) P 240.9(2)	294.5(1,16) 106(2,3)	Mn,Mn 55.43(3) H,O 75(2) H,P 169(2) O,P 115.8(2)
				$\mathrm{MnC_3H_2P}$	OC 181.1(8,36) μH 187(4,3) μ_3H 182(4,6) P 237.5(2,35)	274.0(1) 98(2,0)	C,C 88.5(3,1.9) H,H 80(2,3) C,H 98(2,9) 170(2,4) d
$\mathrm{u^IPPh_3)_2\cdot}$ $\mathrm{\text{-}C(PPh_3)\cdot}$ $\mathrm{{}_5H_4N\text{-}2)\}\cdot}$ $\mathrm{\text{-}Ag^I(\eta^2\text{-}O_2NO)\cdot}$ $\mathrm{OClO_3)]\cdot 3CH_2Cl_2}$ $\mathrm{H_2O}$ at 178K	*m* $P2_1/n$ 4	1119.9(2) 2398.0(7) 2155.2(6)	 91.01(2)	$\mathrm{AgO_3N}$	N not given $\mathrm{O_2NO}$ 241.9(8,23) $\mathrm{O_3ClO}$ 266.3(9)	296.6(1,40)	not given
				AuCP	μC not given P not given		
$\mathrm{(C_6F_5)_3Au^I\cdot}$ $\mathrm{pam)\}_2Ag^I\cdot}$ $\mathrm{OClO_3]}$	*m* $P2_1/n$ 4	1310.3(2) 3788.6(7) 1719.9(3)	 98.19(2)	$\mathrm{AgAs_2O}$	As 252.2(3,2) O 250.0(11)		As,As 145.5(2) As,O 106.8(3,4.8)
				$\mathrm{AuC_3As}$	C 207.1(9,12) As 246.3(2,6)		C,C 88.3(4,2.4) C,As 91.8(3,1.8)
$\mathrm{g^I\{S(CH_2)_2S\}_2}$ $\mathrm{{}_2(cp)_4]\cdot BPh_4}$	*m* $P2_1/n$ 4	871.8(3) 3149.2(9) 1584.7(3)	 92.21(2)	$\mathrm{AgS_4}$	μS 249.5(5,19)	305.3(2,6) 73.8(1,5)	Zr,Zr 170.96(8) S,S 100.7(2,8.9) 129.2(2,4.4)
				$\mathrm{ZrC_{10}S_2}$	μS 259.1(5,31) cpC 249(2,3)		S,S 103.4(2,4)
$\mathrm{g^I\{S(CH_2)_3S\}_2}$ $\mathrm{{}_2(cp)_4]\cdot BPh_4}$	*tr* $P\bar{1}$ 2	1124.2(4) 1279.0(7) 1827.0(10)	112.33(4) 111.23(4) 81.81(4)	$\mathrm{AgS_4}$	μS 262.6(5,36)	330.7(3,27) 79.4(1,1.5)	Zr,Zr 178.05(8) S,S 95.2(2,4.1) 145.1(2,8)
				$\mathrm{ZrC_{10}S_2}$	μS 255.3(5,6) cpC 250(2,5)		S,S 102.6(2,9)
$\mathrm{en)_2Co^{III}}$ $\mathrm{CH_2COO)\}_2Ag^I]\cdot}$ $\mathrm{ClO_4)_3}$	*m* *C*2/*c* 4	1626.7(5) 898.85(7) 2214.5(4)	 99.82(2)	$\mathrm{AgS_2}$	μS 237.0(4,0)		S,S 169.34(9)
				$\mathrm{CoN_4OS}$	N 196.1(3,13) O 190.6(3) μS 224.7(1)		N,N 90.0(1,5.3) N,O 88.8(1,1.4) N,S 91.8(1,1.1) O,S 88.11(8)

$(NH_3)_5Co^{III}\cdot$	*m*	943.1(2)		AgO_2N_2	H_2O 258.5(5,0)		O,N 89.4(2)
$z)\}_2Ag^I(H_2O)_2$	*C*2/*c*	1237.4(2)	92.42(1)		N 232.0(5,0)		
$NO_3)_7\cdot 4H_2O$	4	3371.6(6)		CoN_6	N 197.8(4,0)		N,N 90.0(2,2.7)
					H_3N 195.8(4,16)		178.0(2,2.6)
$PPh_4)_3[\{W^{III}F_5$	*or*	4464(2)		AgI_2	I 339		I,I 115.2
$C_2I_2)\}_2Ag^I]$	$P2_12_12_1$	1074(1)		WF_5C_2	F 192(3,7)		F,F 85.9(14,8.7)
	4	777.6(4)			C 201(4,2)		165.4(13.1)
							C,C 33.3(17)
							163.3(14,2.1)
$Ru^{II}(PEtPh_2)_5$	*m*	2600.5(5)		$AgCl_3P$	P 237.6(6)		not given
$l_5Ag^I]\cdot CH_2Cl_2$	$P2_1/a$	1931.5(6)	106.98(1)		μCl 270.5(6,83)		
	4	1551.5(3)		$RuCl_4P_2$	P 227.9(6,5)		
					μCl 248.0(6,102)		
$cp)(CO)_2Mo$	*m*	1574.5(3)		AgP	P 241.4(4)	e	Mn,Mo 70.2(1)
$-Ag^I(PPh_3)\}$	$P2_1/c$	1538.2(3)	104.69(2)				Mn,P 150.2(1)
$-PPh_2)Mn(CO)_4]$	4	1653.6(3)					Mo,P 139.4(1)
				MnC_4P	OC 182.4(18,69)		C,C 92.9(7,6.8)
					μP 227.2(4)		C,P 91.0(5,3.5)
				MoC_7P	OC 195.2(17,2)		C,C 79.9(6)
					μP 238.7(4)		C,P 81.4(5)
					cpC not given		107,8(5)
$NEt_4)[(PPh_3)_2$	*m*	1035.4(6)		AgS_2P_2	P 247.9(5,1)	f	S,S 88.2(2)
$g^I(\mu\text{-}S)_2Mo^{VI}$	$P2_1/c$	3571(2)	100.76(7)		μS 259.6(5,56)		P,P 122.7(2)
$-S)_2Cu^I(CN)]$	4	1314.4(8)					S,P 110.1(2,4.4)
				CuS_2C	NC 182(2)		S,S 106.1(2)
					μS 221.9(7,4)		S,C 126.9(8,3.7)
				WS_4	μS 219.5(6,12)		S,S 109.5(2,2.2)
$NEt_4)[(PPh_3)_2$	*m*	1036.3(4)		AgS_2P_2	P 248.4(5,1)	g	S,S 88.9(2)
$g^I(\mu\text{-}S)_2W^{VI}$	$P2_1/c$	3574(1)	100.89(5)		μS 258.4(5,46)		P,P 122.5(2)
$-S)_2Cu^I(CN)]$	4	1313.6(9)					S,P 115.5(2,7.0)
				CuS_2C	NC 187(2)		S,S 106.8(2)
					μS 220.9(7,1)		S,C 126.6(8,2.5)
				MoS_4	μS 219.5(6,16)		S,S 109.5(2,2.3)
$NEt_4)[(PPh_3)_2$	*m*	2001.3(6)		AgS_2P_2	P 245.6(4,4)	h	S,S 92.2(1)
$g^IS_2Mo^{VI}OS$	$P2_1/c$	1052.9(3)	101.3(2)		μS 254.0(4)		P,P 126.0(1)
$u^I(CN)]$	4	2272.1(6)			μ_3S 262.7(4)		S,P 108.4(1,2.8)
				CuS_2C	NC 186(2)		S,S 107.2(3)
					μS 220.1(5)		S,C 126.3(5,5.9)
					μ_3S 222.3(4)		
				MoS_3O	O 168(1)		S,S 109.8(2,3.9)
					μS 218.9(5,3)		S,O 109.1(5,1.1)
					μ_3S 226.6(4		

Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the
d the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom or ligand is specified inthese co
g-Ag = 334.6 pm. [d]C-Mn-P = 89.7(2,2.1)° and H-Mn-P = 82(2,3)°.

The next twenty-one examples contain only one silver atom with two identical heterometal atoms, in which the silver atom is centrally located. Four of these examples[29–32] feature an encapsulated two-coordinate Ag(I) atom with a pair of Ir atoms (Ag-Ir = 264.2(1) pm,[29,30] and 265.9(1) pm,[32] or a pair of Rh atoms (Ag-Rh = 264.4(1,8) pm).[31] The M-Ag-M backbone angle ranges from 171.0 to 180°.

A green Ag/Rh_2 derivative exists in two isomeric forms,[35,36] both of which have the three metal atoms in a triangular cluster with two equivalent Ag-Rh distances of 271.9(1) pm[35] and 273.0(1) pm.[36] The corresponding Rh-Rh distances are 277.6(1) pm and 275.1(1) pm. The rhodium atoms are bridged by CO and dppm ligands, and are symmetrically capped by η^5-cyclopentadienyl ligands. An acetate group is chelated to the silver atom.

The core of a white Ag/Pt_2 derivative has the two Pt(II) atoms 326.3(1) pm apart and bridged by a single Ag(I) atom and two chlorine atoms. Each platinum centre also has two terminal *cis*-C_6F_5 groups which complete a distorted square pyramid, sharing a pyramidal face bounded by the two chlorine atoms and the silver atom. The two Ag-Pt distances differ slightly (275.9(1) and 278.2(1) pm). The silver atom is three coordinate, defined by the two Pt(II) atoms and one diethylether molecule.

The structure of the yellow complex $[(ClO_4)Ag(C_7H_4NS_2)_2Rh_2(cod)_2]$[38] is shown in Figure 2. Two Rh atoms and one Ag atom are in a bent arrangement with two molecules of benzothiazole-2-thiolate interacting with all three. Each such ligand is bonded to one Rh atom through its N atom, and bridges one Rh and the Ag atom through its S atom. The Rh atoms complete their coordination shell with 1,5 cycloocta-diene interacting through the two olefinic bonds. The Ag(I) atom completes its coordination with two O atoms of the perchlorate group.

A triangle of $AgPt_2$ has been observed[39] in which the two Ag-Pt bonds (280.4(2) and 281.5(2) pm) are unsupported by a covalent bridge. The two Pt atoms (Pt-Pt = 268.7(1) pm) are bridged by two pentafluorophenyl groups and the silver atom. The two organic moieties are oriented in such a way as to make F· ·Ag contacts of 265.3 and 267.0(10) pm.

The triangular metal core in a Ag/Mn_2 complex[41] is characterized by a Mn-Mn distance of 274.0(1) pm and Ag-Mn distances averaging 294.5(1,16) pm. The metal atoms are triply bridged by one hydrido ligand, and the Mn-Mn edge is bridged by a second hydrido ligand and the dppm ligand (Table 2).

In another two examples[44,45] the central Ag(I) atom is coordinated to four sulphur atoms, pairs of which bridge to a Zr atom. The two Zr centres are also each π-bonded to a cyclopentadienyl ligand. Thus the zirconocene dithiolate acts as a macrocyclic metallo-ligand to encapsulate the Ag(I) atom (Table 2).

Finally, there are four examples[50–52] where in addition to a silver atom, there are two other heterometal atoms. In the Ag·Mn·Mo derivative,[50] the triangle of metal atoms has a Ag-Mn distance of 266.4(2) pm, Ag-Mo disance of 287.4(2) pm and Mo-Mn distance of 319.0(2) pm. The Mo-Mn edge is bridged by a PPh_2 group, and the Ag atom lies 30 pm above the Mo-P-Mn plane. The angle between the Mo-P-Mn and Mo-Mn-Ag planes is 7.59°. There is also a triphenylphosphine ligand, the P atom of which lies 11 pm above the tri-metal plane, and on the same side as the phosphido ligand.

