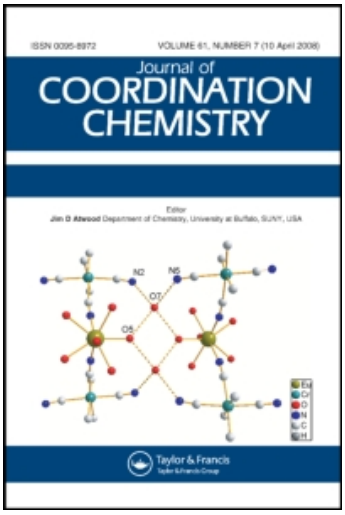

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SILVER COORDINATION AND ORGANOMETALLIC COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

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To cite this Article Holloway, Clive E. , Melnik, Milan , Nevin, W. Andrew and Liu, Wei(1995) 'SILVER COORDINATION AND ORGANOMETALLIC COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA', Journal of Coordination Chemistry, 35: 1, 85 — 178
To link to this Article: DOI: 10.1080/00958979508033088
URL: http://dx.doi.org/10.1080/00958979508033088

J. Coord. Chem., 1995, Vol 35, pp. 85–178
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REVIEW

SILVER COORDINATION AND ORGANOMETALLIC COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

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(Received July 2, 1994; in final form December 12, 1994)

This review summarizes the data for almost six hundred silver coordination and organometallic compounds, with the silver atom occurring in oxidation states of +1, +2, and two examples of +3 in a square-planar environment. The +2 oxidation state is found in digonal, square-planar, tetrahedral and hexa-coordinated environments. The +1 oxidation state is by far the most common in various geometries from two to seven. The nuclearity range from mono- to polynuclear utilizing a variety of ligand types. There are several examples of distortion isomerism, and a few examples of polymerization isomerism. Correlations between bond lengths, bond angles, ligating atom radius and silver oxidation state are discussed.

KEYWORDS: review, silver, crystallography, structures

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CONTENTS

0. Abbreviations

absg	o-aminobenzenesulphonyl glycine
adpo	5-aza-2, 8-dioxa-1-pnictabicyclo[3,3,0]octa-2,4,6-triene
anph	acenaphthylene
bct	3,4:3″,4″-bis(ethylenedithio)-2,2'5,5'-tetrathiafulvalenium
bdtp	1,5-bis(3,5-dimethylpyrazol-1-yl)-3-thiapentane
bp	bis[di(tert-butyl)phosphinomethyl]benzo[c] phenanthrene
bpy	2,2'-bipyridine
bgtp	1,3-bis(8-quinolylthio)propane
Bu^{t}dab	1,4-di-t-butyldiazabuta-1,3-diene
bzttcp	13,14-dibenzo-1,4,8,11-tetrathiacyclopentade-13-ene
c	cubic
cap	caproate

$CF_3CN_5S_3$	7-(trifluoromethyl)-1,3,5-trithia-2,4,6,8,9-penta-azabicyclo[3.3.1] nona-1(9),2,3,5,7-penteene
$C_3H_4NS_2$	2-mercaptothiazoline
$C_3H_6S_3$	1,3,5-trithian
$C_4H_8O_2$	1,4-dioxane
C_4H_8OS	1,4-oxathiane
$C_5H_6N_5$	adeninium
$C_5H_6S_5$	4,5-di(methylthio)-1,3-dithia-2-thione-4-cyclopentene
$C_6H_4N_2$	pyridine-4-carbonitrile
$C_6H_4NCO_2$	nicotinate
$C_6H_5N_3$	benztriazole
C_6H_8OS	1,4-oxathiane
$C_6H_{10}N_2O_2$	cyclosarcosylsarcosine
$C_6H_{10}N_4$	pentamethylenetetrazole
$C_6H_{11}N$	N-cyclohexylamide
$C_6H_{11}S$	cyclohexanethiolate
$C_6H_{12}S_3$	1,4,7-trithiacyclononane
$C_6H_{16}N_{10}$	ethylenebis(biquamide)
C_7H_8	8,9,10-trinorbornadiene
$C_8H_6N_2$	1,8-naphthyridine
C_8H_8	1,2,5,6-cyclooctatetrene
C_8H_{10}	exo-tricyclo[3,2,1,$0^{2,4}$]oct-6-ene
1,5-C_8H_{12}	1,5-cyclooctadiene
C_9H_8	indene
C_9H_{12}	1,4,7-cyclononatriene
$C_9H_{18}S_3$	1,5,9-trithiacyclododecane
$C_9H_{21}N_3$	1,4,7-triazacyclononane
$C_9H_{24}N_2$	N,N,N,N,N',N',-hexamethyl-1,3-propylenediamine
$C_{10}H_6(CO_2)_2$	1,8-naphthalenedicarboxylate
$C_{10}H_7CS_2$	α-dithionaphthoate
$C_{10}H_8$	naphthalene
$C_{10}H_9N_4O_2S$	sulphadiazine
$C_{10}H_{10}$	fullvalene
$C_{10}H_{12}$	1,6-cyclodecadiyne
$C_{10}H_{18}$	cyclodecene
$C_{10}H_{18}OS_4$	3-oxo-1,5,8,11-tetrathiacyclotridecane
$C_{10}H_{20}S_5$	1,4,7,10,13-pentathiacyclopentadecane
$C_{10}H_{20}S_6$	1,3,6,9,11,14-hexathiacyclohexadecane
$C_{10}H_{22}N_2OS_2$	1-oxa-7,10-diaza-4,13-dithiacyclopentadecane
$C_{10}H_{42}N_2S_2$	3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5, 13-diazacyclohexadecane
$C_{11}H_8N_4O_2$	10-methylisoalloxazine
$C_{11}H_{15}As$	o-allylphenyldimethylarsine
$C_{11}H_{30}N_3$	N,N,N,N',N″,N″,N″,-heptamethyl-N-hydrodiethylenetriamine
$C_{12}H_9NO$	4-benzoylpyridine

$C_{12}H_{10}$	benzocyclooctatetraene
$C_{12}H_{16}$	1,7-cyclodecadiyne
$C_{12}H_{16}S_3$	2,5,8-trithia[9]ortho-benzenophane
$C_{12}H_{17}N_3S$	N-(diethylaminothiocarbonyl)benzamidine
$C_{12}H_{18}$	1,5-dimethylcyclodeca-1,5,7-triene
$C_{12}H_{18}S_5$	2,5,7,10-tetrathia[12](2,5)thiophenophane
$C_{12}H_{24}O_5S$	1,4,7,10,13-pentaoxa-16-thiacyclooctadecane
$C_{12}H_{24}S_6$	1,4,7,10,13,16-hexathiacyclooctadecane
$C_{12}H_{26}N_2S_4$	1,4,10,13-tetrathia-7,16-diazacyclooctadecane
$C_{12}H_{28}N_4S_2$	[18]-N_4S_2 coronand
$C_{13}H_{13}N_2S$	thiophene-2-carbaldehyde imine
$C_{13}H_{20}$	1,5,9-cyclotridecatriene
$C_{14}H_{10}$	anthracene
$C_{14}H_{20}$	1,8-cyclotetradecadiyne
$C_{14}H_{26}$	1,1,4,4-tetramethyl-cis-cyclodec-7-ene
$C_{14}H_{28}S_2$	2,2-dimethylbut-3-enyl methylsulphide
$C_{14}H_{28}N_2S_4$	[9]-NS_2 azacoronand
$C_{14}H_{30}N_2S_4$	7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane
$C_{15}H_{15}N_2$	N,N'-di-p-tolylformamidinate
$C_{15}H_{21}OCO_2$	3-hydroxy-4-phenyl-2,2,3-trimethylcyclohexanecarboxylate
$C_{15}H_{23}NO_3S_2$	6,9,12-trioxa-3, 15-dithia-21-azabicyclo [15.3.1]hemicosa-1(21), 17,19-triene
$C_{15}H_{24}$	β-gorgonene
$C_{16}H_{22}N_4S_2$	N-[N-(5-methyl-thenylideneO-L-methionyl]histamine
$C_{16}H_{16}$	1,4-benzodioxan
$C_{17}H_{27}N_5$	quinquedentate macrocyclic ligand
$C_{18}H_{24}S_6$	1,4,7,10,13,16-hexathiacyclooctadecane
$C_{18}H_{36}N_4$	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazatricyclo[9.3.1.$1^{4,8}$] hexadecane
$C_{19}H_{17}N_7Cl$	2,6-diacetylpyridine-bis(6-chloro-2-pyridylhydrazone)
$C_{20}H_{18}$	sac-[2](1,5)naphthalino[2]paracyclophane
$C_{20}H_{24}O_6$	di(benzo-18-crown-6)
$C_{20}H_{27}N_3S_2$	1,12,15-triaza-3,4:9,10-dibenzo-5,8-dithiacycloheptadecane
$C_{21}H_{21}N_7O_2$	1,11-bis(2'-hydroxyethyl)-4,8:12,16:17,21-trinitrilo-1,2,10,11-tetraazacyclohemicosa-2,4,6,9,12,14,18,20-octaene
$C_{24}H_{24}$	[2,2,2]paracyclophane
$C_{24}H_{32}$	pentacyclo[12.2.2.$2^{2,5}$.$2^{6,9}$.$2^{10,13}$]-1,5,9,13-tetracosatetraene
$C_{24}H_{32}N_4O_2S_2$	3,12,19,28-tetraaza-6,9,22,25-tetraoxa-33,34-dithiatricyclo[28.2.1.$1^{14,17}$]tetratriaconta-2,12,14,16,18,28,30, 32-octaene
$C_{25}H_{17}N_5$	2,2':6,2':6″,2‴':6‴,2‴″-quinquepyridine-2,15-dimethyl-7, 10-dithia-3,14,20-triazabicyclo[14,3,1]icosa-1(20),2,14,16, 18-pentaene
$C_{25}H_{24}$	[23](1,4)-cyclophane
$C_{28}H_{34}P_2$	2,11-bis(dialkylphosphinomethyl)benzo[c]phenanthrene

$C_{29}H_{37}NO_5$	phomin
$C_{30}H_{30}$	[26](1,2,4,5)cyclophane
$C_{30}H_{35}N_2O_4$	10-methyl-9-[4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]-acridinium
$C_{30}H_{38}N_4S_4$	2,2'bis{4-(2-(tert-butylthio)ethyl)thio)-2-imidazolyl} biphenyl
$C_{34}H_{53}O_8$	lasalocid A, (antibiotic X-537A)
$C_{34}H_{59}O_{10}$	lysocellin
$C_{36}H_{42}N_8$	N_8 cryptand
$C_{38}H_{46}N_{10}$	N,N-bis(2-aminoethyl)-2-(aminomethyl)pyridine
$C_{38}H_{57}N_8$	N,N-bis(2-aminopropyl)-2-methoxyethylamine
$C_{42}H_{55}N_{10}$	N,N-bis(3-aminopropyl)-2-(aminomethyl)pyridine
$C_{44}H_{74}O_{14}$	emericid
$C_{46}H_{60}N_8O_2$	N,N-(3-aminopropyl)-2-methoxybenzylamine
$C_{47}H_{87}O_{14}$	ionophore X206
C_2O_4	oxalate
cre	creatinine
cry	cryptate
$cy(mt)_2$	cyclo(L-methionyl-L-methionyl)
dbp	dibenzylphosphate
dea	diethylamine
dep	diethylphosphate
dmb	1,8-diisocyano-p-methane
dmcn	3,7-dimethylenebicyclo[3,3,1]nonane
dmpe	bis(dimethylphosphino)ethane
dmpte	bis(2,6-dimethoxyphenylthio)ethane
dmto	1,3-dimethyl-2,4,5,6(1H,3H)-pyrimidinetetrazene-5-oximate
dpac	bis(diphenylarsino)ethane
dppe	bis(diphenylphosphino)ethane
dpph	diphenyl(2-pyridyl)phosphine
dppm	bis(diphenylphosphino)methane
dppp	bis(diphenylphosphono)propane
dppph	bis(diphenylphosphinophenylphosphine)
dtdc	4,7-dithiadecane-1,10-dicarboxylate
dtl	dithiolactone
dtoco	1,10-dithia-4,7,13,16-tetraoxacyclooctadecane
dtt	1,3-dithiane-1,1,3,3-tetraoxide
dttp	2,6-dimethyl-3,15,21-triaza-6,9,12-trithiabicyclo[15.3.1]hemicosa-1(21),2,15,17,19-pentaene
Et	ethyl
Et_2btu	1,1-diethyl-3-benzoylthiourea
fla	flavine
glyH	glycine
gr	grisorixin
hmta	hexamethyltetraamine
htcod	1,4,7,10,13,16-hexathiacyclooctadecane

im	imidazole
iot	2-imino-4-oxo-1,3-thiazolidine
LC	3,4:12,13-dibenzo-1,15-diaza-5,11-dioxa-cyclononadeca-1,14-diene
LN_5	macrocycle, prepared from 2,6,-diacetylpyridine and 1,9-diamino-3, 7,-diazanonane
m	monoclinic
Me	methyl
Me_3aca	trimethylammoniaacetate
Me_3apr	trimethylammoniapropinonate
Mead	methyl-9-adenine
Me_4bpy	4,4',6,6'-tetramethyl-2,2'-bipyridine
Mecyt	1-methylcytosine
9-Mehe	9-methylhypoxantine
meB	monensin B
p-MeOacp	p-methoxyacetophenone
mes	mesityl
Me_4tacd	1,4,8,11-tetramethyl-1,4,8,11-tetracyclotetradecane
Me_6tacd	5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
Metu	N-methylthiourea
mgly	cyclo-1-methionylglycine
ml	(R,S)-1,2-(5-Me-thio-2-CH = $N)_2$-cyclohexadienyl
mor	morpholine
mpsa	[2-(6-methyl)pyridyl]trimethylsilylamido
$4\text{-}NO_2pyNO$	4-nitropyridine-N-oxide
OHqu	8-hydroxyquinoline
or	orthorhombic
otta	1-oxo-1,2^4,2,4λ^4,3,5-trithiadiazole
pa	2-pyridyleneaniline
pctt	pentacyclo[12,2,2,$2^{2,5}$,$2^{6,9}$,$2^{10,13}$]-1,5,9,13-tetracosatetrene
pdp	1-phenyl-3,5-dimethylpyrasole
peA	polytherin A
pfc	pefloxacin; 1-ethyl-1,4-dihydro-7-(4-methyl-1-piperazinyl)-4-oxo-3-quinolinecarboxylate
Ph	phenyl
pic	picrate
pip	piperidine
$Pmes_3$	tris(mesityl)phosphine
pmqu	2-phenyl-8-mercaptoquinolinate
pp	bis(diphenylphosphinomethyl)benzo[c]phenanthrene
ppyp	phenyl-(2-pyridyl)-phosphane
$PrS(CH_2)_2SPr$	1,2-bis(propylthio)ethane
pta	(phenylthio)ethanoate
py	pyridine
pyac	pyridinioacetate
pycac	3-carboxylato-1-pyridinioacetate

pypr	pyridiniopropionate
rfl	riboflavine
sa	2-salicylamide-O-acetate
saca	sulphacetamide
$S_4N_4H_4$	tetrasulphur tetraimide
ste	stearate
sui	succinimide
tacd	1,4,8,11-tetraazacyclotetradecane
tbc	1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne
tch	thiocarbonohydrazide
tg	tetragonal
thf	tetrahydrofuran
tht	tetrahydrothiophene
tmb	2,5-dimethyl-2,5-diisocyanohexane
tmpp	tris(2,4,6-trimethoxyphenyl)phosphine
tosco	α-4,7,13,16-tetraoxo-1,10-disulphocyclooctadecane
tpp	tetraphenylporphyrine
tr	triclinic
trg	trigonal
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
tsc	thiosemicarbazide
ttf	tetrathiafulvalene
tt(9)ob	2,5,8-trithia[9]-o-benzenophane
ttof	8-thiatheophylline
tu	thiourea