In two examples[51,52] the arrangement of the metals atoms (Ag, W, Cu[51] or Ag, Mo, Cu[52]) and the CN ligand is almost linear. The W or Mo atoms are tetrahedrally coordinated by four sulphur atoms. The two metal atoms (Ag and Cu) attached to

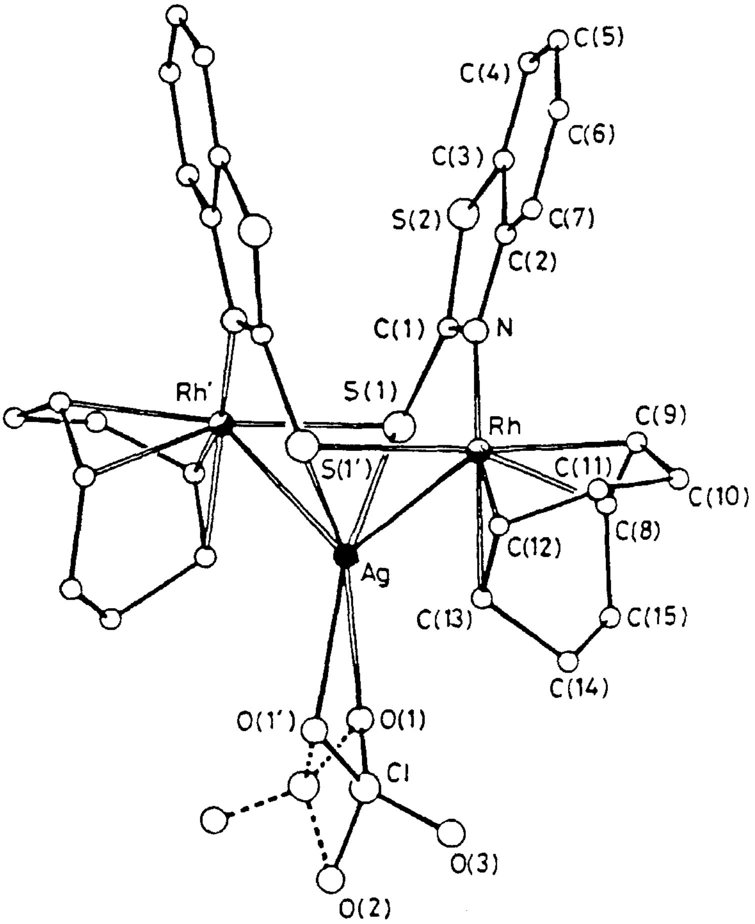

Figure 2 Structure of $[(ClO_4)Ag(C_7H_4NS_2)_2Rh_2(cod)_2]$.[38]

the MS_4 moiety have different geometries. The copper atom has approximately trigonal planar geometry while the silver atom is tetrahedrally coordinated by two μ-S and two PPh_3 ligands (Table 2).

A red complex, $(NEt_4)[(PPh_3)_2AgS_2MoOSCu(CN)]$ has been prepared; the structure is shown in Figure 3.[5] The three different metal atoms and three bridging sulphido ligands are arranged in a butterfly structure. The Ag-Mo-Cu angle is approximately 96°.

The thirty-six heterotrimetallic silver compounds in Table 2 show an oxidation state for silver of +1 exclusively. These atoms are digonal, trigonal, tetrahedral and also hexa-coordinate. The heterometal atoms are found in oxidation states of: zero (Fe, Rh, Ir, Mo, Mn, Zr); +1 (Cu, Au, Mn, Ir); +2 (Ni, Pt, Pd, Ru); +3 (Co, Rh, W): +6 (Mo, W) and one example of +7 (Re). From the stereochemical point of view, there are four, five, six, seven, nine, ten and twelve coordination about the heterometal, the two latter cases being organometallic sandwich compounds. The

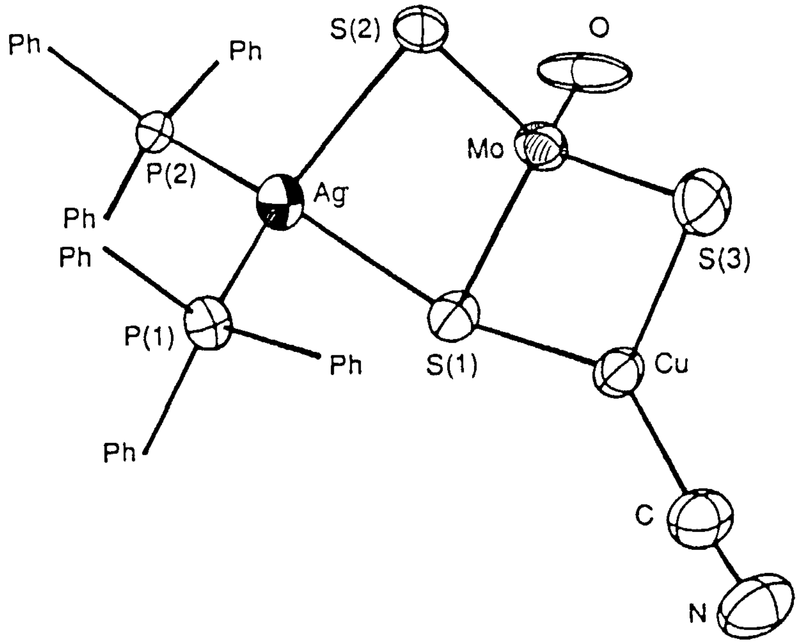

Figure 3 View of the $[(PPh_3)_2AgS_2MoOSCu(CN)]^-$ anion.[52]

mean M-M′ distances which indicate a metal-metal bond are: 263.8(1) pm (Cu-W); 274.0(1) pm (Mn-Mn); and 276.4(13,12) pm (Rh-Rh).

The mean Ag-L bond distances increase with the coordination number and covalent radius of the coordinated atom. For example, three *vs* four coordinated, 236.5 *vs* 247.2 pm (PPh_3); 239.4 *vs* 246.7 pm (bidentate 0 ligands); 246.8 *vs* 257.6 pm (μ-S); 254.6 *vs* 262.7 pm (μ-Se). In general, the mean Ag(I)-L bond distances are longer than those found in thirty two reported heterotrimetallic copper(I) compounds.[20]

The mean Ag(I)-M distances *vs* Cu(I)-M distances, taking only those values less than 300 pm, are: 265.1(9,8) *vs* 250.2 pm (M = Ir); 269.4 *vs* 249.5(8,8) pm (Fe); 272.2 (78,74) *vs* 258.8 pm (Rh); 287.3 (128,127) *vs* 260.7 pm (Re); 286.7 (7,7) *vs* 271.4 (134,88) pm (Mo); and 289.9 (13,12) *vs* 268.3 (81,81) pm (W). The first number in parentheses is the maximum deviation of the smallest, and the second figure is the maximum deviation of the largest. It can be seen that the Ag(I)-M distances are larger which is consistent with the covalent radii of the two metals, 153 pm (Ag) and 138 pm (Cu). The shortest Ag(I)-M distance of 264.2(1) pm (M = Ir) is much larger than the shortest Cu(I)-M distance of 230.9 pm (M = Co).

HETEROTETRANUCLEAR SILVER COMPOUNDS

The structural data for the heterotetranuclear silver complexes are listed in Table 3 in order of decreasing number of silver atoms and then increasing Ag-M distance.

able 3 Crystallographic and structural data for heterotetranuclear silver compounds[a]

OMPOUND	Crys.cl Sp.Grp *Z*	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore	M-L [pm]	Ag-M M-M Ag-Ag [pm]	L-M-L [°]
$PPh_4)_4[Ag^I_3Cu^I I_8]$	*tr*	1343.5(3)	103.12(2)	AgI4	μI[b] 288.0(1,88)	314.7(1)	I,I[b] 109.5(1,10.5)
	$P\bar{1}$	1655.0(4)	104.14(2)	(× 2)		–	69.1(1,1)[c]
	1	1104.7(3)	82.88(2)			322.4(1)	
				MI_3	I 263.8(1)		I,I 120.0(1,4.7)
				(× 2)	μI 267.4(1,4)		68.5(1,9)[d]
$(PPh_3)_2Ag^I\}_3\cdot$	*trg*	1989.6(5)		AgS_2P_2	S 258.9(3,23)		S,S 83.2(1)
$tox)_3Al^{III}]$	$P\bar{3}$	–			P 247.9(4,14)		P,P 113.4(2)
	2	1525.1(6)					S,P 114.4(2,16.4)
				AlO_6	O 188.9(8,6)		O,O 90.3(4,7.9)
							168.7(5)
$(PPh_3)_2Ag^I\}_3\cdot$	*trg*	1989.4(6)		AgS_2P_2	S 258,7(3,21)		S,S 83.3(1)
$tox)_3Fe^{III}]$	$P\bar{3}$	–			P 246.8(2,13)		P,P 115.2(1)
	2	1525.1(6)					S,P 113.7(1,14.6)
				FeO_6	O 200.3(6,7)		
$ClO_4)_2Ag^IAu^I\cdot$	*m*	1328.2(3)		AgO_2	O 226.0(13)	277.2(1,12)	O,O 87.1(5)
$CH_2PPh_3)_2]_2$	$P2_1/n$	1345.8(4)	93.58(8)		247.3(13)		Au,Au 93.8(1)
	2	2201.6(5)		AuC_2	C 208.9(13,10)		C,C 173.9(5)
							Ag,Ag 86.2(1)
$NBu_4)[(C_6F_5)_2Pt^{II}$	*tr*	1243.8(9)	103.53(5)	$AgCl_2$	μCl 240.8(8)	291.8(3,146)	Cl,Cl 141.3(2)
$_2Ag^I]_2$	$P\bar{1}$	1316.0(7)	101.27(6)		272.4(8)	–	Pt,Pt 118.5(1)
	1	1112.8(7)	74.75(6)			299.4(6)	
				PtC_2Cl_2	C 206(3,2)		C,C 173(2)
					μCl 233.2(7,10)		Cl,Cl 175.7(3)
							Ag,Ag 61.5(1)
							C,Cl 90(1,2)
$C_{37}H_{46}N_2O_2S)Pd^{II}$	*m*	1341.6(3)		AgS_2N	N 216(2)	291.9(3)	S,S 118.1(2)
$g^I(PPh_3)]_2\cdot$	$P2_1/n$	2539.7(5)	96.82(2)		μ_3S 250.6(6)	–	S,N 74.5,150.7(4)
$ClO_4)_2\cdot 12\frac{1}{2}\,H_2O$	2	1694.0(3)			286.7(6)	277.9(3)	61.9( )[c]
				PdONSP	O 199(1)		O,N 83.7(5)
					N 202(1)		O,P 88.1(3)
					μ_3S 224.6(5)		N,S 96.7(4)
					P 228.1(6)		S,P 91.5(2)
							75.6(2)[d]

able 3 Continued

OMPOUND	Crys.cl Sp.Grp *Z*	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromophore	M-L [pm]	Ag-M M-M Ag-Ag [pm]	L-M-L [°]
PPh$_3$)Ag^I· hC≡C)$_2$Au^I]$_2$	*m* $P2_1/n$ 4	1153.2(1) 2880.8(3) 2231.3(3)	93.26(1)	AgC$_4$P AuC$_2$	C 227–255(1) P not given C 198.9(16,13)	295.6(1,72)	Au,Au 85.5(1,5) Ag,Ag 94.6(1,2)
PPh$_3$)Ag^I· nt)$_2$Cu^I]$_2$	*m* $C2/c$ 4	1555.9(3) 1193.9(2) 2820.1(6)	94.71(3)	AgS$_2$NP CuS$_2$N	N 224.2(5) P 244.0(2) μS 257.4(2,3) N 204.9(5) μS 227.8(2,53)	297.7(1,29) 281.7(1) 418.8(1)	not given
g$^I_{1.76}$Cu$^I_{2.24}$· -tolylCS$_3$)$_4$	*tr* $P\bar{1}$ 2	1272.7(2) 1315.2(2) 1286.0(3)	103.93(2) 81.64(2) 84.72(2)	MS$_3$	S 231.9(4,46) μS 234.6(4,162)	301.1(2,158)	S,S 94.9(8,3.0) 132.0(2,13.0)
NEt$_4$)$_2$[(PhS)Ag^I $_3$-S)$_2$V^{IV}· OC$_4$H$_8$dtc)]$_2$	*m* $C2/c$ 4	2044.8(3) 1508.6(2) 1792.3(2)	109.32(1)	AgS$_4$ VS$_5$	PhS 239.1(5) μ_3S 248.0(5) 267.0(5,0) S 242.7(7,24) μ_3S 223.2(6,94)	302.6(4,12) 279.3(7) 389.8(3)	not given
PPh$_4$)$_4$· g$^I{}_2$Cu$^I{}_2$I$_8$]	*tr* $P\bar{1}$ 1	1343.4(5) 1653.5(6) 1105.0(5)	103.28(3) 104.08(3) 82.64(3)	AgI$_4$ CuI$_3$	μI 286.3(1,85) I 257.7(1) μI 260.6(2,1)	311.9(2) – 319.5(2)	not given
g^{I}Sb^{III}· C$_6$H$_6$O$_7$)$_2$]$_2$	*m* $P2_1/n$ 2	655.7(4) 1214.9(2) 2050(1)	98.12(3)	AgO$_3$ SbO$_4$	O 231.4(2) μO 232.3(2) 266.1(2) O 205.2(2,44) μO 211.3(2,106)	323.3(1) – 322.1(1)	O,O 61.3(1) 133.3(1,1.2) O,O 76.0–137.5(1) 112.9(1,9.4)^d
g^I(NO$_3$){PPh$_2$· p)}Fe]$_2$·2CHCl$_3$	*m* $P2_1/n$ 22	1390.8(5) 1562.6(9) 1867.4(9)	102.07(2)	AgO$_3$P$_2$ FeC$_{10}$	O 280(1) μO 247.6(8) 287.3(7) P 243.3(3,1) C 204(9)	393.6(2)	O,O 46.0(3) 85.5, 131.6(3) P,P 140.1(1) O,P 101.3(2,8.3) 94.5(2)Z^c
ClO$_4$)Ag^I· C$_6$H$_4$Ncp)$_2$Fe}]$_2$	*tr* $P\bar{1}$ 1	1048.9(2) 1134.0(3) 878.9(2)	91.60(2) 113.29(1) 83.52(2)	AgO$_3$N$_2$ FeC$_{10}$	N 216(1,2) O 297(1) μO 281(1.8) cpC not given		O,O 46.4(2) 68.1, 113.1(2) N,N 163.1(2) O,N 95.8(2,10.7) 111.9(2)

Fe(CO)$_3$(C$_5$Ph$_4$O) g^{I}H$_2$O)]$_2$·(PF$_6$)$_2$	*m* $P2_1/n$ 4	1321.3(7) 1412.8(6) 1980.5(14)	105.75(5)	AgO$_3$	H$_2$O 267(5) μO 227(2) 265(8)		O,O 74.1(5) 105.9(6)^c
				FeC$_8$	OC 182(5,8) η^5C 215(5,16)		C,C 93.6(9,1.3)
PPh$_3$)(ClO$_4$)Ag^I N(PPh$_2$)Au^I}]$_2$	*tr* $P\bar{1}$ 1	1009.2(3) 1071.8(4) 2026.5(6)	99.29(3) 101.69(3) 103.22(3)	AgONP	O 257.0(11) N 223.9(1) P 238.1(2)	287.3	O,N 90.5(3) O,P 104.8(3) N,P 164.3(2)
				AuP$_2$	P 232.2(2,2)		P,P 174.8(2)
CO)$_8$(dppm)$_2$Ru$_3$ -Ag^I(F$_3$CCO$_2$)}] CH$_2$Cl$_2$ (at 140K)	*or* $Pca2_1$ 4	2070.6(9) 1569.3(11) 1844.7(5)		AgO	O 221.1(10)	276.7(1,37)	Ru,Ru 60.0 Ru,O 143.1(3,16.1)
				RuC$_3$P	OC 190.2(13,47) P 232.2(3,5)		C,C 92.3(6,1.7) 171.9(6,2.2) C,P 93.5(4,5.0)
				RuC$_2$P$_2$	OC 189.9(12,16) P 232.4(3,12)		C,C 172.2(5) P,P 108.4(1) C,P 90.8(3,8.5)
CO)$_9$(Bu^{t}C≡C)· u$_3$Ag^I(PPh$_3$)]	*m* $P2_1/N$ 4	1611.7(3) 1679.1(13) 1448.8(3)		AgP	P 240.5(9)	278.7(3,2) 280.6(3,8)	Ru,Ru 60.4(1) Ru,P 148.4(2,2.9)
				RuC$_4$	OC not given μ_3C 220(3)		
				RuC$_5$ (× 2)	OC not given μC 226(3,1) μ_3C 222(3,2)		C,C 33(1,0) 92–160.6(8)
CO)$_9$· PPhCH$_2$PPh$_2$)Ru$_3$· g^I(PPh$_3$)]	*m* $P2_1/n$ 4	1700.9(9) 2269.4(10) 1230.6(5)	91.51(4)	AgP	P 242.2(3)	278.7(1,20) 290.2(1,42)	Ru,Ru 63.8(1) Ru,P 66.9(1) 146.4(1,2.8)
				RuC$_3$P	OC 189.9(9,40) P 237.0(2,62)		C,C 94.6(4,5.1) C,P 98.0(3,13.2) 161.6(3,8.1)
CO)$_3$(Pcy$_3$)$_2$· pp)Pt$_3$· g^I(CF$_3$SO$_3$)]	*m* $P2_1/a$ 4	2722(1) 1474.3(4) 2131.2(3)	107.50(2)	AgO	O 230(3)	284.5(3,155) 268.6(2,33)	Pt,Pt 54.9(1,2.6) Pt,O 144.2(8,14.3) 82.5(2,3.0)^d
				PtC$_2$P (× 2)	P 228(1,1) μOC 197(4,6)		
				PtC$_2$P$_2$ (× 2)	P 231(1,1) μOC 217(4,4)		P,P 98.0(4)

Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is th
d the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these column
lue of the Ag-X-Ag angle. [d] The value of the Ag-X-M angle.

There are three examples which contain three silver atoms plus one heterometal atom, Cu(I),[15] and Al(III) or Fe(III).[53] In the first case[15] the $[Ag_3CuI_8]^{-4}$ anion is centrosymmetric and described as edge shared AgI_4 tetrahedra, each linked by a common edge to an approximately planar Ag/CuI_3 triangle. The metal-metal interactions are: Ag· ·(Ag/Cu) 314.7(1) pm and Ag· ·Ag 322.4(1) pm. The other two examples are isomorphous.[53] The central metal atom (Al or Fe) is octahedrally coordinated by the O,O "bites" of the three dithiooxalato ligands, and the $Ag(PPh_3)_2^+$ cations interact at the S,S "bite" of each ligand.

Thirteen examples contain a pair of Ag(I) atoms plus a pair of heterometal atoms, Au(I),[55,58,65] Cu(I),[15,59,60] Fe(O),[28,63,64] Pt(II),[8,56] Pd(II),[57] V(IV)[61] or Sb(III),[62] in a tetra-metallic core. A white centrosymmetric complex[55] contains the Ag_2Au_2 ring where the Ag-Au bonds (276.0, 278.3(2) pm) are unbridged. The silver(I) atoms are each bonded to two gold atoms and two oxygen atoms of the perchlorate ligands. Another centrosymmetric complex[56] has a central $Ag_2Pt_2Cl_4$ unit. The two $PtCl_2(C_6F_5)_2$ units embrace a central Ag_2 unit in which the Ag-Ag distance is 299.4(6) pm. Each Ag(I) atom has close contact with one Pt(II) atom at 277.2(3) pm, and a longer contact at 306.3(3) pm with the other Pt(II) atom. The first interaction represents a bond while the second does not.

In another example, two $[L_6PdAg(PPh_3)]^+$ units[57] are linked by bonds between the sulphur atom of one and the silver of the other such that each sulphur atom is bonded to one Pd and two silver atoms. The silver atoms are within bonding distance (277.9(3) pm) with a Ag-S-Ag bridge angle of 61.9(1)°.

A nearly square planar arrangement of metal atoms is found in $[(PPh_3)Ag(PhCC)_2Au]_2$,[58] with Au· ·Au and Ag· · ·Ag interactions of 401.3 and 434.3 pm, respectively. The Au-Ag distances range from 289.4 to 302.8 pm. Each gold(I) atom is σ-bonded to two acetylide groups in almost linear coordiantion. Each Ag(I) atom is bonded to PPh_3, and is asymmetrically π-bonded to two alkyne groups (Table 3).

There is one example[59] with a butterfly shaped core of Ag_2Cu_2, with the silver(I) atoms located at the wing tips. A tetrahedral arrangement of copper and silver atoms is found in a red derivative,[60] with the four edges bridged by o-tolylperthiocarboxylate ligands. A cubane core of $V_2Ag_2S_4$ is found in $[(PhS)Ag(\mu_3\text{-}S)_2V(OC_4H_8dtc)]_2$,[61] with a crystallographic C_2 axis passing through the centres of the V_2S_2 and Ag_2S_2 rhombic units. The M-M distances are in the order: 279.3(7) pm (V-V) < 302.6(4,12) pm (Ag-V) < 389.8(3) pm (Ag-Ag). Only the V-V interaction can be considered to be a real bond in this case.

A complex anion $[Ag_2Cu_2I_8]^{-4}$ [15] is isomorphous with another example discussed above, $[Ag_3CuI_8]^{-4}$,[15] with edge-sharing AgI_4 tetrahedra linked via a common edge to an approximately planar CuI_3 triangle.

The structure of monoclinic $[AgSb(C_6H_6O_7)_2]_2$[62] is shown in Figure 4. The only donor atoms involved in bonding are oxygen atoms from the "inner" α-hydroxycarboxyl groups (attached to C(3)), giving two crystallographically independent five-membered chelate rings, with bite angles at the Sb atom of 76.0 and 78.1(1)°.

There are two examples in which two Ag(I) centres are doubly bridged by two staggered $\{PPh_2cpFe\}$[28] or $\{(C_6H_4Ncp)_2Fe\}$[63] ligands. Finally, there are four examples which contain only one silver atom. The three heterometal atoms are Ru[66-68] or Pt.[69] The clusters adopt a butterfly metal-core structure, with the Ag(I) atom occupying one of the wing-tip sites.

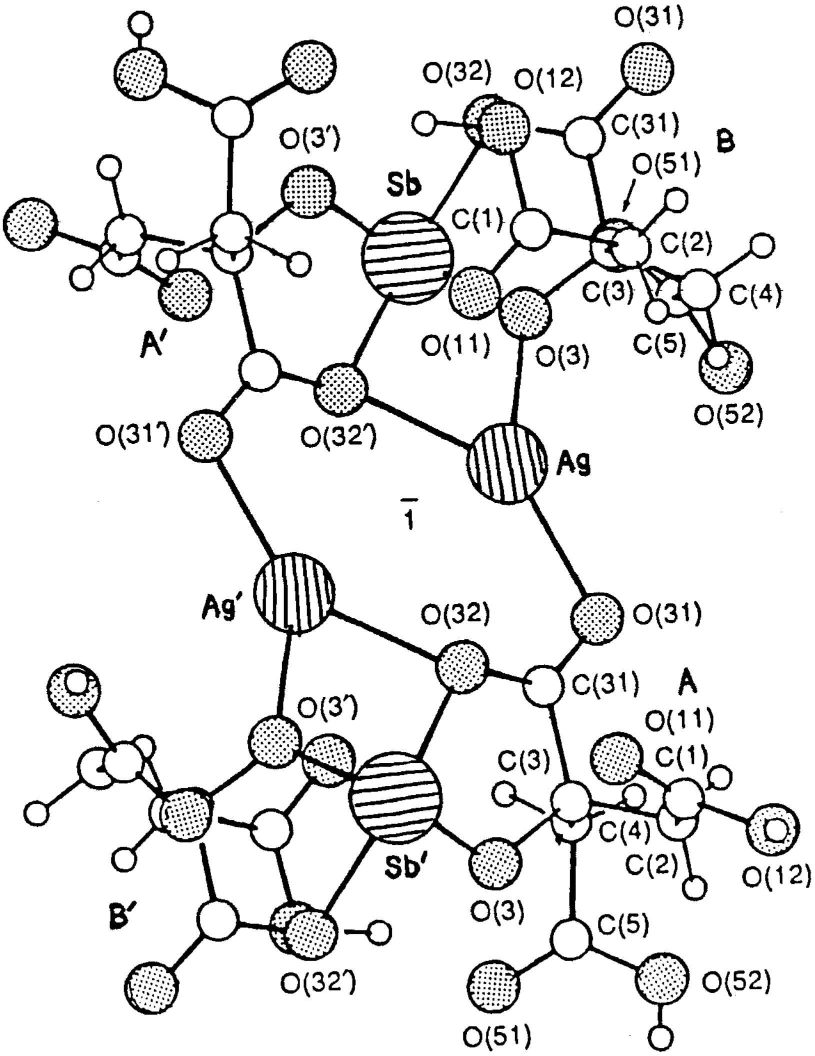

Figure 4 Structure of $[AgSb(C_6H_6O_7)_2]_2$.[62]

The twenty examples in Table 3 indicate prevalence of the butterfly configuration of metal atoms. Silver occurs only in the +1 oxidation state, but its coordiantion number varies from two, to three, four and even five. There are several mean Ag-M distances less than 300 pm, and these increase in the sequence: 278.0(50,27) pm (Ru) < 286.4(104,164) pm (Au(I)) < 288.2(192,182) pm (Pt(II)) < 291.9 pm (Pd(II)) < 297.7(29,29) pm (Cu(I)). There are also some M-M distances within 300 pm, for example: 268.3(33,33) pm (Pt) < 279.3 pm (V) < 281.7 pm (Cu) < 285.4(54,90) pm (Ru) < 287.3(37,37) pm (Au) < 288.7(108,107) pm (Ag). In the comparable Cu(I) compounds there are fifty-five examples[20] which indicated the variety of stereochemical and bonding possibilities open to the "soft" M(I) atoms of the copper subgroup. The Ag(I) derivatives show a similar richness of possibilities.

HETEROPENTANUCLEAR SILVER COMPOUNDS

Structural data for the six examples of this type complex are summarized in Table 4. A trigonal-bipyramidal core, made up of Li(I) atoms at the axial positions of an almost equilateral triangular array of equatorial Ag(I) atoms, has been found in the $[Ag_3Li_2(Ph)_6]^-$ anion.[70] The two Li(I) atoms are approximately equidistant from the silver triangle, with an average Ag-Li distance of 276(3) pm indicating a bonding interaction. By contrast, the separation between the Ag(I) atoms ranges from 337.9(2) to 346.2(2) pm which may be considered non-bonding.

The structure of the Ag_2Fe_3 cluster[28] consists of a (PPh_2cpFe) ligand symmetrically bridged between two {$Ag(PPh_2cpFe)(HCO_2$} moieties. The mean value of the Ag-Fe distances is 287.3(105,299 pm.