1. INTRODUCTION

Silver is quite widely distributed in the environment and appears to have certain uniquely useful properties. The chemistry of silver continues to be a rigorous and diverse area of study, covering coordination complex, organometallic and solid state chemistry. Several review articles have been published during the last few years dealing with various aspects of the solid state chemistry of silver. For example, an analysis of 22 crystal structures of Ag(I) compounds with hard bases showed[1] that the occurrence of a red colouration is related to the coordination number of the silver atoms. The colourless compounds have coordination numbers of 1 or 2, whereas the red compounds always show coordination number 3 or 4. A survey of the literature on organosilver chemistry up to April 1969 was publsihed in 1970.[2] Coordination of compounds of unsaturated and aromatic compounds with silver salts, either in aqueous solution or the solid state, have been studied extensively.[3] Silver(I) oxides with a high ratio of cations to oxygen have been shown to have unusual structural features with respect to the arrangement of the silver atoms.[4] Some silver chalcogenides have been summarized in a separate review.[5]

There have been many structural studies of silver compounds included in annual review over the last few years,[6] but no overall systematic study and classification of these structures yet exists. The purpose of this review is to provide such an overview for structures up to the end of 1991. There are over 600 structures and they are discussed in terms of the nuclearity and coordination number of the silver atoms. The compounds are listed in order of increasing coordination number, increasing complexity of the coordination sphere and increasing covalent radius of the principal coordinating atom. Under varying conditions silver has been isolated with coordination numbers from one to ten, with four being the most common. Some interesting differences between Ag(I), Cu(I) and Au(I) are observed and are discussed in this presentation.

2. MONONUCLEAR SILVER COMPOUNDS

2.1 Coordination numbers one and two

X-ray analysis of colourless air stable Ag(2,4,6-$Ph_3C_6H_2$) shows[7] that the aryl ligand coordinates to the silver atom through one of its ring carbon atoms, giving the silver an unusual coordination number of one. The Ag-C distance of 190.2(5) pm is the shortest of such distances found in organosilver derivatives, and is slightly longer than that of a similar copper(I) complex of 189.0(6) pm.[7] This would be expected on the basis of the larger covalent radius of silver (153 pm) *vs.* copper (138 pm).

Structural data for mononuclear silver compounds with coordination number two are listed in Table 1. There are over forty such derivatives with the two geometries of linear and bent, of which the former is by far the most common. Unidentate N-donor ligands are the most common, building up a homogenous coordination environment about the silver(I) atoms. There is one example of a silver(II) derivative.[17] The mean Ag-L bond distance increases as the covalent radius of the coordinated atom increases. Table 1A shows the mean Ag(I)-L distances, and it is observed that they are longer than those of the comparable Cu(I)[42] and Au(I)[43] values. The mean M-L distances increase with the increasing covalent radius of the metal: Cu(138 pm) < Au (143 pm) < Ag (153 pm). The L-Ag(I)-L angles are in the range 180–145°, which is somewhat wider than that found for the Cu(I) and Au(I) derivatives, 180–154° and 180–155°, respectively.

The compound Ag(C_6F_5)(CH_2PPh_3)[27] exists in two isomeric forms, triclinic and monoclinic, which differ mostly by degree of distortion. In several other derivatives[8,9,19,20,24,28,33,37] two crystallographically independent molecules are present, which again differ by degree of distortion. The coexistence of two or more species of this type within the same crystal is typical of the general class of distortion isomerism.[44] A similar set of examples has been found for Cu(I)[42] and Au(I)[43] derivatives.

2.2 Coordination number three

Structural data for mononuclear silver compounds with coordination number three are given in Table 2, where it can be seen that only oxidation state +1 occurs. A

Table 1 Structural data for mononuclear silver compounds with coordination number one and two.[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	L-M-L [°]	Ref.
$Ag^{I}(2,4,6\text{-}Ph_3C_6H_2)$	m $P2_1/c$ 4	1063.6(2) 1510.5(4) 1253.4(4)	 113.55(2)	AgC	C[b]	190.2(5)		7
$[Ag^{I}(NH_3)_2]NO_3$[c]	or Pnmm 4	1057.3(2) 811.0(2) 628.6(1)		AgN_2 AgN_2	N N	215(2,0) 218(2,0)	180 180	8 9
$[Ag^{I}(NH_3)_2]NO_3$[c] (at 223 K)	or Pnnm 4	808.8(3) 1041.6(5) 626.1(2)		AgN_2 AgN_2	N N	211.6(10) 212.1(10)	180 180	
$[Ag(NH_3)_2]\cdot$ $[Ag_2SeO_3N(NH_3)_3]2H_2O$	or $P2_12_12_1$ 4	1186.4(3) 1455.0(3) 643.3(2)		AgN_2 AgN_2	N See Table 15	213.3(10,18)	170.0(4)	10
$[Ag^{I}(2,6\text{-}Me_2py)_2]ClO_4]$	tg $I4_1/acd$ 9	1523.4(3) — 1442.8		AgN_2	N	216.6(4,0)	180.0	11
$[Ag^{I}(2,6\text{-}Me_2py)_2]NO_3]$	m $P2_1/n$ 4	1323.5(3) 1428.0(3) 828.4(3)	 94.54(2)	AgN_2	N	218.7(6,5)	169.3(2)	11
$[Ag^{I}(2,6\text{-}Me_2py)_2]BF_4]$	tg $I4_1/acd$	1506.9(4) 1439.1(3)		AgN_2	N	216.3(7,0)	18000	12
$Ag(NCCl)_2]SbF_6$	m $P2_1/n$ 2	777.9(3) 887.7(4) 824.0(4)	 113.34(3)	AgN_2	N	214.0(4,0)	180	13
$[Ag^{I}(cre)_2]ClO_4\cdot 2H_2O$	m $P2/c$ 2	1140.5(2) 605.2(2) 1232.5(2)	 95.95(1)	AgN_2	N	210.0(3,0)	177.2(1)	14
$(NMe_4)[Ag_I(NCO)_2]$	or Pnma 4	1086.7(6) 661.4(5) 1385.2(7)		AgN_2	N	204.2(13,27)	177.2(5)	15
$[Ag^{I}(Im]_2]NO_3$	or $P2_12_12_1$ 4	1092.7(2) 1821.5(5) 499.9(1)		AgN_2	N	212.6(8,6)	172.0(3)	16
$[Ag^{II}(ImH]_2]NO_3$	or $P2_12_12_1$ 4	1094(1) 1810(2) 510(1)		AgN_2	N	212(-,0)	172	17
$[Ag^{I}(9\text{-}Mehx)_2]NO_3\cdot 2H_2O$	tr $P\bar{1}$ 2	998.5(3) 1465.5(4) 660.6(2)	107.26(3) 95.92(3) 96.71(3)	AgN_2	N	215.1(7,4)	175.1(3)	18
$[Ag^{I}(9\text{-}Mehx)_2]NO_3\cdot ClO_4H_2O$[c]	tr $P\bar{1}$ 4	927.1(3) 1018.7(7) 1912.4(7)	91.17(4) 94.08(3) 93.78(4)	AgN_2	N	213(1,0)	173.1(4)	19
$Na[Ag^{I}(suc)_2]5H_2O$[c]	or Cmc2 8	685.6(5) 2174(1) 2058.9(6)		AgN_2 AgN_2	N N	207(1,1) 208(1,1)	not given	20
$[Ag^{I}(C_6H_4N_2)_2]NO_3$	tr $P\bar{1}$ 2	2795.4(7) 635.4(2) 371.0(1)	87.55(3) 86.21(2) 89.35(2)	AgN_2	N	220.9(4,6)	162.2(2)	21
$[Ag^{I}(C_{12}HgNO)_2]NO_3\cdot H_2O$	tr $P\bar{1}$ 2	1703.6(5) 869.1(3) 784.9(3)	107.74(2) 97.53(2) 91.11(2)	AgN_2	N	214.7(3,1)	175.3(1)	21
$[Ag^{I}(C_{13}H_{13}N_2S)_2]$ (CF_3SO_3)	m C2 4	1874.6(4) 1246.2(3) 1487.8(4)	 119.71(2)	AgN_2	N	216.1(11,14)	174.7(1)	22

Table 1 *Continued*

$[Ag^I(py)_2]\cdot[Ag^I(py)_4](ClO_4)_2$	tg	2195(1)		AgN_2	N	216(1,1)	173.7(4)	23
	$I\bar{4}$	—						
	4	768.4(3)		AgN_4		see Table 3		
$[Ag^I(C_6H_5N_3)_2]NO_3$[c]	tr	1004.8(2)	98.44(2)	AgN_2	N	214.9(3,3)	158.4(1)	24
	$P\bar{1}$	1031.1(3)	107.23(2)					
	4	1481.7(1)	91.15(3)	AgN_2	N	219.6(3,10)	151.3(3)	
$[N(PPh_3)_2][Ag^I(B_3H_7NC)_2]$	m	1797.6(6)		AgC_2	C	205.3(12,11)	169.8(5)	25
(at 185 K)	$P2_1/c$	1155.9(3)	94.30(6)					
	4	1920(3)						
$K[Ag^I(dtt)_2]H_2O$	m			AgC_2	C	214.7(-,)	180	26a
$[Ag^I(RNC)_2PF_6$	C2/c	2002.2(8)		AgC_2	C	207.5(14,0)	156.1(6)	26b
	4	1082.9(7)	106.4(1)					
		2002.3(6)						
$Ag^I(C_6F_5)(CH_2PPh_3)$	tr	889.1(3)	112.74(3)	AgC_2	C	214.4(5)	178.2(2)	27
	$P\bar{1}$	1168.5(4)	108.89(3)		$(C_6F_5)C$	210.5(6)		
	2	1263.6(5)	97.28(3)					
	m	1213.9(2)		AgC_2	C	213.1(6)	175.4(3)	27
	$P2_1/n$	1248.7(2)	103.06(2)		$(C_6F_5)C$	210.2(6)		
	4	1502.3(3)						
$[Ag^I\{CH(PPh_3)CO_2Et\}_2]\cdot$	tr	983.2(3)	77.10(3)	AgC_2	C	218.3(15,2)	173.4(7)	28
$(ClO_4\cdot 0.5CH_2Cl_2$	$P\bar{1}$	1096.5(4)	78.23(4)					
	2	2179.8(7)	73.07(2)					
$[Ag\{CH(PPh_3)COPh\}_2]\cdot$	tr	1178.1(3)	86.40(2)	AgC2	C	221.9(9,0)	175.6(4)	28
$(NO_3)\cdot 0.25CH_2Cl_2$[c]	$P\bar{1}$	1940.7(4)	89.91(2)					
	4	1951.7(5)	89.65(2)	AgC_2	C	225.6(8,0)	1167.7(4)	
$[Li(thf)_4]\cdot[Ag^I\{C(SiMe_3)_3\}_2]$	tr	942.6(1)	94.49(2)	AgC_2	C	218.07(7,18)	not given	29
	$P\bar{1}$	1204.7(2)	90.09(2)					
	2	2333.1(3)	94.27(2)					
$Ag^I\{CF(CF_3)_2\}_2]\cdot$	or	2114.2(3)		AgC_2	C	201.5(35)	170(1)	30
$[Rh(dppe)_2]$	Pba2	2226.2(2)				219.1(17)		
(at 203 K)	4		1187.7(2)					
$[K(crypt\text{-}2,2,2)][AgCl_2]$	m	1424.2(8)		$AgCl_2$	Cl	232.9(2,1)	178.03(6)	31
	$P2_1/c$	1569.5(4)	95.63(5)					
	4	1161.4(6)						
$[N(PPh_3)_2][Ag^I(Sg)]S_8$	tr	1383.8(4)	62.38(2)	AgS_2	S	236.8(3,1)	166.4(1)	32
	$P\bar{1}$	1429.5(4)	68.05(2)					
	2	1540.5(5)	65.86(2)					
$[Ag^I(C_{12}H_{17}N_2S)_2]NO_3$[c]	m	1254.1		AgS_2	S	240.3(4,5)	159.4(1)	33
	$P2_1/n$	4347.0	106.27					
	8	1109.6		AgS_2	S	240.1(3,5)	158.7(1)	
$[Ag^I(Pmes_3)_2]PF_6$	trg	1537.8(2)		AgP_2	P	246.1(2,0)	179.4(5)	34
	$P3_121$	—						
	3	1994.5(4)						
$[Ag^I\{P(NMe_2)_3\}_2]BPh_4$	m	1197.5(3)		AgP_2	P	239.4(2,1)	166.9(1)	35
	$P2_1/c$	1732.5(3)	107.08(3)					
	4	2007.9(5)						
$[Ag^I\{PPh_2(C_5H_9)\}_2]ClO_4$[c]	m	1057.4(6)		AgP_2	P	242.4(2,7)	145.1(1)	36
	Pn	1714.2(11)	104.34(5)					
	4	1881.2(3)		AgP_2	P	240.8(2,11)	153.0(1)	
$[Ag^I(C_{28}H_{34}P_2)]ClO_4$[c]	m	2356.7(9)		AgP_2	P	237.8(4,1)	164.8(1)	37
	$P2_1/a$	1572.0(3)	96.35(2)					
	4	1524.5(4)		AgP_2	P	239.1(3,2)	167.6(1)	
$[Ag^I(Pcy_3)_2]ClO_4$	tr	950.5(2)	99.03(2)	AgP_2	P	243.1(1,2)	147.34(3)	38
	$P\bar{1}$	979.0(2)	95.44(2)					
	2	2366.7(6)	115.97(1)					
$[Ag^I(by)]ClO_4\cdot$	m	1601.5(4)		AgP_2	P	239.4(2,1)	161.5(1)	39
MeCOMe	Pbca	2005.0(4)	90.0					
	8	2500.2(6)						

Table 1 *Continued*

$[Ag^{I}(pp)]ClO_4$	m	1543.5(3)		AgP_2	P	240.9(3,8)	151.5(1)	40
	$P2_1/c$	1312.9(3)	100.39(1)					
	4	1892.7(3)						
$[Ag^{I}\{As(C_5H_9)_3\}_2]ClO_4$	m	1016.2(4)		$AgAs_2$	As	248.1(2,1)	151.2(1)	36
	$P2_1/n$	2321.(6)	98.37(2)					
	4	1435.1(3)						
Ag^{I}(tmpp)Cl	tg	1531.0(1)		AgClP	Cl	234.2(1)	175.0(1)	41
	$P4_1$	—			P	237.9(1)		
	4	1236.6(1)						
Ag^{I}(tmpp)Br	tg	1531.9(4)		AgPBr	P	237.4(2)	174.40(6)	41
	$P4_1$	—			Br	244.8(1)		
	4	1244.1(6)						

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand. [c]There are two crystallographically independent molecules.