In a Pt/Ag derivative[71] a central Pt atom lies on a centre of symmetry, and has a square planar environment formed by two *trans* chloride and two *trans* tht ligands. The two outer Pt atoms have a slightly distorted square pyramidal coordination with an apical silver at a distance of 281.8(2) pm, indicating a metal-metal bond. In another two examples[72] the three platinum units are located around the threefold Ag· · ·Ag axis. Each Ag(I) atom is coordinated by three μ-S atoms of different dialkyldithio-carbamate ligands.

In the red complex $[Pt_3SAuPPh_3AgCl(dppm)_3]PF_6$,[73] two crystallographically independent cluster cations are present, and their structures are shown in Figure 5. The two cations differ in the orientations of the phenyl ring of the dppm ligand, the conformation and orientation of the PPh_3 ligands, and in the interatomic distances and angles. Both clusters contain metal-metal bonds (Table 4).

The shortest silver-transition metal interaction is found for Ag-Pt at 276.8 pm. A Ag-Ag distance of 273.3(3) pm and Ag-Au distance of 257.6(1,1) pm represent bonding interactions. The Pt-Pt distances range from 261.5(3) to 303.3(5) pm, with an average value of 280.0 pm.

In the structural chemistry of Cu(I)[20] there are twelve examples of pentanuclear clusters. These involve the heterometal atoms Li, Mg, Au, Os, Fe, Co and Ru, representing a somewhat more varied chemistry than presently found in the Ag(I) examples.

HETEROHEXANUCLEAR SILVER COMPOUNDS

The structural data for hexanuclear derivatives are summarized in Table 5 in the order of decreasing number of silver atoms and then increasing Ag-M distances. The highest number of silver atoms is four, for example $M_2(S)_8Ag_4(PPh_3)_4$ (M = Mo,[74] or W[75]). This has been described as a cage (with a centre of inversion) fused by two six-membered SAg_2S_2M rings connected by metal-sulphur bonds. Each metal atom is tetrahedrally coordinated.

The dianion $[Ag_4Au_2(SCH_2CH_2S)_4]^{-2}$ contains the M_6S_6 skeletal framework[76]

able 4 Crystallographic and structural data for heteropentanuclear silver compounds[a]

OMPOUND	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo- phore	M-L [pm]	Ag-M Ag-Ag M-M [pm]	L-M-L [°]
$g^{I}_3Li^{I}_2(Ph)_6]_2\cdot$	*m*	1646.6(9)		AgC_2	μC^{b} 213(1,0)	276(2,0)	Li,Li[b] 88.2(9)
$i^{I}_6Br_4(EtO)_{10}]$	$P2_1/n$	2970.0(15)	100.18(4)			273.3(3)	C,C 174.7(7)
	2	1282.1(5)		LiC_3	μC 227(2)		Ag,Ag 76.9(6)
							C,C 120(1)
$t^{II}Cl_2\{(tht)\cdot$	*tr*	1032.3(3)	104.35(2)	AgC_2Cl	C 238.8(27)	281.8(2)	Cl,Pt 84.5(1)
$_6F_5)_3Pt^{II}\cdot$	$P\bar{1}$	1040.4(3)	103.38(2)		256.7(31)		113.0(2)[c]
$g^{I}(\eta^2\text{-PhMe})\}_2]$	1	1557.2(4)	96.48(2)		μCl 263.7(4)		
				$PtCl_2S_2$	μCl 229.7(4)		Cl,S 85.8(1)
					μS 230.1(3)		115.2(2)[d]
				PtC_3S	C 203.3(14,29)		C,C 88.3(6,2)
				(× 2)	μS 232.8(4)		174.2(60
							C,C 91.5(4,1.2)
							176.1(5)
$t^{II}_3(Pr^{i}_2dtc)_6\cdot$	*or*	1161.6(2)		AgS_3	μS 272.9(6,16)	294.6(2,56)	not given
$g^{I}_2](BF_4)_2$	*Pccn*	2984.4(2)				296.4(2)	
	4	2042.4(3)		PtS_4	S 232.0(2,0)		S,S 175.2(2,4.1)
					μS 232.0(2,0)		
$t^{II}_3(Bu^{i}_2dtc)_6\cdot$	*or*	3124.4(7)		AgS_3	μS 274(1,12)	297.8(4,194)	not given
$g^{I}](ClO_4)_2$	*Pbca*	3067.1(10)				303.3(5)	
	8	1729.1(3)		PtS_4	S 230(1,0)		S,S 174.8(4,4.2)
					μS 230(1,0)		
$t^{II}_3(\mu_3\text{-S})\cdot$	*tr*	1763.9(5)	94.83(2)	AgCl	Cl 241.3(11)	f_1	Cl,Pt 133.5(4,12.0)
$u^{I}PPh_3)\cdot$	$P\bar{1}$	1865.1(5)	98.88(2)				
$_3\text{-}Ag^{I}Cl)\cdot$	4	2832.8(6)	90.33(3)	AuP	P 228.7(11)		P,Pt 174.4(3)
$ppm)_3]\cdot PF^{e}_6$				PtP_2S	P 226.4(10,30)		P,P 110.2(4,1.2)
					μ_3S 230.6(10,77)		
				AgCl	Cl 238.8(10)	f_2	Cl,Pt 134.8(4,4.5)
				AuP	P 226.5(11)		Pt,Pt 174.1(3)
				PtP_2S	P 227.3(11,28)		P,P 110.6(4,8)
					μ_3S 231.5(9,79)		
$g_2(HCO_2)_2\cdot$	*m*	417.9(1)		AgP_3O	P 252.1(5,25)		P,P 113.6(1,4.3)
$Ph_2(cp)Fe\}_3]\cdot$	$C2/c$	1070(1)	110.43(3)		O 265(1)		P,O 104.2(3,15.6)
H_2Cl_2	4	2473(1)		FeC_{10}	cpC 205(2,1)		

Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s. e second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these column g-X-M angle. [d] The M-X-M angle. [e] There are two crystallographically independent molecules. [f1] Ag-Pt = 281.6(4,45) pm; Au-Pt = 257.7(-Pt = 261.5(3) pm; Pt-Ag-Pt = 54.9(1) and 81.3(1,1.1)°; Pt-S-Pt = 70.4(3) and 103.7(4,3)°; P-Pt-S = 100.1(4,5) and 149.3(4,5)°. [f2] Ag-Pt = 281. n; Au-Pt = 257.5(3) pm; Pt-Pt = 261.9(3) pm. Pt-Ag-Pt = 55.0(1) and 82.0(1,1.2)°; Pt-S-Pt = 70.3(3) and 104.0(4,1.9)°; P-Pt-S = 99.6(4, 49.8(4,8)°.

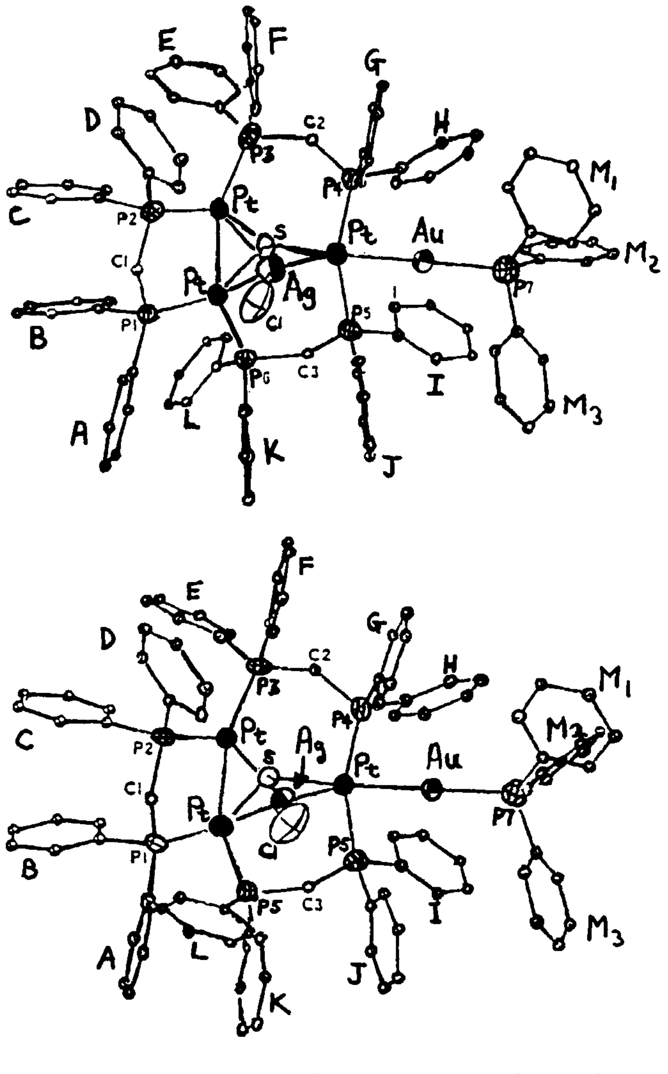

Figure 5 View of the two crystallographically independent $[Pt_3(\mu_3\text{-}S)(AuPPh_3)\mu_3AgCl)(dppm)_3]^+$ cations.[73]

$(D_{2d}$ symmetry) in a somewhat distorted geometry. Each Au(I) atom is linearly coordinated, whereas each Ag(I) atom is inside a trigonal planar array of S atoms. The eight sulphur atoms of the four dithioethyl ligands form two distorted trigonal prisms sharing a common square face. The edges parallel to this plane contain the two Au(I) atoms, and the triangular faces of the S_8 polyhedron are occupied by Ag(I) atoms.

A white Ag/Pt cluster[77] with an inversion centre is formed by two square-planar platinum $[cis\text{-}Pt(C_6F_5)_2(Bu^tCC)_2]$ units linked through two bridging Ag(I) atoms which are coordinated to two C-C triple bonds of the acetylide ligands, one of which

able 5 Crystallographic and structural data for heterohexanuclear silver compounds^a

OMPOUND	Crys.cl Sp.Grp *Z*	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromophore	M-L [pm]	Ag-M M-M Ag-Ag [pm]	L-M-L [°]
[o$_2^{VI}$(S)$_8$·	*tr*	1224.6(2)	97.81(1)	AgS$_3$P	P^b 242.2(3,16)	297.5	S,S^b 101.4(8,8.8)
g$^{I}_4$(PPh$_3$)$_4$	$P\bar{1}$	1290.5(2)	113.31(1)		μ_3S 259.7(3,180)		S,P 116.6(8,12.5)
	1	1321.1(2)	91.52(1)				*c*
				MoS$_4$	S 210.8(3)		S,S 109.4(1,3.6)
					μ_3S 22.7(3,23)		
$_2^{VI}$(S)$_8$·	*tr*	1224.5(6)	97.77(3)	AgS$_3$P	P 242.4(6,17)		92.1–128.3(2)
g$^{I}_4$(PPh$_3$)$_4$	$P\bar{1}$	1292.4(5)	112.35(3)		μ_3S 261.2(6,165)		
	1	1325.0(6)	91.43(3)	WS$_4$	S 212.4(6)		S,S 109.4(1,3.3)
					μ_3S 223.7(5,29)		
Ph$_4$)$_2$[Ag$^{I}_4$·	*m*	3424(2)		AgS$_3$	μS 262.5	299.6	not given
u$^{I}_2$(SCH$_2$CH$_2$S)$_4$]·	*C*2/*c*	1448.6(6)	121.13(3)			317.0	80.8^d
eOH	12	4171(2)		AuS$_2$	μS 229.3		
g$^{I}_2$Pt^{II}(C$_6$H$_5$)$_2$·	*m*	1386.2(2)		Ag$_2$	C 222.3(9,2)	303.1(1,81)	not given
u^{t}C≡C)$_2$(Me$_2$CO)$_2$]$_2$	$P2_1/n$	1729.4(4)	101.56(2)			303.9(2)	
	2	1468.1(5)		AgO$_2$C$_2$	O 229.4(9)		O,O 82.6(4)
					249.0(12)		C,C 26.5(3)
					C 238.2(8,57)		O,C 121.6(4,32.8)
				PtC$_4$	C 203.4(9,12)		C,C 90.0(3,6.4)
g$^{I}_4$·	*m*	3706.2(7)		AgC$_4$	C 242.5(23,88)	310.9(2,82)	C,C 29.0(1,2.5)
$^{II}_2$(Bu^{t}C≡C)$_8$	*C*2	1202.2(1)	107.48(1)		μC 224.8(23,28)	321.8(4,95)	160.4(1,18.2)
	6	2045.9(3)		PtC$_4$	μC 201.8(22,56)		C,C 90.2(1,4.0)
							92.1(1,5.6)^e
g$^{I}_2$(MeCO$_2$)$_2$·	*m*	1037.3(2)		AgO$_3$P	P 234.4(2)	–	O,O 76,4(1)
Ph$_2$(cp)}Fe]$_2$	$P2_1/n$	1759.3(5)	100.66(2)		μO 226.8(2)	310.4(1)	95.6(2,2.6)
	2	1975.4(80			239.5(5,2)		OP 124.7(1,13.2)
							103.6(1)^d
				AgO$_3$P	P 236.5(2)		O,O 51.2(2)
					O 233.7(5,39)		109.9(2,5.3)
					μO 266.7(5)		O,P 121.6(2,7.1)
				FeC$_{10}$	cpC 204(6,0)		75.5(1)^d