Table 1A Mean values of M(I)-L distances in mononuclear two-coordinated derivatives (data for Cu(I)-L are taken from ref. 42, and for Au (I)-L ref. 43; M[covalent radius]).

Coord. atom/ligand	Covalent radius [pm]	Cu(I)-L [pm] [1.38 pm]	Au(1)-L [pm] [1.43 pm]	Ag-L [pm] [1.53 pm]
LN	75	189.7(42,69)	200.4(64,64)	213.7(122,78)
LC	77	194.6(40,124)	207.5(95,124)	215.4(139,102)
Cl	99	207.7(120,41)	227.6(54,54)	233.6(7,6)
LS	102	213.7	228.8(16,50)	240.2(1,1)
LP	106	216.9(8,28)	227.5(85,50)	240.6(33,55)
Br	114	224.4(35,31)	238.2(5,5)	244.8
LAs	120		234.2	248.1

The first number in parenthesis is maximum deviation from the shortest and the second one form the longest distance from the mean value.

regular planar geometry is observed in two cases, one with 1-phenyl-3,5-dimethylpyrazole ligands,[45] and the other with 3,4-di(methylthio)-1,3-dithia-2-thione-4-cyclopentene ligands.[46] Other examples with three identical ligands exhibit some degree of distortion.[47–49] The silver-anion interaction is responsible for the deviation from planarity of the AgP_3 core of the cationic complexes. Distortion from planarity in the $[AgI_3]^-$ anionic complex is due to steric hindrance between the iodine atoms.[50] Highly distorted geometry in the remaining examples in Table 2 is due to the presence of different types of ligand around each silver atom, some of them being bidentate.

The mean Ag(I)-L distances (Table 2A) increase with the covalent radius of the metal, except bidentate N-donor ligands. In general the distances are longer than that of the two-coordinate derivatives, as expected.

The compound $Ag(C_{10}H_{18})_2(NO_3)$ exists in two isomeric forms, *cis*-[53] and *trans*-.[54]

Table 2 Structural data for silver compounds with coordination number three.[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]		L-M-L [°]	Ref.
$[Ag^{I}(pdp)_3]NO_3$	trg R3 3	1530(2) — 1187(1)	 120.0(2)	AgN_3	N^b	224.3(3.0)		119.83(1,0)	45
$[Ag^{I}(C_5H_6S_5)_3]PF_6$	tr $P\bar{1}$ 2	1154.4(3) 1219.7(6) 1322.3(3)	104.31(5) 94.18(5) 114.69(3)	AgS_3	S	250.2(3,12)		119.79(9,1.25)	46
$[Ag^{I}(PPh_3)_3]NO_3$	m $P2_1/n$ 4	1798.0(2) 1370.9(2) 1891.5(3)	 94.91(2)	AgP_3	P	256.8(3,62)		115.6(1,3.2)	47
$[Ag^{I}\{PPh_2(C_5H_9)\}_3]BF_4$	trg P31c 4	1339.8(6) — 3050.9(10)	 	AgP_3	P	254.5(3,0)		117.4(1,0)	48
$[Ag^{I}(PPh_3)_3]BF$	m $P2_1/m$ 4	1902.9(6) 1376.4(4) 1801.8(5)	 94.26(2)	AgP_3	P	250.6(3), 256.0(3,17)		115.1(1,2.0)	49
$(PPh_3Me)_2[Ag^{I}I_3]$	m $P2_1$ 2	1646.9(5) 1251.4(2) 967.3(2)	 103.64(3)	AgI_3	I	274.8(1,7)		120.0(1,4.7)	50
$[Ag^{I}(pa)(NO_3)$	tr $P\bar{1}$ 2	1063.74(10) 862.70(7) 738.31(6)	106.39(7) 83.42(6) 75.01(7)	AgN_2O	N O_2NO	233.8(3,35) 225.9(3)	N,N[b] N,O	72.54(9) 142.7(1,7)	51
$[Ag^{I}(iot)_2]ClO_4$	m $P2_1/c$ 4	1375(5) 735(2) 1588(5)	 119.9(6)	AgN_2O	N O	219.7(16) 228.3(17) 254.3(13)	N,N N,O	144.3(6) 94.0(6) 121.7(6)	52
cis-$Ag^{I}(C_{10}H_{18})_2$ (NO_3)	m C2/*c* 4	532.9 1453 2717	 92.02	AgC_2O	C O	250(-, 1) 250		not given	53
trans-$Ag^{I}(C_{10}H_{18})_2$ (NO_3)	or Pbcn 4	547 1469 2673	 	AgC_2O	C O	244(2,2) 249		not given	54
$[Ag^{I}(C_{14}H_{26})_2$ (NO_3)	or $C2_12_12_1$ 4	587.9 1686 2839	 	AgC_2O	C O	252(-,3) 240		not given	53
$[Ag^{I}(C_6H_{11}Ph)_2$ (ClO_4)	or Pmcn 4	3217(2) 566.6(3) 1267(1)	 	AgC_2O	C O	248(1,0) 266(1)	C,C C,O	109(1) 87(1)	55
$[Ag^{I}(PPh_3)_2\cdot$ $(2,4,6\text{-}Cl_3C_6H_2O)$	m $P2_1/c$ 4	1669.2(4) 1794.2(4) 1285.7(3)	 97.60(1)	AgP_2O	P O	244.8(1,4) 223.5(4)	P,P P,O	131.1(1)56 114.4(3,1.0)	56
$[Ag^{I}(Pcy_3)_2(NO_3)$	tr $P\bar{1}$ 2	925.8(2) 982.8(2) 2338.5(5)	94.73(2) 96.35(2) 116.42(1)	AgP_2O	P O	244.3(3,3) 245(1)	P,P P,O	139.04(9) 108.7(3,3.8)	38
$[Ag^{I}(PPh_3)_2(NO_3)$	tr $P\bar{1}$ 2	1182.1(3) 1199.0(3) 1366.0(3)	102.05(2) 112.80(2) 105.30(2)	AgP_2O	P O	244.2(1,2) 246.4(4)	P,P P,O	138.21(5) 105.8(7,6.0)	57
$[Ag^{I}(PPh_3)_2$ $\{C_5(CO_2Me)_5\}$	or $P2_12_12_1$ 4	2659.2(8) 1863.8(6) 950.7(2)	 	AgP_2O	P O	242.1(2,7) 246.4(5)	P,P P,O	136.64(5) 107.5(1,13.4)	58
$[Ag^{I}(pp)(NO_3)$	m $P2_1/n$ 4	949.8(1) 1765.9(2) 2181.6(3)	 98.34(1)	AgP_2O	P O	241.7(2,7) 247.6(12)	P,P P,O	148.6(1) 104.3(3,8.7)	40
$[Ag^{I}(pp)Cl$	m $P2_1/c$ 4	940 1720 2210	106.15 	AgP_2Cl	P Cl	243.4(1,22) 251.2(1)	P,P P,O	142.2(1) 108.5(1,5.0)	40, 59

Table 2 *Continued*

$[Ag^{I}(bp)Cl]CH_2Cl_2$	m	1116.3(3)		AgP_2Cl	P	244.2(2,15)	P,P	142.6(1)	39
	$P2_1/n$	2438.28(7)	76.88(2)		Cl	256.9(2)	P,Cl	108.6(1,8.0)	
	4	1409.4(4)							
$[Ag^{I}(bp)Br]CH_2Cl_2$	m	1117.4(3)		AgP_2Br	P	244.8(5,15)	P,P	141.6(2)	39
	$P2_1/n$	2432.3(9)	102.69		Br	268.1(2)	P,O	109.1(1,7.7)	
	4	1417.8(4)							

[a]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.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom/ligand is specified in these columns.

Table 2A Mean values of M(I)-L distances [pm] in mononuclear three-coordinated deriatives (Cu(I)-L[42] and Au(I)-L[43]; M[covalent radius]).

Coord. atom/ligand	Covalent radius [pm]	Cu(I)-L [pm] [1.38 pm]	Au(1)-L [pm] [1.43 pm]	Ag-L [pm] [1.53 pm]
LO	73	206.9(152,151)		241.7(182,83)
LN	75	199.2(48,33)		224.3
		205.8(74,22)[a]	228.6(120,120)[a]	227.3(76,110)[a]
Cl	99	223.2(106,103)	261.5(115,203)	
LS	102	224.5(31,90)	246.8	250.2(12,12)
LP	106	224.3(109,52)	237.3(161,58)	248.3(73,147)

The first number in parenthesis is maximum deviation from the shortest and the second one from the longest distance from the mean value.
[a]For bidentate ligands.

2.3. Coordination number four

Structural data for mononuclear silver compounds of coordination number four are summarized in Table 3. There are over seventy examples, with electronic configurations from d^{10} to d^8, the latter having only one example[75] and the former being by far the most common. Silver(I) prefers a tetrahedral environment, but silver(II) and silver(III) use the square planar arrangement as expected. The ligands range over uni-, bi-, tri- and tetradentate and various degrees of distortion are consequently observed, especially in the silver(I) derivatives. For the bidentate ligands there are different sizes of the metallo-ring causing variations in the bite angles. The effects of both electronic and steric factors can be seen in the variation of the L-Ag-L bond angles. For the four-membered metallocycles, the L-Ag-L bond angles range from 48° to 53° for O-donor ligands, and from 65° to 68° for S-donor ligands, reflecting the difference in covalent radius of oxygen (73 pm) and sulphur (102 pm). For the five-membered metallocycles, the L-Ag-L angles range from 72° to 77° for the N-donors, from 84° to 88° for the S-donors and around 84° for the P-donor ligands.

Comparison of the Ag-L bond distances (Table 3) shows several trends. The mean Ag-L bond distance increases with decreasing oxidation state of the silver. For example the mean Ag-L distance increases in the sequence: 216 pm (Ag(II)) < 232.6 pm (Ag(I)) for bidentate N donors; 240.7 pm (Ag(II)) < 273.5 pm (Ag(I)) for bidentate S-donors; and 197.9 pm (Ag(III)) < 214.4 pm (Ag II))< 240.7 pm (Ag(I))

for tetradentate N-donors. This reflects the ionic radius of the respective silver ions. When the ligand is unidentate, the mean Ag(I)-L distance increases in the sequence: 176 pm (H, 37 pm) < 230.8 pm (N, 75 pm) < 247.3 pm (O, 73 pm) < 253.3 pm (Cl, 99 pm) < 255.2 pm (S, 102 pm) < 256.1 pm (P, 106 pm) < 264.8 pm (Br, 114 pm) < 266.3 pm (As, 120 pm) < 277.5 pm (I, 133 pm). This reflects, except for N and O (see below), the trend in covalent radius of the coordinating atom.

Steric effects on the Ag(I)-P bond lengths can be seen clearly in the PPh_3 derivatives, representing the most common unidentate ligand in silver(I) chemistry. Table 3 contains examples of derivatives with one, two, three or four such ligands. The mean Ag(I)-P bond distances vary with the chromophore in the sequence: 239.2 pm ($AgPX_3$) < 246.8 pm (AgP_2X_2) < 255.5 pm (AgP_3X) < 264.9 pm (AgP_4). A similar trend is observed in the $AsPh_3$ derivatives: 262.2 pm ($AgAs_3X$) < 267.3 pm ($AgAs_4$). It is noted that the mean Cu(I)-P bond distance also varies in the same manner,[42] but are in general shorter than those of the silver derivatives: 222.9 pm ($CuPX_3$) < 226.5 pm (CuP_2X_2) < 233.2 pm (CuP_3X) < 246.1 pm (CuP_4).

Some other trends were found between the uni- and multidentate ligands. For example, the mean Ag-N distance increases with the dentate character of the N-donor ligands: 230.8 pm (uni-) < 232.6 pm (bi-) < 239.0 pm (tri-) < 240.7 pm (tetradentate). However, the opposite trend is observed for O-donor or C-donor ligands: 243.4 pm (O, bi-) < 247.3 pm (O, unidentate); 243 pm (C, tri-) < 250 pm (C, bidentate). A more random order is observed for S or P donors, for example: 255.0 pm (S, tetra-) < 255.2 pm (S, uni-) < 259.9 pm (S, tri-) < 273.5 pm (S, bidentate); 249.4 pm (P, bi-) < 253.1 pm (P, tri-) < 256.1 pm (P, unidentate).

The mean M(I)-L bond distances for the Group IB metals are shown in Table 3A. In general, the mean M(I)-L bond lengths increase with the covalent radius of both L and M, as well as with coordination number (see Tables 1A and 2A). The most common ligand found with the +1 metals of this subgroup is triphenylphosphine, and the most common coordination environment is tetrahedral. It should be noted that there is some degree of confusion regarding M-O bond distances. Some authors have considered an oxygen to be bonding when the M-O distance is over 270 pm, while others have cut off bonding at 260 pm. Considering the covalent radii of copper, silver and oxygen to be 138, 153 and 73 pm, respectively, it would seem appropriate to consider any distance over about 250 pm as something less than a full bonding interaction.

There are some derivatives, $Ag(PPh_3)_3I$[49,101] and $Ag(PPh_3)_2pyX$[120,121] which exist in two isomeric forms differing mostly by degree of distortion. In the former[49] the triclinic form has two crystallographically independent molecules present. In several other examples[61,72,93,110] two, or even three,[63] crystallographically independent molecules are present, again differing only by degree of distortion. There is one example which has been studied independently by two different groups, one in 1989[89] and the other in 1990,[87] with similar results.

2.4 Coordination number five

The mononuclear pentacoordinate silver compounds are presented in Table 4, the silver atom being only in the +1 oxidation state. The structures of these derivatives lie between the two limiting geometries of square pyramidal and trigonal bipyramidal. The conversion of one structure into the other requires only minor distortion. Both of the limiting geometries, with varying degrees of distortion, are

Table 3 Structural data for mononuclear silver compounds with coordination number Four[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	L-M-L [°]	Ref.
$[Ag^{I}(4\text{-}NO_2pyNO)_2(NO_3)$	m C2/*c* 8	2407.3(4) 529(1) 2339.6(4)	98.73(2)	AgO_4	O[b] $(NO_3)O$	234.1(3,23) 251.3(6,60)	48.1(2), 78.3(1) 120.0(1,2.3) 153.9(2)	60
$[Ag^{I}(NO_3)_2]$[c] $[Rh(py)_4Cl_2]$	or Pbcn 4	765.8(2) 2148.6(3) 1495.3(3)		AgO_4	O	224.8(3,0) 259.7(5,0)	52.7(1) 124.6(1,10.6) 169.3(2)	61
				AgO_4	O	231.3(7,0) 241.3(10,0)	54.7(1) 135.9(1,7.0) 150.8(1)	
$[Ag^{I}(py)_4]ClO_4$ (at 260 K)	tg $I\bar{4}$ 2	1247.1(3) — 689.4(2)		AgN_4	N	232.2(3,0)	110.2(2,2.1)	62
$[Ag^{I}(py)_4][Ag^{I}(py)_2]$ $(ClO_4)_2$	tg $I\bar{4}$ 4	2195(1) — 768.4(3)		AgN_4 AgN_2	N N	230(1,0) 216(1,1)	107.1(4,7.8) 173.7(4)	23
$[Ag^{I}(MeCN)_4]ClO_4$[d] (at 240 K)	or $Pn2_1a$ 2	2450(1) 2075.6(8) 856.7(3)		AgN_4 AgN_4 AgN_4	N N N	224(3,6) 228(2,7) 226(2,3)	109.4(10,4.7) 109.3(8,6.6) 109.4(9,6.7)	63
$[Ag^{II}(bpy)_2](NO_3)_2 \cdot H_2O$	m $P2_1/c$ 4	695.3(3) 2751.2(9) 1153.9(5)	103.25(5)	AgN_4	N	216(1,2)	105.4(4,8)	64
$[Ag^{I}(Me_4bpy)_2]BF_4$	or Pbcn 4	1673.7(2) 1370.3(2) 1191.6(2)		AgN_4	N	232.1(5,3)	72.1(2) 122.3(2,5) 140.5(2)	65
$[Ag^{I}(Br_2C_{16}H_{14}N_2)_2] \cdot (CF_3SO_3)$	m $P2_1/c$ 4	1449.1(3) 2100.5(7) 1367.7(3)	108.75(2)	AgN_4	N	233.3(8,16)	76.4(3,3) 128.2(3,7.8)	66
$[Ag^{I}\{Me_2C(pz)_2\}_2]$ ClO_4	tr $P\bar{1}$ 2	1329.2(2) 1162.5(1) 756.90(5)	94.764(6) 86.320(6) 102.183(6)	AgN_4	N	228.7(4,40) 243.2(4)	83.2(1,6) 109.8(1,5.8) 140.5(1,4.7)	67
$Ag^{II}(tpp)$	tr $P\bar{1}$ 1	637 1123 1247	100.5(1) 82.2(1) 113.(1)	AgN_4	N	not given		68
$Ag^{II}(tpp)$	tr $P\bar{1}$ 1	1050.3(2) 1248.5(2) 635.1(2)	97.72(1) 100.68(1) 97.15(1)	AgN_4	N	209.2(3,10)	89.9(1)	69
$\{Ag^{II}(tpp)_{0.54}\}(tpp)_{0.46}$	tg I4/m 2	1338.4(5) — 971.7(5)		AgN_4	N	206.3(5,0)	not given	70
$[Ag^{II}(Me_4tacd)](ClO_4)_2$	m $P2_1/n$ 2	926.53(7) 936.26(8) 1285.16(8)	90.740(5)	AgN_4	N	219.5(3,1)	94.2(1)	71
$[Ag^{II}(tacd)](ClO_4)_2$[c]	or Pbnm 4	1302.4(2) 1451.0(1) 959.4(1)		AgN_4 AgN_4	N N	219.2(11,0) 215.8(2,0)		72
$[Ag^{II}(Me_6tacd)](NO_3)_2$	m C2/c 4	1322.2(3) 1162.9(4) 1547.1(3)	111.87(2)	AgN_4	N	216.1(3,2)	90.0(1,4.6)	73
$[Ag^{II}(ml)](CF_3SO_3)$	tr $P\bar{1}$ 2	990.0(4) 1146.5(4) 1942.3(6)	106.10(3) 99.95(3) 90.38(3)	AgN_4	N	227.8(3,3) 253.6(3,19)	72.3(1) - 153.3(1)	74
$[Ag^{III}(C_6H_{16}N_{10})] \cdot (SO_4)(HSO_4) \cdot H_2O$	tr $P\bar{1}$ 2	864.5(5) 917.7(5) 1336.3(6)	104.2(2) 117.5(2) 99.4(2)	AgN_4	N	197.7(8,10)	90.0(4,3.6)	75

Table 3 *Continued*

$[Ag^{III}(C_6H_{16}N_{10})]$ $(ClO_4)_3$	tr $P\bar{1}$ 2	1155.6(5) 1145.2(5) 807.6(4)	107.96(4) 93.65(3) 103.77(4)	AgN_4	N	198(1,1)	not given	76
$[Ag](C_{24}H_{32})$	m $P2_1/c$?	1618.9(2) 981.4(1) 1670.4(2)	60.92(2)	AgC_4	C	250	90	77a
$[Ag^I(1,5\text{-}C_8H_{12})_2]BF_4$	or Pnma 4	1797.3(3) 1019.0(3) 920.1(2)		AgC_4	C	250(1,2)	not given	77b
$Ag^I(SH)(Et_2btu)_3$	m $P2_1/n$ 4	818.1(1) 2021.6(2) 2503.5(3)	98.21(1)	AgS_4	HS S	279.3(2) 205.2(2,39)	97.5(1,1.5) 115.0(1,6) 124.9(1)	78
$[Ag^I(C_{10}H_{18}OS_4)_4]$ $CF_3SO_3)$	or $P2_12_12_1$ 4	825.8(6) 1437.1(4) 1618.9(3)		AgS_4	S	261.7(2,44)	109.30(7,19.7)	79
$[Ag^I(S_8)_2]AsF_6$	m C2/c 4	1760.6(4) 786.6(2) 1547.6(3)	102.58(2)	AgS_4	S	277.2(3,29)	71.5–142.2(2)	80
$[Ag^I(S_4N_4H_4)_2]\cdot$ $ClO_4\cdot 1.5H_2O$	m $P2_1/c$ 4	1168.4(5) 1462.3(6) 1148.7(5)	105.39(54)	AgS_4	S	274.5(3,49)	64.0–150.2(1)	81
$[Ag^I(C_{12}H_{16}S_3)_2]$ (CF_3SO_3)	tr $P\bar{1}$ 2	1239.0(2) 1415.8(4) 929.0(4)	91.04(3) 109.64(2) 83.87(2)	AgS_4	S	247.6(3)[e1] 258.7(3,17)[e2]	84.9(1,3) 107.3(1)	82
$Ag^{II}(dtdc)_2$	tr $P\bar{1}$ 2	1257.4(4) 1034.8(3) 1026.5(5)	90.12(2) 90.65(2) 84.70(2)	AgS_4	S	255(2,5)	86.0–126.0(8)	83
$[Ag^I(C_{10}H_{20}S_6)]ClO_4$	or Pbca 8	984.2(2) 2574.8(4) 1521.7(2)		AgS_4	S	255.0(3,14)	87.7(1,9) 121.4(1,8.5)	84
$[Ag^I(PPh_3)_4ClO_4$	rh $R\bar{3}$ 2	1908.5(5)	43.90(1)	AgP_4	P	265.9(4,9)	109.4(2,1)	85
$[Ag^I(PPh_3)_4]NO_3$	trg $R\bar{3}$ 2	1907(2)	— 43.77(5)	AgP_4	P	265.7(4,14)	109.47(11,2)	57
$[Ag^I(PPh_3)_4]PF_6$	trg $R\bar{3}$ 6	1433.0(6) 1433.0(6) 5157(1)		AgP_4	P	265.7(2,18)	109.21(2)	86
$[Ag^I(PPh_3)_4]PF_6$	rh $R\bar{3}$ 2	1911.0(10)	44.04(3)	AgP_4	P	266.0(3,13)	109.47(9,28)	87a
$[Ag^I(PPh_3)_4]\cdot$ $[SnPh_2(NO_3)_2Cl]$	tr $P\bar{1}$ 2	2243(2) 1413(1) 1396(1)	90.59(5) 69.82(4) 64.58(8)	AgP_4	P	265.9(5,87)	109.5(2,3.6)	87b
$[Ag^I(adpo)_4]SbF_6$	tg P4/mcc	1619.2(2) —		AgP_4	P	261.2(1,0)	90.00(1)	88
(at 203K)	4	2385.6(2)						
$[Ag^I(dppe)_2]NO_3$	m $P2_1/n$ 4	1483.4(2) 1979.5(2) 1585.6(3)	93.09(1)	AgP_4	P	251.5(3,27)	84.2(1,4) 116.9(1,1.0) 129.2(1,4)	89
$[Ag^I(dppe)_2][SnPh_3$ $(NO_3)_2]$	tr $P\bar{1}$ 2	1747.5(8) 1032.7(5) 1775.8(7)	95.00(3) 77.43(2) 88.75(3)	AgP_4	P	247.3(2,10)	84.0(1,1) 123.4(1,5.6)	90
$[Ag^I(AsPh_3)_4]\cdot$ $[SnPh_2(NO_3)_3]$	tr $P\bar{1}$ 2	2257(2) 1422(1) 1407(1)	90.9(1) 69.9(1) 65.6(1)	$AgAs_4$	As	267.0(4,30)	109.4(3,4.9)	91
$[Ag^I(AsPh_3)_4]\cdot$ $[SnPh_2(NO_3)_2Cl]$	tr $P\bar{1}$ 2	2268(2) 1424(1) 1424(1)	90.66(6) 69.17(5) 64.36(4)	$AgAs_4$	As	267.6(3,22)	109.4(2,3.7)	91