able 5 Continued

OMPOUND	Crys.cl Sp.Grp *Z*	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore	M-L [pm]	Ag-M M-M Ag-Ag [pm]	L-M-L [°]
$Ag^{I}Rh^{III}(H)_3\cdot$ ripod)]$_3\cdot$ $CF_3SOI_3)_3$	*m* $P2_1/n$ 4	2900.7(6) 1678.6(5) 2709.5(6)	 90.87(3)	AgH_x	H not given	285.5(4,79) 298.3(4,15)	not given
				Rh_xP_2	not given		
$g_3^0Nb_3^0(CO)_{12}\cdot$ lmpe)$_3$	*rh* $R\bar{3}c$ 6	1432.3(1) – 4477.2(4)				288.79(2) 284.24(5)	Nb,Nb 178.8(1)
				NbC_4P_2	OC 209.2(4,11) P 257.26(8,0)		P,P 76.5(1) Ag,Ag 59.0(1)
$g_3^0Ta_3^0(CO)_{12}\cdot$ lmpe)$_3$	*rh* $R\bar{3}c$ 6	1427.4(5) – 4455(3)				288.84(2) 284.18(8)	Ta,Ta 178.9(1)
				TaC_4P_2	OC 206.6(4,17) P 255.6(1)		P,P 76.8(1) Ag,Ag 58.9(1)
$Ag^{I}(\delta\text{-hcqd})_2\cdot$ $i^{II}]_3\cdot 2\frac{1}{2}CHCl_3$	*or* $P2_12_12_1$ 4	1599.0(5) 3844(1) 1343.7(5)		AgN_3 (× 2)	N 220(4,10)	364.5(8,29) 305.6(6,4) 628.0(9,583)	not given
				AgO_6	μO 249(3,11)		O,O 56.5(9,7) 112.7(2,30)^e
				NiO_2N_2	N 186(4,7) μO 188(3,5)		O,O 77,8(2,2.7) N,N 97.3(2,1.4) O,N 92.5(2,3.9) 169.4(2,2.9)
$Ag^{I}(\sigma\text{-hcqd})_2\cdot$ $d^{II}]_3\cdot 2CHCl_3$	*or* $P2_12_12_1$ 4	1611.0(6) 3892(1) 1339.3(3)		AgN_3 (× 2)	N 227(3,12)	365.3(3,15) 317.6(3,3) 628.1(3,681)	not given
				AgO_6	μO 245(2,2)		O,O 62.0(6,2.0) 109.3(7,1.9)^e
				PdO_2N_2	N 199(2,6) μO 200(2,3)		O,O 78.6(7,6) N,N 95.0(1,1.0) O,N 93.3(9,1.6) 171.3(9,1.6)
$Ag_2Ru_4(\mu\text{-CO})_3\cdot$ $O)_{10}(PPh_3)_2]$	*tr* $P\bar{1}$ 2	2468.5(3) 1071.0(2) 1013.7(3)	102.03(2) 96.20(2) 86.47(2)	AgP	P 241.8(3,1)	287.7(1,100) not given 290.6(2,168)	Ru,Ru 60.5(1,5.2) Ru,P 143.7(1,8.3)
				RuC_4	OC 186.1(4,62) μOC 227.1(4,3(8)		

$g^{I}{}_{2}Ru_{4}(\mu_{3}\text{-}H)_{2}\cdot$	tr	1395.4(4)	72.21(2)	AgP	P 242.1(3)	289.4(1,86)	Ru,Ru 61.4(1,1.2)
$O)_{12}(PPh_{3})_{2}]\cdot$	$P\bar{1}$	1492.8(3)	72.64(2)			285.7(1)	Ru,P 144.9(1,4.3)
$H_{2}Cl_{2}$	2	1510.3(3)	73.36(2)			288.3(1,102)	113.7(37,5.4)[e]
				$AgH_{2}P$	P 238.2(4)		H,H 57.5(33)
					μ_{3}H 172.5(93,33)		H,P 137.1(3,5.1)
				RuC_{3}	OC 188.5(12,13)		C,C 93.9(5,6.0)
				$RuC_{3}H$	OC 181.9(11,33)		H,H 56.3(36)
					μ_{3}H 181.9(66,17)		C,H 96.8(25,10.7)
				$RuC_{3}H_{2}$	OC 189.4(11,34)		160.8(26,8)
					μ_{3}H 176.0(68.6)		112.4(54,2)[f]
$g^{I}{}_{2}Ru_{4}(\mu_{3}\text{-}H)_{2}\cdot$	tr	1415.9(4)	70.59(3)	AgP	P 243.6(10)	293.2(6,165)	Ru,Ru 60.2(2,2.6)
$O)_{12}(dppm)]$[g]	$P\bar{1}$	1431.7(5)	71.98(3)			275.6(6)	Ru,P 142.3(3,13.5)
	4	2582.8(10)	67.59(2)	$AgH_{2}P$	P 241.2(10)	288.0(6,107)	
					μ_{3}H 172		
				AgP	P 245.2(10)	293.3(6,218)	Ru,Ru 60.2(2,2.5)
				$AgH_{2}P$	P 239.0(10)	275.6(6)	Ru,P 141.9(2,14.6)
					μ_{3}H 172	288.0(6,118)	
$g^{I}Cu^{I}Ru_{4}(\mu_{3}\text{-}H)_{2}$	tr	1373.9(2)	75.11(2)	AgP	P 240.0(2)	h	Ru,Ru 63.1(1)
$O)_{12}(PPh_{3})_{2}]\cdot$	$P\bar{1}$	1442.9(2)	74.22(2)				Ru,Cu 57.4(1,0)
$H_{2}Cl_{2}$	2	1507.4(2)	75.02(2)				Ru,P 143.5(1,3.9)
							Cu,P 148.3(1)
				$CuH_{2}P$	P 220.3(3)		H,H 70.5(30)
					μ_{3}H 164.8(78,37)		H,P 128.8(24,9)
				RuC_{3}	OC 188.5(12,8)		C,C 90–133
				$RuC_{3}H$	OC 188.9(10,26)		C,C 93.3(5,1.9)
					μ_{3}H 178.6(56,12)		
				$RuC_{3}H_{2}$	OC 189.7(11,21)		C,C 94.7(5,2.4)
					μ_{3}H 177.1(60,42)		H,H 65.0(32)
							C,H 87–167
$NBu_{4})_{2}]Pt^{II}{}_{2}Ag^{I}\cdot$	m	1452.8(9)				276.3(4,18)	Pt,Pt 163.3(3,1)
$\text{-}Cl)_{2}(C_{6}Cl_{5})_{4}]_{2}$	$P2_{1}/n$	4261.5(12)	96.08(5)			387	
	?	1994.2(10)				326.9(3,4)	
				$PtC_{2}Cl_{2}$	C 201.2(23,73)		not given
					μCl 241.8(12,22)		85.0(4,7)[f]
$t^{II}{}_{2}Ag^{I}(\mu\text{-}S)_{2}\cdot$	m	2463.8(7)		AgS_{2}	μS 238.9(9,10)	368.7(3,218)	S,S 175.2(3,1.1)
$Ph_{3})_{4}]_{2}\cdot(BF_{4})_{2}\cdot$	P2/a	1972.2(7)	94.40(4)			281.5(4)	
25 $CHCl_{3}$	4	3261.9(9)				331.4(2,36)	
				$PtS_{2}P_{2}$	P not given		S,S 82.4(3,1.0)
					μS 235.5(8,29)		

Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is th
d the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these co
Ag-S-Ag = 75.1(7,1.7) and 118.5(1)°; Ag-S-Mo = 76.7(8,6) and 117.3(1,4.3)°. [d] The Ag-X-Ag angle. [e] The Ag-X-M angle. [f] The M-X-M angle.
e two crystallographically independent molecules. [h] Ag-Cu = 276.4(1) pm; Ag-Ru = 282.2(1,3) pm; Cu-Ru = 272.2(1,74) pm;Ru-Ru = 287.7(1,

is associated with a platinum atom. Also, a terminal Ag(I) atom is bonded to each square-planar platinum unit through the two C-C triple bonds. Two molecules of acetone complete the coordination sphere of each terminal Ag(I) atom (Table 5).

The six metal atoms of $Ag_4Pt_2(Bu^tCC)_8$[78] are arranged in a slightly irregular octahedron, with Pt atoms mutually trans and the Ag(I) atoms in the equatorial plane. Each Pt atom is in an almost square planar environment formed by four Bu^tCC ligands. Each acetylenic fragment also forms an asymmetric π-interaction with one Ag atom so that each Ag atom is bonded to two such fragments. The molecular structure of an orange Ag_4Fe_2 cluster[28] is shown in Figure 6. The molecule is a fusion of three metallocyclic rings, consisting of a planar four-membered $\{Ag_2O_2\}$ ring sandwiched by two six-membered rings.

The next segment of Table 5 contains the Ag_3M_3 derivatives, such as the $Ag_3M_3(CO)_{12}(dmpe)_3$ molecule (M = Nb or Ta)[80] which has D_3 point symmetry with a planar heterometallic raft. Two derivatives $[Ag^I(hcdq)_2M^{II}]_3$ (M = Ni, green; M = Pd, yellow)[81] are isomorphous. Each molecule consists of three individual $M(hcqd)_2^-$ units which act as multidentate ligands coordinating to a linear chain of three silver atoms. Each MO_2N_2 unit is square-planar. The Ag in the centre of the

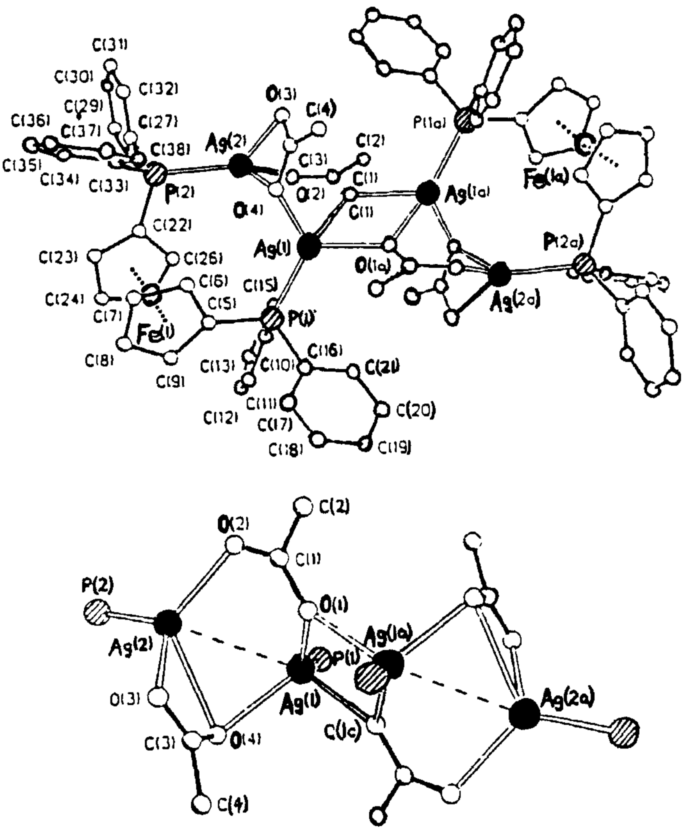

Figure 6 Molecular structure of $[Ag_2(MeCO_2)_2\{PPh_2cp\}Fe]_2$ (top); perspective view of the coordination modes of the acetato ligands in the cluster (bottom).[28]

molecule is six coordinate AgO_6. The two silver atoms at the ends of the chain are trigonally coordinated AgN_3.

In another four examples[82–85] clusters exhibit a capped trigonal bipyramidal metal framework. This consists of a tetrahedron of ruthenium atoms with two Ru_3 faces capped by $M(PP_3)$ (M = Ag[82–84] or Ag and Cu, respectively[85]). The Ag-Ru distance ranges from 280.6(1) to 297.7(1) pm, and the Ru-Ru distances from 278.5(1) to 315.1(6) pm. Two crystallographically independent molecules in one case[84] differ mostly by degree of distortion, involving both interatomic distances and interbond angles.

In another example[86] two $[Pt_2(\mu\text{-}Cl)_2(C_6Cl_5)_4]$ units doubly bridge two Ag(I) atoms with Pt-Ag-Pt angles of 163.3(3,1)°. Another platinum derivative[87] has two binuclear hinged $\{Pt_2S_2(PPh_3)_4\}$ moieties bridging the silver atoms via the sulphido ligands. The silver atoms are close to linear coordination (mean S-Ag-S = 175.2(3,1.1)°). The small bite angle of the $Pt_2S_2(PPh_3)_4$ ligand leads to a Ag-Ag bond distance of only 281.5(4) pm.