Table 3 *Continued*

$[Ag^{I}(AsPh_3)_4]\cdot$	tr	2121.2(9)	95.91(3)	$AgAs_4$	As	267.4(2,26)		109.4(1,5.0)	92
$[Sn_2Ph_4(NO_3)_4(OH)_2]$	$P\bar{1}$	1453.2(6)	77.76(4)						
2MeCN	2	1330.4(5)	75.47(3)						
$Ag^{I}(C_9H_{21}N_3)(SCN)$[c]	or	949.7(5)		AgN_3S	N	240.4(9,9)	N,N[b]	74.3(3,8)	93
	Pcmn	1183.7(8)			S	236.0(4)	N,S	135.6(2,4.1)	
	8	2600(1)							
				AgN_3S	N	237.7(11,54)	N,N	74.5(4,3)	
					S	236.8(5)	N,S	135.3(3,4.2)	
$Ag^{I}(C_{30}H_{30})(CF_3SO_3)$	m	1869.6(1)		AgC_3O	C	243(1,5)			94
	$P2_1/n$	999.8(1)	93.37(1)		O	249(1)			
	4	1402.2(1)							
$[Ag^{I}(Metu)_3Cl$	or	1482.4(2)		AgS_3Cl	S	252.0(2,0)	S,S	111.65(5)	95
	Pmcn	852.4(1)				266.5(3)	S,Cl	85.69(7)	
	4	1267.1(1)			Cl	264.9(3)		114.47(6)	
$[Ag^{I}(C_6H_{12}S_3)Cl$	m	1414.4(2)		AgS_3Cl	S	260.5(1,13)	S,S	84.43(4,28)	96
	12/*a*	668.4(1)	91.65(1)		Cl	238.9(1)	S,Cl	128.9(1,7.2)	
	8	2227.7(2)							
$[Ag^{I}(tt(9)ob)(PPh_3)]$	m	817.04(8)		AgS_3P	S	257.3(1,27)	S,S	84.45(5,4)	97
ClO_4	$P2_1/c$	1623.9(1)	101.36(1)		P	238.2(1)		106.55(1)	
	4	2334.9(2)					S,P	123.87(5,6.1)	
$[Ag^{I}(\{(S)PPh_2\}_3C)$	m	1819.2(3)		AgS_3P	S	263.1(2,46)	S,S	100.4(1,2.0)	98
(PBu^{n}_3)	$P2_1/c$	1298.6(2)	109.42(1)		P	240.2(3)	S,P	117.2(1,8.4)	
	4	2119.4(5)							
$Ag^{I}(PPh_2Me)_3(BH_4)$	m	1276.7(6)		AgP_3H	P	248.2(2,36)	P,P	116.6(6,11.4)	99
	$P2_1/n$	1983.8(7)	97.19(4)		H	176(7)	P,H	85(5)	
	4	1466.1(6)						118(5)	
$Ag^{I}(PPh_3)_3(NO_3)$	m	1898.4(5)		AgP_3O	P	256.7(2,63)	P,P	115.6(5,3.6)	57
	$P2_1/n$	1371.0(3)	94.94		O	268.4(6)	P,O	83.7(1)	
	4	1790.0(4)						124.4(1)	
$Ag^{I}(PPh_3)_3Cl$	m	1022.1(1)		AgP_3Cl	P	254.3(1,23)	P,P	115.1(1,2.0)	100
	$P2_1/n$	3373.5(1)	89.78(1)		Cl	255.2(1)	P,Cl	103.0(1,6.4)	
	4	1337.4(3)							
$[Ag^{I}(PPh_3)_3Cl]$	tr	1365.4(4)	84.82(2)	AgP_3Cl	P	257.2(4,14)	P,P	114.3(1,1.4)	101
$2Me_2CO$	$P\bar{1}$	1405.9(4)	87.71(2)		Cl	253.3(4)	P,Cl	103.4(1,1.4)	
	2	1397.0(4)	75.68(2)						
$Ag^{I}(PPh_3)_3Br$	trg	1936.6(6)		AgP_3Br	P	253.6(6,13)	P,P	109.8(2,5)	101
	P3	—			Br	268.0(6)	P,Br	109.2(1,4)	
	3	1078.7(6)							
$Ag^{I}(PPh_3)_3I$	m	1899.3(8)		AgP_3I	P	255.9(2,15)	P,P	112.0(1,5.0)	101
	$P2_1/n$	1380.7(4)	96.11(4)			278.0(3)	P,I	106.7(6,2.3)	
	4	1778.1(8)			I	285.8(1)			
$Ag^{I}(PPh_3)_3I$[c]	tr	1409.7(5)	92.61(2)	AgP_3I	P	258.8(4,19)	P,P	113.1(1,1)	49
	$P\bar{1}$	1438.4(4)	91.85(2)		I	285.5(1)	P,I	105.3(1,1.6)	
	4	2341.3(7)	91.12(2)						
				AgP_3I	P	260.4(3,22)	P,P	112.7(1,1.9)	
					I	286.4(1)	P,I	106.0(1,3.0)	
Ag^{I}(triphos)I	or	2053.4(6)		AgP_3I	P	253.1(5,24)	P,P	89.0(2,2.2)	102
	$Pna2_1$	1036.3(3)			I	269.1(3)	P,I	125.7(1,10.2)	
	4	1772.4(4)							
$[Ag^{I}(AsPh_3)_3Cl]$	tr	1343.8(2)	95.45(2)	$AgAs_3Cl$	As	262.2(2,15)	As,As	112.9(8,1.1)	103
$0.5Me_2CO$	$P\bar{1}$	1405.5(3)	87.01(2)		Cl	251.8(5)	As,Cl	105.7(1,4.2)	
	2	1416.6(3)	103.92(1)						
$H[Ag^{I}(absg)_2]$	m	573(2)		AgO_2N_2	O	259.9(12,0)	O,N	88.1(1,1)	104
	$P2_1/n$	1216(1)	94.9(1)		N	228.0(12,0)			
	2	1394(3)							
$[Ag^{I}(fla)_2](NO_2)_2\cdot$	m	2176.4(11)		AgO_2N_2	O	260.0(9,0)	O,N	67.0(3)	105
$4H_2O$	C2/*c*	700.5(4)	107.57(2)		N	237.3(9,0)			
	8	1733.6(9)							

Table 3 *Continued*

$[Ag^{I}(fla)_2]\cdot$	m	2173.2(6)		AgO_2N_2	O	261.2(7,0)	O,N	67.8(2)	105
$(NO_2)_{1.1}(NO_3)_{0.9}\cdot 4H_2O$	C2/*c*	709.2(2)	107.63(1)		N	230.3(6,0)			
	8	1750.3(4)							
$[Ag^{II}(pydc)_2]2H_2O$	m	600.2(4)		AgO_2N_2	O	213	O,O	75.5	106
	$P2_1/n$	1068.2(7)	90.83(15)		N	212	O,N	75.1(-,2.9)	
	2	1284.2(8)							
$[Ag^{I}(OHqu)(OHquH)]py$	m	1087(1)		AgO_2N_2	O	247.8(5,27)	O,O	109.9(2)	107
	$P2_1/a$	1065(1)	92.6(2)		N	215.0(4,5)	N,N	167.7(2)	
	4	1670(1)					O,N	115.6(2,1.7)	
$[Ag^{I}(2\text{-}COOpy)\cdot$	m	1394.4(3)		AgO_2N_2	O	252.4(4,0)	O,O	79.9(2)	108
$(2\text{-}COOHpy)]H_2O$	C2/*c*	794.9(1)	125.70(1)		N	220.7(3,0)	N,N	166.3(2)	
	4	1428.7(3)					O,N	70.6(1)	
								121.0(2)	
$[Ag^{I}(otta)_2]AsF_6$	or	920.3(1)		AgO_2	O	251.7(7,0)		not given	109
	Pcca	1021.7(1)			N	230.1(6,0)			
	4	1483.6(1)							
$[Ag^{I}(rfl)]ClO_4\cdot 0.5H_2O^{c}$	m	1946.4(10)		AgO_2N_2	O	252.1(5,0)		not given	110
	C2	788.6(4)	107.34(2)		N	229.5(5,0)			
	4	1545.9(8)							
				AgO_2N_2	O	255.9(6,0)		not given	
					N	230.4(5,0)			
$Ag^{I}(PPh_3)_2(NO_3)]C_6H_6$	tr	1227.9(1)	102.51(1)	AgO_2P_2	O	251.8(2,55)	O,O	50.4(1)	111
	$P\bar{1}$	1626.0(1)	114.28(1)		P	242.6(1,10)	P,P	139.4(1)	
	2	1113.4(1)	101.79(1)				O,P	107.3(1,10.9)	
$Ag^{I}(PPh_3)_2(NO_3)$	tr	1177.2(3)	61.76(2)	AgO_2P_2					112
	$P\bar{1}$	1200.7(2)	62.77(2)						
	2	1415.7(3)	74.57(2)						
$Ag^{I}(PPh_3)_2(HCOO)$	m	2495.2(2)		AgO_2P_2					113
	Cc/*a*	917.9(1)	116.34(1)						
	4	1526.2(1)							
$[Ag^{I}(PPh_3)_2(MeCOO)$	tr	1006	92.0	AgO_2P_2					114
	$P\bar{1}$	2434	99.9						
	4	1383	89.7						
$Ag^{I}(tch)_2]NO_3$	m	1595.5(8)		AgN_2S_2	N	251(1,0)	N,N	98.7(4)	115
	C2/*c*	892.2(5)	98.7(1)		S	244.2(4,2)	S,S	153.1(1)	
	8	1717.1(8)					N,S	77.2(3)	
								124.0(3)	
$[Ag^{I}(C_{30}H_{38}N_4S_4)]\cdot$	m	1042.8(1)		AgN_2S_2	N	229.7(5,5)	N,N	113.3(2)	116
(CF_3COO)	$P2_1/n$	2314.5(5)	99.71(1)		S	258.6(2,0)	S,S	110.98(7)	
	4	1551.7(3)					N,S	108.4(1,10.0)	
$[Ag^{I}(tdoco)]NO_3$	or	1749.0(8)		AgN_2S_2					117
	Pbca	1506.8(7)							
	8	1384.7(6)							
$[Ag^{I}(PPh_3)_2(EtOCS_2)$	or	940.1(3)		AgS_2P_2	S	264.4(4,43)	S,S	68.0(1)	118
	$P2_12_12_1$	1869.1(4)			P	247.04(4,1)	P,P	115.6(1)	
	4	2011.4(3)					S,P	115.9(1,4.6)	
$Ag^{I}(PPh_3)_2(Bu^{t}SCS_2)$	tr	1057.1(1)	88.75(2)	AgS_2P_2					119
	$P\bar{1}$	1363.8(3)	72.84(1)						
	2	1439.1(3)	80.58(1)						
$Ag^{I}(PPh_3)_2(py)Cl$	m	981.4(3)		AgP_2NCl	P	247.2(2,0)	P,P	123.55(4)	120
	$P2_1/m$	2001.6(2)	97.60(3)		N	258.5(5)	P,N	101.20(6)	
	2	903.9(4)			Cl	251.1(2)	P,Cl	114.37(3)	
							N,Cl	95.0(1)	
$Ag^{I}(PPh_3)_2(py)Cl$	m	1964(1)		AgP_2NCl	P	247.67(2,2)	P,P	123.60(7)	121
	$P2_1/a$	2003(1)	97.66(6)		N	259.3(4)	P,N	105.4(1)	
	4	905.6(7)			Cl	251.7(2)	P,Cl	114.4(1,1.2)	
							N,Cl	94.6(1)	

Table 3 *Continued*

$Ag^{I}(PPh_3)_2(py)Br$	m	980.3(2)		AgP_2Br	P	247.6(1,0)	P,P	124.44(5)	120
	$P2_1/m$	2005.7(4)	97.31(2)		N	257.5(5)	P,N	102.10(6)	
2	2	915.5(2)			Br	262.9(1)	P,Br	112.86(3)	
							N,Br	96.8(1)	
$Ag^{I}(PPh_3)_2(py)Br$	m	1962(1)		AgP_2NBr	P	247.8(3,5)	P,P	124.4(1)	121
	$P2_1/a$	2007.2(9)	97.42(4)		N	257.2(7)	P,N	106.0(2)	
	4	916.6(5)			Br	263.6(2)	P,Br	112.9(1,2.2)	
							N,Br	96.2(2)	
$Ag^{I}(PPh_3)_2(2\text{-}SHpy)Cl$	m	1436.2(2)		AgP_2ClS	P	247.9(1,3)	P,P	123.0(0)	122
	$P2_1/c$	1030.2(1)	93.38(1)		Cl	259.5(1)	P,Cl	105.9(0,5.1)	
	4	2505.4(3)			S	262.5(1)	P,S	108.3(0,4.6)	
							Cl,S	104.2(0)	

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns. [c]There are two crystallographically independent molecules. [d]There are three crystallographically independent molecules. [e1]The unidentate ligand. [e2]The tridentate ligand.

Table 3A Mean values of M(I)-L distances in mononuclear four-coordinated derivatives (Cu(I)-L[42] and Au(I)-L[43] M[covalent radius])

Coord. atom/ligand	Covalent radius [pm]	Cu(I)-L [pm] [138 pm]	Au(I)-L [pm] [143 pm]	Ag(I)-L [pm] [153 pm]
LO	73	224.5(230,34)		247.3(155,211)
		217.0(164,170)[a]		243.4(186,163)[a]
LN	75	204.0(120,105)		230.8(285,68)
		202.9(119,481)[a]		232.6(79,106)[a]
		208.0(60,365)[b]		239.0(67,23)[b]
		205.5(118,177)[c]		240.7(129,148)[c]
LC	77	198.8(91,45)[a]		250(2,2)[a]
		206.0[b]		243(5,5)[b]
Cl	99	234.4(109,130)	271.0	253.3(144,116)
LS	102	234.0(150,64)	286.5(74,73)	255.2(192,241)
		233.9(88,118)[a]		273.5(134,66)[a]
		232.7(34,16)[b]		259.9(53,78)[b]
		230.3(54,56)[c]		255.0(14,14)[c]
LP	106	229.6(116,270)	246.3(73,139)	256.1(179,219)
		232.3(57,46)[a]		249.4(31,48)[a]
		229.4(20,48)[b]		253.1(24,23)[a]
Br	114	248.6(175,99)		264.8(19,32)
LAs	120	238.7(65,48)		266.3(41,37)
		235.7(24,14)[a]	247(11,10)[a]	
I	133	262.8(138,82)		277.5(84,83)

The first number in parenthesis is the maximum deviation from the shortest and the second from the longest distance from the mean value. [a]For bidentate ligands. [b]For tridentate ligands. [c]For tetradentate ligands.

observed. There are eleven purely coordination silver(I) compounds, with no CO or other C-donor ligands. Some of the others cannot be classified because the full data have not been published. In all these species, the coordination environment around the silver atom is built up by penta-dentate O[23–125] or N-donors.[126] There is an example where a near planar arrangement of the pentadentate N-donor ligand

is observed,[127] with the maximum deviation of a nitrogen from the AgN_5 plane being 36 pm. Trigonal-bipyramidal geometry occurs in several cases[128,129,132] with a high degree of distortion because the pentadentate ligands[128–129] and tetradentate ligands[132] span both equatorial and axial positions (Table 4). A distorted square pyramidal coordination around the Ag(I) atom is observed in other examples.[91,130,131] In the trigonal bipyramidal derivatives the Ag-N and Ag-S bond distances in the axial positions are longer than those in the equatorial plane.

Orthorhombic $Ag(C_{10}H_{22}N_2OS_2)(SCN)$ exists in two isomeric square pyramidal forms, both having the axial position occupied by the SCN group, with Ag-S distances of 253.9(2) pm[130] and 252.6(2) pm,[131] respectively, and the square plane is defined by the tetradentate ligand. The mean Ag(I)-L distances are again longer than those found in the comparable Cu(I) compounds.[42] For example, the mean M(I)-N distance is 245.5(85,95) pm for Ag(I) and 212.6(249,408) pm for Cu(I) when the ligand is a pentadentate N-donor, where the first number in parenthesis is the difference between the shortest and the mean values, and the second number between the longest and the mean. A similar trend can be observed for another pentadentate ligand, a 3N- and 2S-donor, giving mean M-L distances of 243.0(113,107) pm (L = N) and 263.0(75,83) pm (L = S) for Ag(I), and 230.0 (197,219) pm and 232.0(2,2) pm, respectively, for Cu(I).

2.5. Coordination numbers six and higher

Structural data for mononuclear silver compounds with coordination numbers six and higher are given in Table 5. Among the series of hexa-coordinated species there are examples in which the silver atom is in a distorted octahedral environment, sandwiched between two tridentate ligands.[93,96,136,138,141,143,144,149] There are two neutral complex species in which Ag(II) is found,[143,144] the remaining examples being cationic complexes of Ag(I) with anions normally considered too "hard" for the Ag(I) ion. Silver(I) atoms are found sitting in the cavity of a macrocyclic ligand, giving an octahedral arrangement of the six donor atoms of the macrocycle.[133–135,137–139,142,147,148,150–152] In one case the silver(I) atom is coordinated by five macrocyclic donor atoms and the N atom of acetonitrile from the solvent. There are both neutral and cationic complexes, the latter coexisting with non-coordinated "hard" anions.

The mean Ag-L distances in the tridentate ligand series increases with the covalent radius of the donor-atom, in the sequence: 267 pm (C, 77 pm) < 272.5 pm (S, 102 pm) < 293 pm (Se, 116 pm). However, in the hexadentate ligand series the order is: 256 pm (S, 102 pm) < 257.5 pm (N, 75 pm) < 260 pm (C, 77 pm) < 262 pm (O, 73 pm), which indicates the influence of the architecture of the macrocyclic ligand.

There are two examples in which the silver(I) atom is hepta-coordinated.[53] Unfortunately the data available at the time of writing was limited to those obtainable from Chemical Abstracts. It is surmised that the Ag(I) atom is in a capped octahedral environment with the AgO_7 chromophore, in which the cap is an oxygen atom of the unidentate NO_3 group, and the octahedron consists of the hexadentate crown O-donor atoms. A similar capped-octahedral environment about silver(I) is found in one other example.[94] Another two derivatives[154,155] have an octa-coordinated silver(I) atom, bonded to eight oxygen atoms in one case,[154] consisting of the two tetradentate ligands and resulting in a square antiprismatic structure with a Ag-O distance of 257 pm. In the other case[55] the coordination

Table 4 Structural data for mononuclear silver compounds with coordination number five[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	L-M-L	[°]	Ref.
Ag^{I}(qr)	or $P2_12_12_1$ 4	2001.1 1726.6 1333.0		AgO_5	O[b]	220 240–270	not given		123
Ag^{I}(peA)	or $P2_12_12_1$ 4	2376.2(4) 1459.1(2) 1208.0(2)		AgO_5	O 247	226 263(-,3)	not given		124
$[Ag^{I}(meB)]\cdot H_2O$	or $P2_12_12_1$ 4	1227.8(6) 1498.1(9) 2043.1(9)		AgO_5	O	not given			125
$[Ag^{I}(C_{17}H_{27}N_5)]$ ClO_4[c]	m $P2_1/c$ 8	1164.3(10) 1619.4(9) 2420.6(11)	117.70(9)	AgN_5 AgN_5	N N	239–251(3) 237–255(2)	not given not given		126
$[Ag^{I}(C_{25}H_{17}N_5)]$ PF_6	m A2/*a* ?	749.7(8) 2646.7(17) 1215.1(11)	104.5(1)	AgN_5	N	246.1(17,22) 131.9(6,1.1.)		66.5(6,1) 157.1(6)	127
$[Ag(C_{17}H_{25}N_3S_2)]$ BPh_4	m $P2_1/c$ 4	1313.2(11) 2500.1(12) 1247.9(12)	105.7(1)	AgN_3S_2	Ne Se N_a	231.7(9) 257.8(4,23) 248.9(10,48)	S,S[b] S,N_e S,N_a N_e,N_a N_a,N_a	85.8(1) 136.9(1,9.2) 107.2(3,20.2) 68.2(3,6) 135.5(3)	128
$[Ag^{I}(C_{20}H_{27}N_3S_2)]$ ClO_4	m $P2_1/n$ 4	1270.8(9) 948.3(7) 1956.9(13)	103.95(6)	AgN_3S_2	N_e S_e N_a S_a	238.0(6,13) 265.2(3) 252.2(6) 271.3(2)	N_e,N_e N_e,S_e N_e,N_a N_e,S_a S_e,N_a S_e,S_a N_a,S_a	123.6(2) 86.4,145.0(1) 74.6(2,1.2) 82.4,142.1(1) 100.8(1) 82.3(1) 145.0(1)	129
$[Ag^{I}(C_{10}H_{22}N_2OS_2)$ (SCN)]	or Pbca 8	2668.1(9) 853.3(5) 1433.2(8)		AgS_3N_2	N_e S_e NCS_a	249.4(7,41) 267.5(2) 285.5(2) 253.9(2)	N,N N,S_e S_e,S_e N,S_a S_e,S_a	73.9(2) 75.9(1,8) 136.2(1,7.6) 109.59(7) 119.2(1,2.0) 102.2(1,7.5)	130
$[Ag^{I}(C_{10}H_{22}N_2OS_2)$ SCN)]	or Pbca 16	1984.4(5) 1978.8(4) 1663.4(2)		AgS_3N_2	N_e S_e NCS_a	250.4(5,56) 270.5(2) 300.5(2) 252.6(2)	N,N N,S_e S_e,S_e N,S_a S_e,S_a	102.9(2) 74.2 130.1(1,5.2) 72.7(1) 114.0(1,5.3) 118.4(1,2.3)	131
$[Ag^{I}(AsPh_3)_3(NO_3)$	m $P2_1/n$ 4	1919.3(8) 1400.3(7) 1789.3(7)	96.4(1)	$AgAs_3O_2$	As O As,O	263.4(2,44) 257.5(15,32) 82.9–126.0(4)	As,As O,O	114.0(1,3.1) 43.8(4)	91
$[Ag^{I}(C_{20}H_{42}N_2S_2)\cdot$ $(MeCO_2)]\cdot 2H_2O$	tr $P\bar{1}$ 2	1081.8(2) 1266.2(2) 1045.7(1)	101.11(1) 103.23(1) 89.77(2)	AgN_2S_2O	S_e O_e N_a	258.9(1,0) 268.6(2) 245.5(2,2 6)	S,S S,O S,N O,N N,N	160.6(1) 99.7(1,1.7) 90.0(1,8) 90.0(1,3.9) 179.3(1)	132

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specific in these columns. [c]There are two crystallographically independent molecules.

sphere consists of a hexadentate C-donor liand and a bidentate NO_3 group with an O-Ag-O angle of 50° and Ag-O distance of 251.3(5,42) pm.

Finally, there is one example[156] in which two tetradentate C-donor ligands sandwich a Ag(I) atom and two additional positions are taken up by a bidentate NO_3 group, giving deca-coordination about the silver(I) atom (Table 5).

Table 5 Structural data for mononuclear silver compounds with coordination number six and higher[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore	M-L [pm]	L-M-L [°]	Ref.
$[Ag^{I}(C_{34}H_{59}O_{10})]$	or	1625.9		AgO_6	O[b] 240–300	not given	133
$0.5H_2O$	$P2_12_12_1$	2646.0					
	4	891.6					
$Ag^{I}(C_{44}H_{74}O_{14})$	m	1501.1		AgO_6	O 256(-,21)	not given	134
	$P2_1$	1340.2	111.3				
	2	1278.9					
$Ag^{I}(C_{47}H_{87}O_{14})$				AgO_6	O 260(-,22)	not given	135
$[Ag^{I}(C_9H_{21}N_3)_2]PF_6$	tg	1013.4(1)		AgN_6	N 254.3(10,0)	70,2(3,1.1)	93
	$P4_2/m$	—			260.7(7,0)	109.8(3,1.4)	
	2	1277.1(2)				180.0(5,0)	
$[Ag^{I}(C_{10}H_{10})_3]BF_4$	m	1244(2)		AgC_6	C 267(3,22)	not given	136
	$P2_1/c$	1018(2)	95.4(1)				
	4	1947(2)					
$[Ag^{I}(C_{24}H_{24})]ClO_4$	m	1870.0(8)		AgC_6	C 260(2,7)	not given	137
	Cc	633.1(6)	123.9(1)				
	4	1845.6(8)					
$[Ag^{I}(C_6H_{12}S_3)_2]$	or	788.4(2)		AgS_6	S 272.5(2,29)	80.0(1,7)	96,
(CF_3SO_3)	Pnam	1239.6(5)				100.0(1,7)	138
	4	2354.6(7)					
$[Ag^{I}(C_{12}H_{24}S_6)]PF_6$	m	529.5(4)		AgS_6	S 266.6(1,0)	78.9(1,1.5)	139
	I2/m	1395.9(10)	95.15(10)		278.1(1,0)		
	2	1395.1(9)					
$[Ag^{I}(C_6H_{12}S_3)_2]\cdot$	hx	1591(2)		AgS_6	S 272.5(5,28)	82.8(2,7.3)	140
$[Ag^{I}(C_6H_{12}S_3)]_3$	$P6_3$	—				116.0(2)	
$(ClO_4)_4$	2	1345.9(2)		AgS_4	see Table 10	159.7(2)	
$[Ag^{I}\{(SeCH_2)_3\}_2]$	m	2880(4)		$AgSe_6$	Se 293(1,15)	66.2-162.5(2)	141
AsF_6	C2/c	942(1)	137.4(1)				
	8	2240(4)					
$[Ag(C_{30}H_{35}N_2O_4)]\cdot$	m	1486.1(8)		AgO_5N	O 253(2,6)	O,O[b] 65.4-142.0(8)	142
$(ClO_4)_2\cdot 2CH_2Cl_2$	$P2_1$	1481.0(8)	101.86(5)		N 258(1)	O,N 69.1(4,1)	
	2	915.7(4)				132.3(9,3.8)	
$[Ag^{II}\{2,6\text{-}(CO_2)$	or	787.4(5)		AgO_4N_2	O 220(1,0)	O,O 97.6(5)	143
$(CO_2H)py\}_2]\cdot H_2O$	Pnna	1094.2(7)			253(1,0)	O,N 74.1(3,2.5)	
	4	1773.4(12)			N 215(2,6)		
$[Ag^{II}\{2,6\text{-}(CO_2)$	m	600.2(4)		AgO_4N_2	O 213.4(10)	O,N 78.1(3)	144
$(CO_2H)py\}_2]\cdot 2H_2O$	$P2_1/n$	1068.2(7)	90.83(10)		O 298		
	2	1284.2(8)			N 211.8(10)		
$[Ag^{I}(C_{30}H_{35}N_2O_4)$	m	1180.5(5)		AgO_4N_2	O 253(1,3)	O,O 65.8(3,1)	145
$(MeCN)]\cdot(ClO_4)_2$	$P2_1/a$	2677.0(18)	100.37(4)		N 272(1)	112.9(3,10.4)	
	4	1147.5(5)			MeCN 221(1)	N,N 105.0(4)	
						O,N 67.6(3,1)	
						121.2(4,22.0)	
$Ag^{I}(C_{16}H_{14}N_2)_2$	m	568.5(3)		AgO_4N_2			146
(NO_3)	$P2_1/c$	792.8(1)	94.90(2)				
	2	3050.2(5)					

Table 5 *Continued*

$Ag^{I}(C_{29}H_{37}NO_5)]$	or	1395		AgO_4C_2	O	230-280		not given	147
$(BF_4)\cdot 2Me_2CHOH$	$P2_12_12_1$	2748			C	not given			
	4	1006							
$[Ag^{I}(C_{12}H_{28}N_4S_2)]$	or	1085.9(22)		AgN_4S_2	N	257.1(11,18)	N,N	104.3(4)	148
PF_6	Pbca	2024.7(26)			S	265.8(5,0)		164.3(5)	
	4	974.2(10)					S,S	124.5(2)	
							N,S	75.9(3)	
								113.2(2)	
$[Ag(C_{14}H_{28}S_2)_2]$	m	1083.8(2)		AgC_4S_2	C	257.0(11,10)	C,C	30.7(3)	149
BF_4	C2/c	1172.0(2)	105.02(1)		S	250.4(3,0)	S,S	128.5(2)	
	4	1635.5(2)					C,S	78.9(3)	
								105.2(3)	
$[Ag(C_{14}H_{28}N_2S_4)]$	tg	1012.8(3)		AgS_4N_2	S	261.1(2,0)	S,S	87.0(1,6.0)	150
PF_6	$P4_12_12$	—				280.2(2,0)	N,N	73.7(1)	
	4	2171.1(4)			N	258.6(3,0)	S,N	74.0(1)	
								149.62(6)	
$[Ag^{I}(C_{12}H_{26}N_2S_4)]$	or	1673.3(2)		AgS_4N_2	S	269.7(4,77)	S,S	81.3(1,1)	151
PF_6	Pcab	1750.2(1)			N	253.3(10)		108.5(1,2.3)	
	8	1470.3(1)				281.7(15)		146.2(1,2.7)	
							S,N	73.1(3,2.9)	
								106.9(3,6.7)	
							N,N	172.9(4)	
$[Ag(C_{14}H_{30}N_2S_4)]$	m	1075.3(1)		AgS_4N_2	S	264.0(4,57)	S,S	82.3(1,1.4)	151
BPh_4	$P2_1/n$	1905.7(2)	106.04(1)			281.9(3)		96.7(1,8)	
	4	1893.6(2)			N	251.7(11)		169.2(1,2.3)	
						277.8(10)	S,N	73.8(3,1.6)	
								116.1(3)	
$[Ag^{I}(dttp)]BPh_4$	tr	1386.3(9)	109.0(1)	AgN_3S_3	N	241.0(8,12)	N,N	65.5(2,5.0)	152
	$P\bar{1}$	1096.5(11)	99.2(1)			261.3(9)		130.5(3)	
	2	1499.0(12)	65.0(1)		S	266.2(3,8)	S,S	81.9(1,6.0)	
						294.9(4)	N,S	73.4(2)-	
								156.1(2)	
$[Ag^{I}(C_{20}H_{24}O_6)$	m	1842.7(4)		AgO_7	O	270			153
$(NO_3)]\cdot$	$P2_1/n$	1407.9(2)	93.56(3)		O_2NO	250			
$0.5BuOH\cdot 0.5H_2O$	8	1847.1(3)							
$Ag^{I}(C_{25}H_{24})$	m	3742.6(3)		AgC_6O	C	259(1,19)		not given	94
(CF_3SO_3)	$P2_1/a$	1044.8(2)	90.3(1)		O	249(1)			
	16	2390.9(2)							
$[Ag^{I}([12]crown\text{-}4)_2]$	m	1047.1(3)		AgO_8	O	257		not given	154
AsF_6	C2	1153.9(3)	91.83(3)						
	2	980.1(3)							
$[Ag(C_{13}H_{20})(NO_3)$	m	1207.4(2)		AgC_6O_2	C	240.4(6,69)[c]	O,O	49.9(1)	155
	$P2_1/c$	807.1(2)	93.49(2)		O	251.3(5,42)		*c*	
	4	1422.9(4)							
$Ag^{I}(C_8H_8)_2(NO_3)$	m	1029.6(2)		AgC_8O_2	C	271.8(4,24)		d	156
	C2/c	975.2(1)	95.59(2)		O	251.8(3,0)			
	4	1512.2(4)							
Ag^{I}(pctt)	m	1618.9(2)							157*a*
	$P2_1/c$	981.4(1)	60.92(2)						
	4	1670.4(2)							
$[Ag^{I}(tbc)_2](CF_3SO_3)\cdot$	m	1536.9(3)		AgC_x	C	274(2,7)		not given	157*b*
$tbc\cdot 0.5C_6H_{14}$	$P2_1/n$	2817.7(5)	90.61(1)						
	4	2675.1(4)							

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specific in these columns. [c]The value of midpoint C=C bond; O-Ag-(C=C) = 97.5-148.1(2)° and (C=C)-Ag-(C=C) = 97.3(2,1.6) and 119.8(2)°. [d] (C-C)-Ag-(C-C) = 71.1, 100.2, 113.6 and 164.7°.