In these seventeen heterohexanuclear derivatives the silver atom is found in both oxidation state +1 and zero. There are two, three, four and six coordiante silver atoms observed. The shortest Ag-M distance is 276.4(1) pm (M = Cu),[85] and the shortest Ag-Ag distance is 275.6 pm.[84] The most common heterometal atoms are Pt and Ru, with one example each of Cu, Au, Nb, Ta, Ni, Pd, Fe, Rh, Mo and W. The mean Ag-M distances are: 276.4 pm (Cu); 285.5 pm (Rh); 288.8 pm (Nb or Ta); 289.2 pm (Ru); 297.5 pm (Mo) and 299.6 pm (Au). The other metal-metal distances are greater than 300 pm and are not considered bonding. There are several examples which contain M-M distances below this limit, for example: 281.9 pm (Ag); 284.2 pm (Nb or Ta); 288.0 pm (Ru) and 298.5 pm (Rh). There is also a Cu-Ru interaction of 272.2 pm. In general the Ag-M distances are longer than the corresponding Cu-M distances[20] as might be expected. In the latter case[20] twenty-eight examples of hexanuclear complexes were found.

HETEROOLIGONUCLEAR SILVER COMPOUNDS

The data for these compounds are given in Table 6 in order of increasing nuclearity. There is only one example of a heteroheptanuclear derivative[88] in which a Ag(I) atom links two $Os_3H(CO)_{10}$ fragments. The central $AgOs_4$ moiety is planar (Ag-Os = 286.4(1,12) pm), and all of the CO ligands are bonded to the Os atoms.

There are five octanuclear clusters, one having six silver atoms and two molybdenum atoms.[89] Two cubane like fragments are linked by two Ag-$SCMe_3$ bonds in which the $SCMe_3^-$ ligand acts as a triple bridge. The coordination geometry of the four silver(I) atoms is a distorted tetrahedral AgS_3P, while the remaining two silver atoms are approximately triangular planar. The Ag-Mo distances range from 288.8(5) to 310.0(1) pm.

The structure of $[AgCo(CO)_4]_4$[54] consists of an eight-membered ring with Co atoms bridged by Ag atoms. The mean Ag-Co distance is 259.2(1,3) pm, the Co-Ag-Co angle value is 161.25(4)°, and the Ag-Co-Ag angle is 70.8(1,9)°. Each Co atom carries four CO ligands.

The structure of $[Ag(Me_2am)Fe(cp)_2]_4$[90] is shown in Figure 7. The metal atoms form an essentially planar square with substituted pentadienyl rings acting as bridges. The Ag-Ag distance of 274.0(2) pm in the Ag_4 metallic cluster indicates

able 6 Crystallographic and structural data for heterooligonuclear silver compounds[a]

OMPOUND	Crys.cl Sp.Grp *Z*	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo- phore	M-L [pm]	Ag-M M-M Ag-Ag [pm]	L-M-L [°]
$N(PPh_3)_2\}\cdot$	*m*	2785.1(4)				286.4(1,12)	Os,Os[b]55.6(1,4)
$Os_3H(CO)_{10}\}_2Ag^I$	*C*2/*c*	1821.8(2)	112.10(1)			277,8(1,112)	
	8	2663.0(4)		OsC_3	C[b] not given		not given
				OsC_4			
$g^I{}_6Mo_2^{VI}(\mu_3\text{-}S)_6\cdot$	*tr*	1351.4(2)	102.02(2)	AgS_3	μS 239.4(3,4)	299.6(1,111)	S,S 97.2(1)
$Ie_3CS)_2(O)_2\cdot$	$P\bar{1}$	1577.9(6)	103.00(1)	(× 2)	μ_3SL 238.9(3)		130.3(1,4)
$Ph_3)_4]$	1	1142.5(2)	67.06(2)				75.2(1,2)[c]
				AgS_3P	P 239.4(3,4)		S,S 94.7(1,14.5)
				(× 4)	μ_3S 263.3(3,129)		102.0(1,18.1)[d]
					μ_3SL 258.5(3,60)	–	77.2(1,1.5)[c]
				MoS_3O	O 184.3(6)	–	Ag,Ag 79.9(1,7.5)
					μ_3S 233.4(3,10)		S,S 111.6(1,9)
							S,O 107.2(3,1.8)
$g^0Co^0(CO)_4]_4$	*m*	1192.3				259.2(1,3)	
	*C*2*m*	1783.7	95.61	CoC_4	OC 178.1(9,21)		C,C 101.8(5,2.4)
	8	637.4					141.1(6,3)
$g(Me_2am)Fe(cp)_2]_4$	*tg*	1581.7(3)		AgC_2	μC 217(2,3)	309.1(3)	C,C 170.7(6)
	$P42_1c$	–				–	78.3(6)[d]
	8	1018.6(11)				274.0(2)	
				FeC_{10}	cpC 204(3,8)		
$h_6C(CO)_{15}\cdot$	*m*	1811.0(3)		AgN	N 214(1)	282.2(1,1)	not given
$g(MeCN)\}_2]\cdot$	*C*2/*c*	1045.5(3)	125.99(1)			278,7(1,36)	
MeOH	4	2055.3(4)		RhC_5	OC 191(1,1)		
					μOC 211(1,6)		
					μ_6C 213(1,1)		
$h_6C(CO)_{15}$	*tr*	1139.7(3)	116.07(1)	AgP	P 237.6(3,7)	282.3(1,38)	not given
$g(PPh_3)\}_2]$	$P\bar{1}$	1651.9(2)	98.86(2)			279.2(1,36)	
	2	1687.9(5)	87.77(2)	RhC_5	OC 192(1,2)		
					μOC 211(1,7)		
					μ_6C 213.4(6,15)		

g$_6${Fe(CO)$_4$}$_3$·	*m*	1216.8(2)		AgP	P not given	268.0(1,51)	not given
Ph$_2$P)$_3$CH}]·	$P2_1/c$	2047.3(4)	91.65(2)			–	
(C$_3$H$_6$O)	4	2442.5(3)		FeC$_4$	C not given	301.4(1,401)	C,C 91(1.1)
							120(1)
t^{II}(Ag^{I}NO$_3$)·	*m*	2800.7(18)		AgO	O 225(4)	*e*	Pt,O 145.9(10)
u^{0}PPh$_3$)$_8$(NO$_3$)$_2$	$P2_1/c$	1774.8(3)	99.12(3)				
	4	2821.6(4)		AuP	P 226.9(15,65)		Pt,P 163.2(1,11.8)
t^{II}(CO)(Ag^{I}NO$_3$)	*tr*	1743.6(2)	94.18(2)	AgO	O 230.5(26)	*f*	Pt,O 162.2(6)
u^{0}PPh$_3$)$_8$]·(NO$_3$)$_2$	$P\bar{1}$	2035.8(7)	93.20(1)	AuP	P 230.8(9,33)		Pt,P 168.0(1,11.1)
	2	2050.0(3)	99.64(2)	PtC	OC 187.7(32)		
Ph$_4$)$_2$[Ag$_4$·	*or*	1376.8(4)				275.4(5,48)	
e(C$_4$H$_3$S)}$_6$]	$P2_12_12_1$	2427.6(7)				–	
	4	2518.3(6)		TeC	C 217(4,11)	313.0(5,117)	Ag,Ag 69(2)
(PPh$_3$)$_2$}]Ag$^I_6$·	*m*	1395.0(3)		AgC$_2$	C 216.8	297.2(–,57)	not given
u$^I_7$(PhC≡C)$_{14}$]	$P2_1/n$	3478.7(8)	99.03(4)		228.9	282.6	
	4	2568.1(4)		CuC$_2$	C 186.1		
Ph$_4$)$_3$[Ag^I·	*tr*	1935.9(2)	85.105(2)			298.3(1,113)	not given
h$_6$(CO)$_{15}$C}$_2$]	$P\bar{1}$	1778.6(2)	100.337(2)			279.2(1,42)	
	2	1675.3(2)	100.194(2)	RhC$_5$	OC 186(1,2)		
					μC 209(1,9)		
Bu$_4$)$_5$[{AgRe$_7$·	*m*	2230.2(6)		AgBr	μBr 251.6(4,6)	288.2(3,50)	121.6(2)^d
O)$_{21}$C}$_2$Br]	$P2_1/n$	2270.1(5)	95.07(2)			299.7(3,105)	
	4	3099.7(7)		ReC$_3$	OC not given		not given
					μC 213		
Ph$_3$)$_{10}$Au$_{13}$·	*m*	1658.6(2)		AgBr	Br 250(1)	282.5	
g$_{12}$Br$_8$·(SbF$_6$)	$P2_1/m$	2412.1(2)	103.22(4)	(× 2)		278.2	
	2	2996.9(3)		AgBr$_2$	μBr 263(1,5)		
					μ_4Br 278.2(8)		
				AuP	P 230		

able 6 Continued

OMPOUND	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	M-L [pm]	Ag-M M-M Ag-Ag [pm]	L-M-L [°]
(p-tol)$_3$}$_{10}$·	tr	1697.1(2)	78.20(6)	AgBr	Br 249.1(9)	290.5(5,202)	
u$_{13}$Ag$_{12}$Br$_8$](PF$_6$)	$P\bar{1}$	1743.1(2)	72.33(6)			282.8(3,186)	
0EtOH	1	2182.5(2)	72.13(4)			308.0(6,273)	
				AgBr$_2$	μBr 261.3(9,9)		Br,Br 102.7(2,1.7)
					μ_3Br 264.7(6,84)		68.2(2,13.2)[d]
					312.6(6,58)		
				AuP	P 231(1,2)		
(p-tol)$_3$}$_{16}$·	tg	2051.0(6)		AgCl	Cl 243(3)	283.1	
u$_{13}$Ag$_{12}$Cl$_7$]	$P4_32_12$	-				282.5	
bF$_6$)$_2$·nEtOH	4	6178(1)				295.3	
				AgCl$_2$	μCl 244		
				AuP	P 235		
P(p-tol)$_3$}$_{12}$·	tr	2464.7(10)	77.87(2)	AgBr$_x$	Br 239	273–301	
u$_{18}$Ag$_{19}$Br$_{11}$]·	$P\bar{1}$	2621.8(8)	81.92(4)		μBr 256(–,4)	266–320	
sF$_6$)$_2$	2	3030.9(2)	65.94(4)		μ_3Br 272(–,10)	279–334	
				AuP	P not given		
(p-tol)$_3$}$_{12}$·	tr	2324.0(8)	112.15(5)	AgCl$_x$	Cl 229(–,8)	270–314	
u$_{18}$Ag$_{20}$Cl$_4$	$P\bar{1}$	3193(2)	90.38(5)		μCl 248(–,22)	268–320	
	2	3398(2)	98.38(5)		μ_3Cl 266(–,20)	281–329	
				AuP	P 221(–,17)		

Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is th nd the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these column g-X-M angle. [d] The Ag-X-Ag angle. [e] Ag-Au = 276.1(5,47) pm; Ag-Pt = 272.2(5) pm; Au-Pt = 265.0(3,45) pm; Au-Au = 285.0(3,19 -M-M = 64.5(1,5.7) and 89.3(1,7.7)°. [f] Ag-Au = 294.1(2,133) pm; Ag-Pt = 276.2(3) pm; Au-Pt = 273.2(1,63) pm; Au-Au = 293.0 -M-M = 64.9(1,4.0)°.

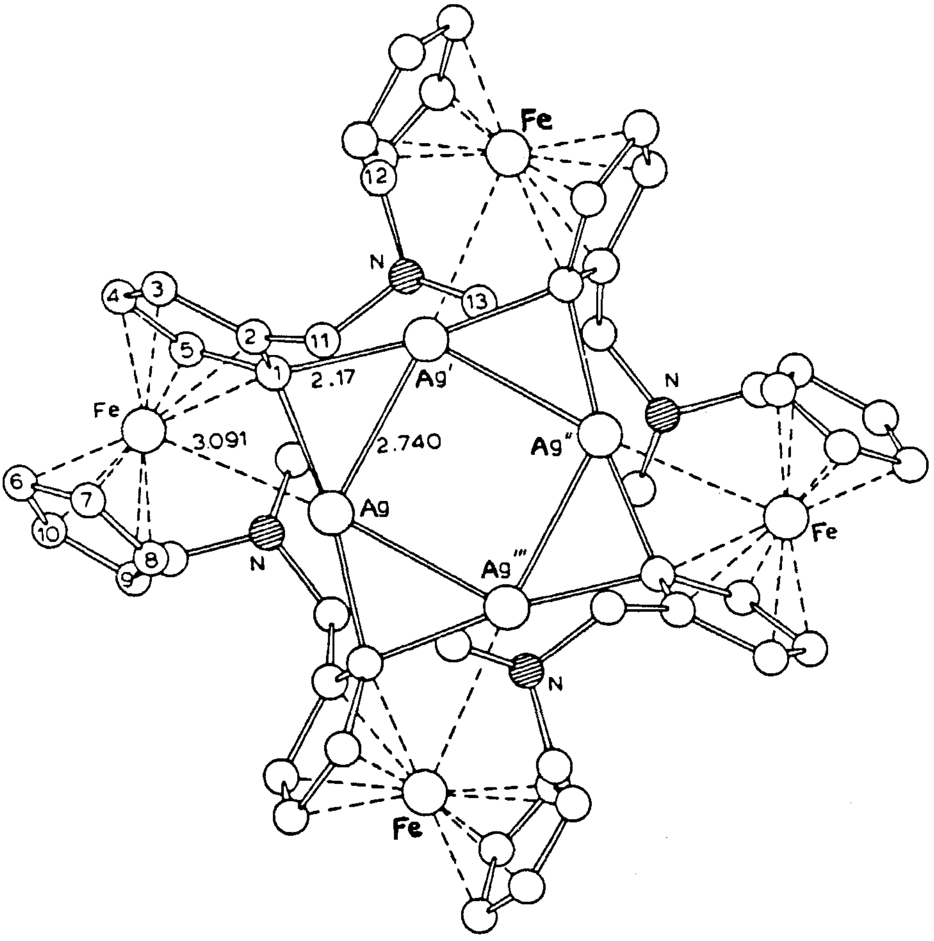

Figure 7 Structure of $[Ag(Me_2am)Fe(cp)_2]_4$.[90]

metal-metal bonding. The mean Ag-C distance of 217(2,3) pm almost coincides with the value of a sigma-bonded organosilver compound. The cyclopentadienyl ligands are planar but not quite parallel within each of the ferrocenyl fragments, the corresponding dihedral angle being 8.18°, and mean Fe-C distance 204(3,8) pm.