3. BINUCLEAR SILVER COMPOUNDS

3.1 Coordination number two

Structual data for these complexes are summarized in Table 6. The structures are arranged in order of increasing Ag-Ag distance. Bidentate ligands, each forming three-atom bridges, bring the two silver(I) atoms within 265.4(1) pm in the colourless derivative $[Ag\{2\text{-}(Me_3Si)_2C\}(py)]_2$[158] which is the shortest Ag(I)–Ag(I) distance observed in the series of binuclear silver compounds. The associated N-Ag-C angles are 174.5(1)°. This type of bridging is common to binuclear di-coordinated silver compounds, the exceptions being $[Ag(tolN_5tol)]_2$ (Table 6) and (costunolide) $AgNO_3$[171] where the silver(I) atoms are linked by the C atoms of costunolide.

Bidentate ligands and a silver oxidation state of +1 are the only features of these derivatives. The mean Ag-L bond distances are; 215.5(50,40) pm (L = N, 75 pm) < 217.6(7,7) pm (C, 77 pm) < 222.3(13,27) pm (O, 73 pm) < 238.3(3,3) pm (P, 106 pm); which largely follows the trend of covalent radius of the coordinated atom. The L-Ag-L bond angles are in the range 150° to 178°. The Ag(I)–Ag(I) distances range from 265.4(1) to 354(2) pm, compared to the corresponding Cu(I)–Cu(I) distances of 241.2 to 635.0 pm[42] and the Au(I)–Au(I) distances of 276.1 to 296.7 pm[43]

Two crystallographically independent molecules, differing mostly by degree of distortion and Ag–Ag distance are recorded.[164] The derivative $[Ag(C_8H_6N_2)]_2(ClO_4)_2$ has been independently studied by two groups[162,163] with comparable results.

3.2. Coordination number three

Structural data for these derivatives are listed in Table 7. Two of the derivatives[185,187] have one of the silver(I) atoms in a tetrahedral environment. The twenty-two derivatives are listed in order of increasing Ag–Ag distance.

In dark yellow $[Ag\{EtOC_6H_4)_2N_3\}(py)]_2$,[172] two triarsenido ligands bridge two Ag(I) atoms with each of their N atoms forming an eight-membered heterocycle Ag_2N_6, with a Ag–Ag distance of 272.6(1) pm. To each Ag(I) atom an additional pyridine ligand is coordinated, the Ag-N distance being 245.5(5) pm. The AgAg distance in this complex represents the shortest value found in the binuclear tri-coordinated silver(I) derivatives. This type of bridging is also found in other cases.[173–175,181,187]

In the $[Ag_2I_4]^{-2}$ anion[31,176] two iodine atoms serve as bridges between Ag(I) atoms. This type of bridging, involving two bridging ligands, is the most common in this series. Other halogens also serve as bridges, for example, two bromine atoms[179,180] and two chlorine atoms.[179,180] In two cases bridging is accomplished by a pair of sulphur atoms.[177,178] The Ag–Ag distances and angles are interrelated in the above examples. As the Ag–Ag distance increases, the Ag-L-Ag angle opens and the μL-Ag-μL angle closes. For example: 302.1 pm, 65.6° and 114.4°;[176] 355.7 pm, 79.0° and 101.0°;[31] 365.9 pm, 88° and 92°.[179] In the colourless crystals of $[Ag'(C_8H_6N_2)_2]_2(NO_3)_2$[163] each Ag(I) atom is trigonally surrounded by the N atoms of one unidentate and two bridging phtalarsine molecules to form a six-membered metallocycle Ag_2N_4 with a long Ag–Ag distance of 349.1(1) pm. In the remaining three examples[182,184,185] the Ag(I) atoms are each bridged in a unique fashion.

Table 6 Structural data for nuclear two-coordinate silver compounds[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm]	L-M-L [°]	Ref.
$[Ag^I\{2\text{-}C(SiMe_3)_2\cdot C_5H_4N\}]_2$	or Pcab 4	1631.8(9) 1611.5(10) 1203.3(6)		AgNC	N[b] C	216.0(5) 215.4(5)	265.4(1)	174.5(1)	158
$[Ag\{(Me_3SiN)_2CPh\}]_2$ (at 263 K)	tr $P\bar{1}$ 2	1132.5(5) 1221.4(6) 1407.9(8)	107.85(5) 106.63(4) 91.54(3)	AgN_2	N	212.4(2,6)	265.5(2)	170.2(1,1)	159
$[Ag^I(PhN_3Ph)]_2$	m C2/*c* 4	2602.3(7) 547.1(7) 1693.4(6)	118.13(2)	AgN_2	N	215.0(4,5)	266.86(1)	167.7(1)	160
$[Ag^I(C_{15}H_{15}N_2)]_2$	or Pnaa 4	703.97(8) 1368.9(2) 2903.9(3)		AgN_2	N	210.5(5,11)	270.5(1)	168.8(2)	161
$[Ag^I(C_8H_6N_2)]_2(ClO_4)_2$	m $P2_1/n$ 2	1601.7(7) 1042.7(4) 575.2(2)	99.90(3)	AgN_2	N	219.5(15,16)	274.8(2)	167.82(50)	162
$[Ag^I(C_8H_6N_2)]_2(ClO_4)_2$	m $P2_1/a$ 2	1611.4(3) 1046.2(2) 577.2(1)	100.77(2)	AgN_2	N	218.8(3,3)	275.6(1)	not given	163
$[Ag^I(C_{15}H_{21}OOO_2)]_2\cdot 2H_2O$[c]	m $P2_1/c$ 4	1576 1871 1839	103.1	AgO_2 AgO_2	O	225(2,5)	277.8(5) 283.4(5)	158(1)	164
$[Ag^I(PhCO_2)]_2$	or $P2_12_12_1$ 4	629.7(5) 898.7(6) 2377.1(15)		AgO_2	O	222(2,2)	290.2(3)	158.6(7,1.7)	165
$[Ag^I(pfb)]_2$	m C2 2	646(1) 901(2) 1311(4)	100.2(3)	AgO_2	μO	225(-,0)	290(2)	160	166
$[Ag^I(4\text{-}OHC_6H_4CO_2)]_2\cdot H_2O$	m $P2_1/a$ 2	611.3(7) 906.7(17) 1421.8(20)	103.74(9)	AgO_2	μO	221.0(8,4)	291.5(8)	157.9(7)	165
$[Ag^I(C_6F_5OCH_2CO_2)]_2$	m $P2_1/a$ 2	599.2(3) 3022(2) 527.7(2)	106.42(5)	AgO_2	O	221.7(3,14)	294.3(1)	161.6(2)	167
$[Ag^I\{CH(CO_2Et)_2PPh_2\}]_2$	tr $P\bar{1}$ 1	961.1(2) 1001.0(2) 1125.3(2)	83.74(2) 83.42(2) 69.99(2)	AgC_2	C	217.6(2,7)	295.3(1)	178.2(1)	168
$[Ag^I(CH_2PPh_2S)]_2$	m C2/*c* 4	2420(1) 906.7(4) 1210.1(6)	105.79(1)	AgCS	C S	218.3(9) 238.2(3)	299.0(2)	173.7(3)	169
$[Ag^I(tmpm)]_2(PF_6)_2$	or Pbca 4	1117(1) 1768(5) 1315(2)		AgP_2	P	238.3(4,3)	304.1(2)	174.3(2)	170
$[Ag^I(to\ lN_5tol)]_2$	m $P2_1/n$ 4	525.7(4) 1236.1(3) 2189.6(9)	90.88(5)	AgN_2	N	217.0(10,10)	354.17(2)	155.0(5,5.4)	160
$[Ag^I{}_2(gly)(glyH)]NO_3$	m $P2_1/c$ 2	504(1) 2802(3) 578(1)	93.83(1)	AgO_2	O	219		160	17

[a] 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.d., and the second is the maximum deviation from the mean. [b] The chemical idenity of the coordinated atom/ligand. [c] There are two crystallographically independent molecules.

Table 7 Structural data for binuclear three-coordinate silver compounds[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm] M-L-M [°] μL-M-μL [°]		L-M-L [°]	Ref.
$[Ag^I\{(EtOC_6H_4)_2N_3\}py]_2 \cdot (py)_2$	m $P2_1/n$ 2	1067.1(7) 1764.5(9) 1373.0(9)	 106.46(7) 	AgN_3	N^b (py)N	218.1(5,5) 245.5(5)	272.6(1)		107.(2,1) 158.5(2)	172
$[Ag^I(2\text{-}OHC_6H_4CO_2)]_2$	m $P2_1/c$ 2	740.3(1) 882.4(7) 1066.1(1)	 107.74(2) 	AgO_3		285.5(1)				173
$[Ag^I(2\text{-}OHC_6H_4CO_2)]_2$	m $P2_1/c$ 2	740.5(1) 882.6(2) 1068.3(2)	 107.48(4) 	AgO_3						174
$[Ag^I\{2,6\text{-}(OH)_2 \cdot C_6H_3CO_2\}]_2$	m $P2_1/n$ 2	732.2(1) 1030.7(2) 970.1(2)	 111.98(2) 	AgO_3						174
$[Ag^I(C_5H_6N_5)(ClO_4)]_2 \cdot (ClO_4)_2$	m $P2_1/c$ 4	1553.3(12) 735.6(6) 1301.9(8)	 117.43(5) 	AgN_2O	N O	217.5(10,20) 263.5(5)	300.2(4)	N,N[b] N,O	164.1(2) 84.7(2) 109.9(2)	175
$[Ag^I_2I_4] \cdot [Cu(C_{13}H_{14}N_2O)_2]$	tr $P\bar{1}$ 1	854.0(1) 1002.8(1) 1058.4(2)	110.22(1) 95.47(1) 93.42(1)	AgI_3	I μI	267.9(1) 279.0(1,10)	302.1(1) 65.6(1) 114.4(1)	I,μI	122.8(1,1.3)	176
$[Ag^I(tu)(SCN)]_2$	m C2/c 8	1107.2(3) 1383.8(4) 1398.3(4)	 111.65(3) 	AgS_3	NCS μS	260.8(2) 247.2(2,10)	309.7(1) 66.1(1) 122.2(1)	S,μS	116.3(1,8)	177
$[Ag^I(S_6)]_2(PPh_4)_2$	m $P2_1/c$ 2	1093.8(4) 1397.7(5) 1701.7(6)	 105.11(3) 	AgS_3	S μS	241.5(2) 250.0(2) 269.3(2)	344.2(1) 82.9(1) 97.1(1)	S,μS	114.6(1) 148.1(1)	178
$[Ag^I(C_8H_6N_2)_2]_2(NO_3)_2$	m $P2_1/a$ 2	1360.3(2) 1596.1(2) 732.8(1)	 99.10(2) 	AgN_3	N	226.3(5,14) 233.2(4)	349.1(1)	N,N	124.1(2)	163
$[Ag^I_2Br_4](PPh_4)_2$	m $P2_1/n$ 2	1454.6(4) 807.2(2) 1985.4(5)	 102.73(2) 	$AgBr_3$	Br μBr	248.1(1) 261.4(1) 274.(1)	354.9(2) 82.96(3) 97.04(3)	Br,μBr	123.69(4) 139.16(4)	179
$[K(crypt\text{-}2,2,2)]_2 \cdot [Ag^I_2I_4]$	tr $P\bar{1}$ 1	1133.0(2) 1236.5(2) 1034.3(2)	103.49(1) 101.72(2) 86.66(1)	AgI_3	I μI	267.2(2) 279.5(1,6)	355.7(2) 79.02(3) 100.98(3)	I,μI	129.2(1,1.6)	31
$(PPh_4)_2[Ag^I_2Br_4]$	m $P2_1/n$ 2	1452.5(9) 791.4(3) 2001.0(10)	 103.16(5) 	$AgBr_3$	Br μBr	249.1(1) 261.7(1) 275.2(2)	357.8(2) 83.53(4) 96.47(4)	Br,μBr	122.99(4) 140.38(3)	180