The structure of $[Rh_6C(CO)_{15}(AgL)_2]$,[91] where L is MeCN or PPh_3, is based on a trigonal-prismatic framework of Rh atoms capped on both triangular faces by the silver atoms carrying the linear acetonitrile or triphenylphosphine ligand. The mean Ag-Rh and Rh-Rh distances are 282.3 and 279.0 pm, respectively.

There is one example of a heterononanuclear cluster, which is shown in Figure 8. The silver atoms define a distorted octahedron with the tripodal ligand coordinated to three silver atoms on the face of the octahedron. The three $Fe(CO)_4$ fragments cap three of the octahedral faces in a symmetrical fashion. The brown and red

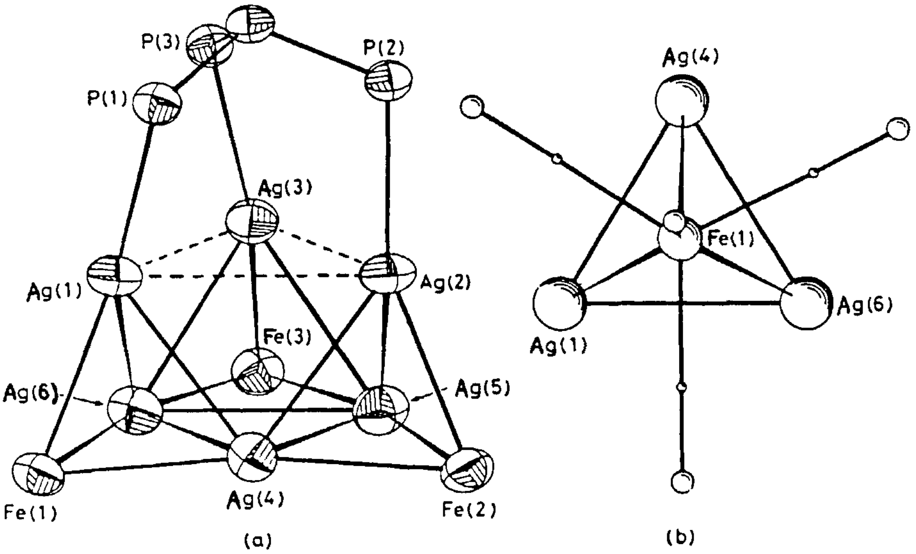

Figure 8 (a) The skeletal geometry of $[Ag_6\{Fe(CO)_4\}_3\{(Ph_2P)_3CH\}]$; (b) The geometry of a single $Ag_3Fe(CO)_4$ tetrahedron.[92]

heterodecanuclear clusters[93] show a central Pt atom surrounded by eight Au atoms and one Ag atom, with several M-M distances within bonding range (Table 6).

The structure of orange-red $\{N(PPh_3)_2\}[Ag_6Cu_7(PhCC)_{14}]$[95] reveals a well separated cation and a tridecanuclear cluster anion. A central, linearly-coordinated copper atom is linked via Cu-Ag interactions to three tetranuclear $[Ag_2Cu_2(PhCC)_4]$ sub-clusters, and within each unit of the sub-cluster, copper and silver atoms are bonded through metal-metal interactions and bridged phenylethynyl ligands.

In another tridecanuclear cluster anion[96] a silver atom is sandwiched between trigonal faces of two staggered Rh_6 trigonal prismatic units. Interstitial carbon atoms are found in the prismatic cavities, and 30 CO ligands are coordinated on the prism surfaces. In another anion cluster,[97] $[\{AgRe_7(CO)_{21}C\}_2Br]^{-5}$ to Re_7Ag moieties of *trans*-bicapped octahedral geometry are joined through a bromide interacting with two Ag atoms.

There are 25-nuclear bis-icosahedral clusters[98–100] containing 13 Au atoms and 12 Ag atoms. There are also 37- and 38-nuclear super-clusters[101,102] which conform to idealized C_{3v} and D_{3h} symmetry, respectively. In the former, there are two types of Au atoms, 12 on the cluster surface and six in the interior. Twelve tri(p-tolyl)phosphines coordinate to the surface Au atoms. Eleven bromide ligands (six double-bridging, four triply-bridging and one terminal) are coordinated to the silver atoms. In the latter derivative, the Au atoms are arranged as previously. The Ag atoms are arranged with 12 on the cluster surface, six inside and another two on the idealized threefold axis. All 12 phosphine ligands are coordinated to the surface Au atoms, and 14 chloride ligands are coordinated to the 20 Ag atoms (six double-bridging, six triply-bridging and two terminal).

HETEROPOLYNUCLEAR SILVER COMPOUNDS

The structural data for these derivatives are given in Table 7. Two yellow complexes $AgLAu(C_6F_5)_2$,[103] where L is C_4H_8S or C_6H_6, consist of $(AgAu)_2$ rings which have Au· ·Au contacts of 288.9(2) and 301.3(2) pm, and Ag-Au distances of 272.2(2,4) and 274.7(2,45) pm, respectively. The C_6F_5 ligands are coordinated to the Au atoms, and the L ligand to the Ag only. In another golden yellow platinum derivative, [104] 1-methyluracil ligands provide coordination for three metals simultaneously through N and O_4 for the two Pt atoms, and through O_2 for the one Ag atom. A second Ag atom links two trinuclear Pt_2Ag units without being directly coordinated to the 1-methyluracil ring. As a result, four Ag atoms take part in a 12-membered ring which also contains bridging NO_3 groups and an aquo bridge. The intramolecular Pt-Pt and Ag-Pt distances are 288.5(1) and 286.0(3) pm, respectively.

The structure of yellow $(NBu_4)[(C_6Cl_5)_2PtCl_2Ag]$[7] consists of a band-like polymeric anion and tetraalkylammonium cations. The $(\text{-Cl-Ag-Cl-Pt-})_n$ backbone of the polymer is planar and lies on the crystallographic *yz* plane with its propagation along the z axis.

The structure of a green complex[105] contains a centrosymmetric tetranuclear $\{Cu_2(C_8H_4O_2)_2(OH)\}_2^{-2}$ unit linked in a polymeric chain by bridging or phthalate anions, Ag(I) atoms and water molecules. There are two independent Cu(II) atoms linked by triply bridging hydroxo O atoms, and by carboxylate bridges from phthalate anions. One Cu atom (1) is in a trigonal bipyramidal environment, and the other (2) has a square pyramidal geometry (Table 7).

The structure of a dark red complex[107] contains ferric acetylacetonate moieties arranged in a staggered array along the *z* direction to form a bulky sheet-like structure in the *bc* plane. These sheets create 'cylindrical holes' in a direction parallel to *y*. These holes are filled with Ag(I) atoms and ClO_4^- ions. A similar structure was observed for a blue-green complex.[108]

Colorless pseudo-hexagonal crystals of $[Ag_4Sb_4(C_4H_2O_6)_4(H_2O)_4]$ were described[109] in terms of a repeating tetramer which extends into a polymer network. There are four independent and different silver and antimony centres. Each of the remaining examples[110–116] is unique from a structural point of view, and contain no significant degree of bonding between silver and the heterometal atoms.

CONCLUSIONS

Almost one hundred and forty heteronuclear silver compounds have been characterized by X-ray diffraction. The number increases by nuclearity in the order: heterotri- < -tetra-, -bi- < -hexa-, -poly- < -penta- < -octa- < -oligonuclear. There are a few examples of silver in the zero oxidation state, the rest contain Ag(I) with geometries, in increasing number of examples: hepta- < penta- < octa- < di- < tri- < tetracoordinate.

One example, $Ag(MeCO_2)Rh_2(CO)(dppm)(cp)_2$,[35,36] exists in two isomeric forms differing mostly by degree of distortion. Two crystallographically independent molecules, again differing mostly by degree of distortion, have been found in $[Pt_3SAuPPh_3AgCl(dppm)_3]PF_6$[73] and $Ag_2Ru_4(H)_2(CO)_{12}(dppm)$.[84] The coexistence of two species, differing only by small deviations in M-L distances and bonding able 7 Crystallographic and structural data for heteropolynuclear silver compounds[a]

OMPOUND	Crys.cl Sp.Grp *Z*	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore	M-L [pm]	Ag-M M-M [pm]	L-M-L [°]
$g^I (C_4H_8S)\cdot$	*or*	1118.5(3)		AgS	S^b 245.4(4)	272.2(2,4)	Au,Au 111.9(2)
$u^I(C_6F_5)_2$	*Pccn*	2247.5(6)				288.9(2)	AuS 120.3(2,1.4)
	8	1480.2(4)		AuC_2	C 205.8(12,1)		C,C 176.5(7,4)
							C,Ag 69.1(4,1.6)
							99.8(4,9.2)
$g^I(C_6H_6)\cdot$	*m*	2423.1(5)		AgC_2	C 248.9(11,9)	274.7(2,45)	Au,Au 112.0(2)
$u^I(C_6F_5)_2$	*C*2/*c*	757.0(1)	117.49(2)			301.3(2)	C,C 31.6(6)
	8	2261.3(5)					Au,C 102–145.0(4)
				AuC_2	C 205.7(11,6)		Ag,Ag 68.0(2,1.3)
							C,C 176.1(5,1)
							Ag,C 89.9(3,20.4)
$NH_3)_2\cdot$	*tr*	1347.0(4)	104.89(3)	AgO_4	O 242(2,6)	286.0(3)	O,O 90(1,8)
$^{II}(1\text{-Meur})\}_2\cdot$	$P\bar{1}$	1165.6(5)	107.29(2)		O_2NO 236(3,3)	302.5(1,140)	
$g^I{}_2(NO_3)_4]\cdot H_2O$	1	1018.5(3)	104.99(4)	AgO_4	O_2NO 247(2,9)		O,O 50(1); 103(1,17)
				PtN_4	N 204(2,2)		N,N 90(1,8)
				PtO_2N_2	O 204(2,2)		O,O 92(1)
					N 202(3,1)		N,N 88(1)
$Bu_4)\cdot$	*m*	1930.0(3)		$AgCl_2$	μCl 247.7(5)	320.3(1)	Cl,Cl 180.0
$_6Cl_5)_2Pt^{II}\cdot$	*C*2/*c*	2652.3(4)	103.53(2)		301.0(8)		83.6(2)[c]
$_2Ag^I]$	4	845.0(2)		PtC_2Cl_2	C 208(2)		C,C 175.8(8)
					μCl 232.4(5)		Cl,Cl 177.0(2)
							C,Cl 90.0(5,1)
$u^{II}_2(C_8H_4O_4)_2\cdot$	*tr*	1138.8(11)	100.3(1)	AgO_3C_2	μO 226.4(12)		O,O 93.9(7,12.2)
$H)Ag^I\cdot(H_2O)_5$	$P\bar{1}$	1177.2(12)	80.2(1)		H_2O 243.2(26,104)		O,C 118.8(6,25.4)
	2	787.5(9)	102.2(1)		C 252.9(17,43)		
				CuO_5	O^{eq} 212.8(11,105)		O,O 86.5–173.5(4)
					O^{ax}191.7(11,6)		
				CuO_5	O^{eq} 193.9(9,16)		O,O 83.2–175.3(4)
					μO^{ax} 235.2(13)		

$g^{I}Cu^{I}(tu)_4Cl_2$	*m*	3626.9(5)		AgS_3Cl	μCl 285.6(1)	306.2	not given
	$P2_1/a$	826.3(2)					
	4	588.3(2)		CuS_3Cl	not given		
$e^{III}(acac)_3\cdot$	*m*	1227.4(5)		AgO_2C	C 229(2)		O,O 119.4(7)
$g^{I}(ClO)_4(H_2O)]$	$P2_1/a$	1176.1(5)	120.64(12)		H_2O 225(2)		OC 106.2(8)
	4	1723.5(5)			ClO_4 250(2)		132.7(5)
				FeO_6	O 200(1,3)		O,O 90.0(4,3.6)
							176.7(4,3.1)
$g^{I}Ni^{II}(acac)_3\cdot$	*tg*	1505.3(5)		AgO_3	O 246(7)		not given
$g^{I}{}_2(NO_3)_2(H_2O)]$	$P4_1$	–			C 232(9)		
	4	1080.0(7)		NiO_6	O 204(6)		O,O 90(3)
$g^{I}{}_4Sb_4^{III}\cdot$	*or*	894.2(2)		AgO_4	O 216.8(8,12)	*d*	O,O 74.5–169.5(3)
$_4H_2O_6)_4\cdot$	$P2_12_12_1$	1527.2(6)			μO 257.1(8,11)		
$I_2O)_4$	4	2155.2(7)		AgO_4	μO 236.9(7,21)		O,O 70.3–144.3(3)
					μ_3O 252.6(8)		
				AgO_5	O 258.4(7)		O,O 79.3–161.5(3)
					μ_3O 249.9(7)		
					H_2O 239.9(8,26)		
					μH_2O 251.4(8)		
				AgO_6	O 266.6(8)		O,O 64.8–159.0(3)
					μO 251.4(8,120)		
					H_2O 252.1(8)		
				SbO_4	O 204.6(7,84)		O,O 74.4–152.9(3)
					μO 215.8(7,188)		
					μ_3O 238.1(7)		
$g^{I}Hg^{II}(C_4H_6NO)_2$	*or*	1553.2(3)		AgO_3	O 227.6(10,9)	304	O,O 46.5–162.8(5)
$O_3)]_2$	*Pbcn*	1624.4(2)			μ_3O 240.3(9,34)		
	8	1975.5(2)			270.7(10,44)		96.8(3,1)[e]
				HgO_2N_2	N 202.6(11,24)		O,O 46.8(4,3)
					O_2NO 271.4(11,83)		N,N 174.3(5,3)
							O,N 92.5(4,3.3)
$g^{I}Ga^{III}Cl_4\cdot$	*or*	1136.3(2)		AgC_4Cl_2	C 250.8(8,134)		not given
$-C_6H_4CH_2CH_2)$	$P2_12_12_1$	1176.7(2)			μCl 277.8(2,59)		
t 238K)	4	1376.6(2)		$GaCl_4$	not given		

able 7 Continued

OMPOUND	Crys.cl Sp.Grp *Z*	*a* [pm] *b* [pm] *c* [pm]	*α* [°] *β* [°] *γ* [°]	Chromo-phore	M-L [pm]	Ag-M M-M [pm]	L-M-L [°]
$_6H_6)Ag^IAl^{III}Cl_4$	*m*	909(3)		$AgCl_4C_2$	C 257(6)		Cl,Cl 70.3–144.0(6)
	$P2_1/c$	1022(3)	95.05(15)		μCl 280(2,24)		C,C 30.0(4)
	4	1273(3)		$AlCl_4$	μCl 214(2,2)		109(1,3)
$g^IBa(C_3H_2O_6P)\cdot$	*m*	657.8(3)		AgO_4	μO 225.3(4,8)	*f*	O,O 77.3–156.4(2)
$_2O)_3$	$P2_1/a$	2381.1(9)	90.57(3)		249.5(4)		
	4	661.0(3)			H_2O 270.3(5)		
				BaO_9	μO 267.3–295.8(4)		O,O 49.8–174.5(2)
$g^I{}_4(NH_3)_5\cdot$	*tr*	974.6	102.5	AgN_4	CN 226.7(10,50)	*g*	N,N 109.4(4,6.7)
$o^{IV}(CN)_8\cdot 1\frac{1}{2}H_2O$	$P\bar{1}$	1477.6	94.6	AgN_3	H_3N 215.5(10,4)		N,N 98.2(4,3.3)
	2	775.5	81.5		CN 254.0(12)		163.3(5)
				AgN_3	H_3N 214.9(10)		N,N 104.9(4,9.7)
					CN 230.0(11,155)		150.0(4)
				AgN_2	H_3N 213.4(12,4)		N,N 174.2(3)
				MoC_8	NC 215,7(12,23)		
$a[Ag^I(CN)_2]$	*m*	657.2(1)		AgC_2	C 200.9(16.0)	*h*	C,C 180
	$C2/c$	371.0(1)	92.05(1)				
	4	1734.6(2)		NaN_6	N 255.6(15,24)		
$nAg^I{}_2(SCN)_4$	*m*	1972.0(9)		AgS_4	S 255.3(2,1)		S,S 103.5(1,7.8)
178K	$C2/c$	770.3(3)	96.57(4)		264.8(2,16)		135.7(1)
	4	775.3(3)					108.1(1,5.0)[e]
				ZnN_4	N 196.4(2,1)		N,N 108.5(1,11.0)

Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is th
d the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these column
g-X-M angle. [d] Ag-Ag = 299.2(1) pm and Ag-O-Ag = 97.0(3)°. [e] The Ag-X-Ag angle. [f] Ag-Ag = 291.3(2) pm; Ag· ·Ba = 379.9(2), 533.6(3) and 5
n; Ba· ·Ba = 452.0(3) pm. [g] Ag-Ag = 312.8(1,37), 386.7(1) and 466.6(1) pm. [h] Ag-Ag = 374.2(–,32) pm.

Table 8 Summary of the Ag^I- and Cu(I)-ligand(atom) (pm) bond distances[a]

COORD. ATOM	Covalent Radius [pm]	Metal	2-Coordination [pm]	3-Coordination [pm]	4-Coordination [pm]
H	37	Ag	μ-H 180	μ_3H 180(11,11)	
		Cu		μ_3H 183(30,46)	μH 157(6,44)
					μ_3H 190(10,12)
O	73	Ag	LO 224(9,6)	LO 244(19,23)	
			LO 242(18,10)[b]	LO 238(12,23)	LO 257 (14,13)
		Cu	μO 190(10,10)	μO 211(37,42)	μOL 223.7
					LO 204(2,2)[b]
N	75	Ag	LN 212(12,11)	LN 228(14,26)	LN 227(5,5)
				LN 218(3,3)[b]	LN 232.0[b]
		Cu	LN 201.0(134,174)	SCN 186.8(8,12)	SCN 192.4(54,86)
			190(1,1)[b]	LN 202.3(72,82)	LN 202.5(115,84)
				207(3,7)[b]	209(7,11)[b]
C	77	Ag	LC 209(8,8)	LC 229	LC 234
			LC 237(2,1)[b]	LC 248(9,9)[b]	LC 249[b]
			μCL 213	NC 209(6,5)	
			μCL 217[b]		
		Cu	μCO 227(1,1)	μCO 218.5(153,166)	μCO 227.3(154,187)
			LC 196.0(40,110)	NC 189.2(12,10)	
			μCL 200.0(84,340)	μCL 204.7(113,283)	
Cl	99	Ag	237(6,6)		240(1,1)
				μCl 263.7	μCl 270(8,8)
		Cu	210.5(26,113)	214.8(57,163)	218.0(26,72)
			μCl 221.3(8,8)	μCl 244.8	μCl 242.2(146,353)
					μ_3Cl 266.0(203,195)
S	102	Ag	μS 238(1,1)	S 245	μS 257(4,7)
			LS 241(1,1)	μS 248(2,3)	μ_3S 262(20,16)
			μSL 237	μ_3S 248	μSL 269(21,22)
				μSL 262.5	μ_3SL 258(6,6)
				μ_3SL 239	
		Cu		S 215.0	NCS 257.2(248,544)
				μS 222.6(29,163)	μS 231.2(84,149)
				μ_3S 224.6(45,38)	μ_3S 232.4(124,168)
				μ_4S 227.1(33,73)	μ_4S 232.0(23,46)
				LS 218.0(9,8)	μSL 232.0(57,89);
				μSL 225.8(25,116)	241.1(2,149)[b]
				μ_3SL 222.5	μSL 242.0(46,80)[b]
P	106	Ag	LP 238(3,3)	LP 238(3,5)	LP 243(8,9)
				LP 242(4,8)[b]	LP 248(8,6)[b]
		Cu	LP 223.1(28,19)	LP 222.4(30,94)	LP 224.9(98,88)
			LP 222.2(8,7)[b]	LP 227.7(1,1)	LP 226.6(40,38)[b]
Br	114	Ag	246(7,4)	240	
			μBr 256(6,5)	μBr 262(7,7)	
			μ_3Br 283(26,35)		
			μ_4Br 278		
		Cu	226.7	229.9(18,18)	230.7
				μBr 238.5(39,17)	μBr 246.2(275,465)
					μ_3Br 279.1(5,5)
I	133	Ag		279.6	
				μI 266(2,2)	
		Cu	μI 266.4(82,81)	252.6(56,31)	246.5(17,29)
				μ_3I 252.2(125,126)	μI 272.8(135,396)
					μ_3I 263.8(83,300)

[a] The first number in parenthesis is the deviation from the mean of the shortest value and the second is the deviation from the mean of the highest value. [b] Bidentate ligands.

angles, within the same crystal is typical of the general class of distortion isomerism.[117]

A comparison of the mean M-L bond distances of the silver heteronuclear and corresponding copper(I) derivatives,[20] of which there are almost two hundred and forty, can be found in Table 8. In general, the mean Cu-L bond distances are shorter than the equivalent Ag-L values, as might be anticipated. In the series of copper clusters there is a greater variety of ligands, probably because this has been a more active area of investigation. For both copper and silver the tetrahedral and trigonal-planar geometries are most common. From a structural architecture point of view the clusters are very complex, with supraclusters being more common wth silver, particularly in the presence of gold.

Table 9 summarizes Ag-M and Cu-M distances in their respective heteronuclear clusters, excluding any value over 300 pm. Both metals have similar heterometal partners, with the Ag-M distances longer than the Cu-M values. Niobium, nickel and palladium are found in the silver clusters at distances less than 300 pm, but not in the copper clusters. Titanium and vanadium are present in the copper clusters but not in the silver ones.

Table 10 summarizes the M-M distances for the heterometal atoms in the copper and silver clusters, excluding those greater than 300 pm. The mean Au-Au, Ru-Ru and Os-Os distances found in the silver clusters are smaller than those found in the copper ones. For all the other metal atoms the opposite trend is observed.

Table 9 Summary of the Ag-M and Cu(I)-M distances[a].

M	Ag-M [pm]	Cu-M [pm]
Cu	290.4(140,125)	265.3(250,281)
Ag	286.5(132,209)	286.5(132,209)
Au	285.6(142,218)	280.8(179,200)
Li	276	275.3(23,22)
Ti		283.0(27,17)
V		267.8(82,42)
Nb	288.8	
Ta	288.8	281.4(26,30)
Mo	293.6(76,171)	268.3(103,247)
W	292.3(39,138)	269.8(131,283)
Mn	280.5(141,156)	269.6(131,91)
Re	287.8(133,123)	265.2(43,56)
Fe	270.9(80,93)	251.4(195,138)
Co	259.2	247,8(169,204)
Ni	297.0(63,40)	
Ru	283.6(121,261)	267.4(113,319)
Rh	282.8(184,268)	280.0(212,284)
Pd	291.9	
Os	283.2(33,44)	280.0(292,212)
Ir	276.1(119,113)	275.4(252,330)
Pt	277.5(134,397)	264.2(44,165)

[a] The first number in parenthesis is a deviation from mean of the shortest value, and the second number is the deviation from mean of the longest value.

Table 10 Summary of the M-M distances of heteronuclear Ag and Cu complexes[a].

M-M	SILVER CLUSTERS [pm]	COPPER CLUSTERS [pm]
Cu-Cu	282.2(5,4)	
Cu-W	263.8	
Cu-Mo	263.4(12,11)	
CuRu	272.2(74,74)	
Au-Au	285.4(196,188)	288.1(102,135)
Au-Pt	265.3(48,142)	
V-V	279.3	
Nb-Nb	284.2	
Ta-Ta	284.2	
Mo-Mo		276.3(41,95)
W-W		279.0(103,62)
W-Pt		277.9
Mn-Mn	274.0	
Re-Re	299.7(105,105)	257.0(2,2)
Fe-Fe		272.0(183,180)
Co-Co		251.3(6,6)
Co-Ru		262.8(6,6)
Ru-Ru	286.3(101,101)	287.4(175,125)
Ru-Ag		282.2(3,3)
Rh-Rh	282.4(73,176)	278.3(47,40)
Os-Os	277.8(112,112)	288.7(119,49)
Os-Ni		256.1(6,6)
Ir-Ir		277.9(68,49)
Pt-Pt	274.6(96,287)	267.3(25,39)

[a] The first number in parenthesis is a deviation from mean of the shortest value, and the second number is the deviation from mean of the longest value.

This review is part of a series which includes copper(I) clusters,[20] copper(I) coordination and organometallic compounds, and the corresponding silver compounds.[2] An analysis of copper(II) compounds is currently in progress. Despite the increasing availability of data retrieval systems, the collection of such data is not always straightforward. Many examples remain effectively invisible due to their associated keywords; others do not include full structural information. Some authors do not include bonding parameters about the central metal atom, M-M distances, bridge angles or an adequate description of the ligands. It is hoped that this review will serve to concentrate the available material, highlight areas of particular interest and point out areas where more attention is warranted.

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