Table 7 *Continued*

$(PPh_4)_2[Ag^I{}_2Cl_4]$	m	1419.0(9)		$AgCl_3$	Cl	235.8(2)	365.7(2)	Cl,μCl	118.74(5)	180
	$P2_1/n$	806.2(3)	101.64(4)		μCl	244.7(1)	88.27(5)		149.53(5)	
	2	1917.7(10)				279.2(2)	91.73(5)			
$(AsPh_4)_2[Ag^I{}_2Cl_4]$	m	1428.0(6)		$AgCl_3$	Cl	235.9(2)	365.9(2)	Cl,μCl	118.91(6)	179
	$P2_1/n$	820.0(4)	101.19(3)		μCl	244.6(2)	87.97(6)		149.06(6)	
	2	1911.8(8)				280.9(2)	92.03(6)			
$[Ag^I(CF_3CN_5S_3)_2]_2\cdot$	tr	747.8(8)	99.98(2)	AgN_3	N	225.2(5,29)		N,N	105.6(1,11.2)	181
$(AsF_6)_2$	$P\bar{1}$	985.9(7)	90.75(2)			249.7(4)			148.1(2)	
	1	1440.5(8)	99.70(3)							
$[Ag^I(Ph_2S_2)_2]_2$	tr	1090.2(4)	112.82(4)	AgS_3	S	253.4(2)		S,μS	94.1(2)	182
$(AsF_6)_2$	$P\bar{1}$	1097.6(6)	92.43(2)		μS	257.1(2,68)			138.4(2)	
	1	1330.8(7)	107.69(3)				119.8(2)			
$[Ag^I\{\mu\text{-}(PhPH_2)\}\cdot$	tr	919.0(4)	97.48(3)	AgP_3	P	244.3(4)		P,μP	122.8(2,9.2)	183
$(PhPH_2)]_2(AsF_6)_2$	$P\bar{1}$	1109.8(4)	107.25(3)		μP	246.8(3,23)				
	1	1316.4(5)	102.71(3)				114.5(2)			
$[Ag^I(Ph_2Se_2)]_2(AsF_6)_2$	tr	1067.6(3)	66.40(2)	$AgSe_3$	Se	261.6(2)		Se,μSe	94.3(2)	182
	$P\bar{1}$	1125.3(3)	89.67(2)		μSe	258.0(2)			138.3(2)	
	1	1362.5(4)	71.40(2)			271.1(2)	119.8(2)			
$[Ag^I{}_2(C_{24}H_{32}N_4O_2S_2)\cdot$	m	2794.1(16)		AgN_2O	N	222(4,5)		N,N	163.5(15)	184
$(H_2O)_2](ClO_4)_2$	C2/c	861.2(6)	102.92(5)		H_2O	272(7)		N,O	96.7(2,3.0)	
	4	1535.9(9)								
$[Ag^I{}_2\{S_2C_2(CN)_2\}\cdot(PPh_3)_4]$	m	1228.9(8)		AgP_2S	P	248.4(7,21)	439.2	P,P	123.1(2)	185
	$P2_1/c$	2383.3(9)	101.32(4)		μS	247.8(7)	117.7(2)	P,S	118.4(2,9,8)	
	4	2317.9(11)					82.2(2)			
				AgS_2P_2	P	250.7(7,39)		P,P	119.1(2)	
					S	256.8(7)	P,S	111.4(2,5.0)		
					μS	265.3(7)	S,μS	102.3(2)		
$[Ag^I{}_2(pp)_2F]BF_4$	tr	1255.5(2)	97.97(1)	AgP_2F	P	243.3(6,44)	500.9(1)	P,P	144.2(2,7)	186
	$P\bar{1}$	1332.2(2)	109.31(2)		μF	254.9(9,1)	158.6(5)	P,F	107.2(3,8.9)	
	1	1394.9(3)	117.32(1)							
$[Ag^I(C_9H_8)(ClO_4)]_2(ClO_4)$	or	1539.0(2)		AgC_2O	C	247(2,0)		C,C	128.0(1.2)	187
	Pbnm	852.5(1)			O	246(2)		C,O	116.0(1.4)	
	8	1521.3(1)								
				AgC_4	C	241(2,5)		C,C	99.2(9)	
									162.2(1.0)	

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns.

From Table 7 it can be seen that silver occurs only in the oxidation state of +1, but the ligands involved are uni-, bi-, tri- and tetradentate.

In general, the mean Ag-L(terminal) distances are shorter than the Ag-L(bridge) distances. For example, in the series where L is halogen they both follow the trend of the covalent radius of the halogen, the values being 235 pm (Cl) < 248.6 pm (Br) < 267.6 pm (I), and 262.4 pm (Cl, 99 pm) < 267.6 pm (Br, 114 pm) < 279.3 pm (I, 133 pm), for terminal and bridging, respectively.

The derivative $(PPh_4)_2[Ag_2Br_4]$ exists in two isomeric forms[179,180] which are distortion isomers of each other.

3.3. Coordination number four

Structural data for over fifty binuclear silver(I) compounds with coordination number four are summarized in Table 8. Some examples[214,223,229] contain two silver(I) atoms of higher coordination number, which are cross listed with the appropriate table. Two of the examples[230,231] are organometallic compounds.

There are several types of bridging, with the distorted edge-shared bis-tetrahedral structure being the most common. The crystal structure of $[Ag(tu)_3]_2(ClO_4)_2$[188] has two bridging S-atoms of thiourea molecules bringing the silver(I) atoms to within 284.5(1) pm, and Ag-S-Ag angles of 64.3(1)°. This is the shortest Ag(I)–Ag(I) distance found in this series of compounds. In another five examples[194,203,206,208,214] two sulphur ligands also serve as bridges. In three examples the bridges involve two oxygen ligands.[212,213,216] A pair of halogen atoms also serve as bridges in several cases, for example, chlorine,[195,196,204,207,209,210] bromine,[195,197,205] and iodine.[121,194,195,211] In this series there are relationships between the Ag–Ag distance, the Ag-L-Ag angles and the μL-Ag-μL angles similar to those found in the binuclear tri-coordinate species of the previous section. The Ag–Ag distance increases as the Ag-L-Ag angle opens and the μL-Ag-μL angle closes. For example, in the sulphur-bridged cases the values are; 284.5 pm, 64.3° and 112°,[188] 307.6 pm, 70.5° and 109.5°,[94] 344.1 pm, 80.3° and 99.7°;[203] 373.8 pm, 89.2° and 90.8°.[206] For the chlorine bridges the values are; 307.4 pm, 71.2° and 98.1°,[196] 350.7 pm, 84.2° and 95.8°,[195] 375.0 pm, 90.9° and 89.4°[207] In the bromine-bridged examples the values are 308.0 pm, 68.5° and 111.6°,[197] 349.8 pm, 80.1° and 99.8°.[195]

A second type of bridging involves two bidentate ligands serving as tri-atom bridges, to give an eight-membered metallocycle $Ag_2O_4C_2$,[189,190] $Ag_2S_4C_2$[193] $Ag_2P_4C_2$[198] $Ag_2O_2N_2C_2$[202] and $Ag_2N_2S_2C_2$.[220] In one case,[189] two carboxylate groups of β-alaninate moieties bring the silver(I) atoms to within 285.5(4) pm, with μO-Ag-μO angles of 161.6(8)°. This is the shortest Ag–Ag distance found in this series.

In a third type, the bridging consists of two bidentate ligands forming a ten-membered heterocycle $Ag_2N_4C_4$[192] and $Ag_2P_4C_4$.[221] A twelve-membered heterocyclic ring is also found with the chromophores $Ag_2N_4C_6$[191,224] and $Ag_2P_4C_6$[225] and $Ag_2S_4C_6$[79] and in one case a sixteen-membered heterocycle is found.[191]

There are some examples where single bidentate ligands serve as a bridge, for example, Ag-P-P-Ag,[218] Ag-S-C-Ag[223] and Ag-P-C-C-P-Ag.[222] There is one example where two silver(I) atoms are bridged by a single chlorine atom and by the two bis(diphenylphosphino)methane ligands in a syn-syn arrangement.

The data in Table 8 indicate silver atoms in only the +1 oxidation state. The ligands range over uni-, bi-, tri-, tetra- and octadentate. In the series of uni- and bidentate ligands the mean Ag-L distances increase in the sequence: 235.9 pm (uni-) and 233.4 pm (bi-, N) < 245.0 pm (uni-) and 245.2 pm (bi-, P) < 250.5 pm (uni-) and 250.8 pm (bi-, O) < 253.9 pm (unidentate) and 252.5 pm (bidentate, S). In the series of N multidentate ligands, the mean Ag-N distance increases in the sequence: 233.4 pm (bi-) < 235.9 pm (uni-) < 236.7 pm (tetra-) < 239.2 pm (octadentate). The mean Ag–L(bridge) distances increase in the order: 250.0 pm (LO) < 265.0 pm (Cl) < 273.2 pm (Br) < 274.2 pm (LS) < 286.5 pm (I). Thus for singly-bridging atoms the bond distances follow the order of covalent radii of the respective atoms, 99 pm (Cl) < 114 pm (Br) < 133 pm (I). However, this does not follow for the O- and S-donor ligands suggesting that steric hindrance of the rest of the ligand is a factor in these bridge distances. Steric effects can also be seen in the series of triphenylphosphine adducts, this molecule being the most common unidentate ligand in this series of silver(I) derivatives. For the AgP_2X_2 derivatives, the mean Ag–P distance of 248.1(33,65) pm is about 6.5 pm longer than those found in the $AgPX_3$ derivatives at 241.6(24,29) pm).

There are hetero-, bi-, tri- and tetradentate ligands, with O plus N atoms and N plus S atoms in the first case, two O atoms plus one N atom in the second case, two O plus two S atoms and two N plus two S atoms in the third case. The mean Ag–L distances increase with covalent radius of the coordinated atom. The shortest Ag(I)–Ag(I) distance of 284.5(1) pm found in the binuclear tetrahedrally-coordinated derivatives is longer than either of those found previously in the digonally and trigonally-coordinated Ag(I) derivatives, at 272.6(1) pm and 265.4(1) pm, respectively. These shortest Ag(I)–Ag(I) distances are themselves longer than the corresponding values in the Cu(I) derivatives,[42] which are 241.2(1) pm (digonal), 243.3(1) pm (trigonal) and 237.1(1) pm (tetrahedral). This corresponds with the relative values of the covalent radii of the metal atoms at 138 pm (Cu) and 153 pm (Ag). It is also noted that while the Ag–Ag distance increases with coordination number, this is not the case for Cu(I)–Cu(I) distances.

The compound $[Ag(PPh_3)(py)I]$[195] exists in two isomeric forms differing by degree of distortion. There is one example, $[Ag(dppm)(NO_3)]_2$ which was independently studied by two groups,[198,199] however the latter information was only obtainable from Chemical Abstracts[199] and a full comparison was not possible.

3.4 Coordination numbers five and higher

Structural data for binuclear silver compounds with coordination numbers five, six and seven are given in Table 9. In $[Ag(glyH)(NO_3)]_2$ two silver(I) atoms are bridged by the carboxylate oxygens of the glycine molecules in a syn-syn arrangement, bringing the Ag(I) atoms to within 287.7(6) pm with μO-Ag-μO angles of 163.1(7)°. This represents the shortest metal–metal distance observed in this series and is about 3.2 pm longer than the shortest values found in tetrahedrally-coordinated binuclear derivatives (Table 8). In other examples, two nitrogen atoms of a macrocyclic ligand,[191] two sulphur ligands,[234] and two oxygen ligands[91,235] serve as bridges. There are eight examples in which both silver atoms are penta-coordinate, and two examples[191,233] in which one of the silver atoms is hexa-coordinate. There are four examples[239–242] with both silver atoms hexa-coordinated, and one derivative containing hepta-coordinate silver(I).[243] In an example with a

Table 8 Structural data for binuclear tetra-coordinated silver compounds[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm] M-L-M υL-M-μL [°]		L-M-L [°]	Ref.
$[Ag^{I}(tu)_3]_2(ClO_4)_2$	m	1953.7(8)		AgS_4	S^b	254.7(2,23)	284.5(1)	S,S^b	115.9(1)	188
	C2/*c*	1343.6(6)	103.57(5)		μS	267.4(2,11)	64.3(1)	S,μS	107(1,6.5)	
	8	1079.1(5)					112.3(1)			
$[Ag^{I}(\beta\text{-ala})(NO_3)]_2$	m	665.6(5)		AgO_4	O_2NO	258(3,1)	285.5(4)		not given	189
	$P2_1/n$	828.0(5)	94.90(3)		O	220.4(19,6)	—			
	2	1297.5(4)					161.6(8)			
$[Ag^{I}(pfc)(H_2O)]_2 \cdot 2H_2O$	tr	871.46(9)	69.17(1)	AgO_3N	H_2O	245.4(4)	290.1(1)	O,N	93.0(2)	190
	$P\bar{1}$	988.5(1)	67.54(1)		O	230.7(3,22)	—	O,μO	95.4(1,9.5)	
	2	1381.2(2)	84.69(1)		N	243.1(3)	140.8(2)	N,μO	108.1(2,10.7)	
$[Ag^{I}_2(C_{36}H_{57}N_8)](ClO_4)_2 \cdot 0.5H_2O$	tr	1417.1(14)	99.20(12)	AgN_4	N	234.9(8,27)	290.7(4)		65.7-	191
	$P\bar{1}$	1832.3(16)	120.13(11)			248.1(9,68)			150.0(4)	
	2	1249.5(23)	116.35(7)							
$[Ag^{I}(tch)]_2(CF_3SO_3)_2$	m	1726(1)		AgN_2S_2	N	215.6(10,6)	290.9(1)	N,N	169.1(4,1)	192
	$P2_1/n$	1508(2)	106.15(4)		S	295.5(4,40)		S,S	82.1(1,1.3)	
	4	1996.0(17)						N,S	77.0-	
									115.6(3)	
$[Ag^{I}(\mu\text{-}Et_3PCS_2) \cdot (Et_3PCS_2)](ClO_4)_2$	tr	1337.8(8)	80.38(4)	AgS_4	S	248.1(2,13)	291.4(4)		65.5(1)	193
	$P\bar{1}$	1356.2(8)	85.60(4)		S	266.8(2)			107.0(1,7.9)	
	1	761.7(5)	67.44(4)			281.2(2)			136.5(1)	
$[Ag^{I}(PPh_3)(py)I]_2$	m	2714.5(6)		AgI_2NP	N	233.5(7)	295.6(1)	I,N	99.6(2,4)	121
	C2/*c*	1454.8(3)	94.83(2)		P	243.8(2)	62.2(3,3)	I,P	110.8(1,9)	
	4	1131.6(4)			μI	286.4(1,13)	117.83(3)	N,P	117.6(2)	
$[Ag^{I}(tsc)_2I]_2$	m	1288.6(3)		AgS_2I_2	S	259.0(2,20)	295.9(2)		not given	194
	C2/*c*	868.7(1)	105.36(3)		μI	285.4(1,36)	62.43(3)			
	4	2000.6(16)					117.6(1)			
$[Ag^{I}(PPh_3)(py)I]_2$	m	1133.3(7)		AgI_2NP	N	233.8(6)	295.9(2)	I,N	99.6(1)	195
	C2/m	1456.9(6)	108.47(4)		P	244.5(2)	62.09(3)	I,P	110.83(3)	
	4	1427.9(5)			μI	286.9(1,0)	117.91(4)	N,P	117.6(2)	
$[Ag^{I}_2(dpph)_3Cl_2]$	m	1459.9(3)		$AgCl_2P_2$	P	234.2(3,10)	307.4(2)	P,P	125.4(1)	196
	$P2_1/c$	1838.8(5)	125.12(1)		μCl	266.0(6,42)	71.2(1,4)	P,Cl	107.4(1,5.3)	
	4	2113.4(4)					98.1(1)			
				$AgCl_2NP$	P	243.6(4)		N,P	126.7(2)	
					N	245.1(9)		N,Cl	106.7(2,9.6)	
					μCl	262.0(7,19)		P,Cl	100.2(1)	

Table 8 *Continued*

$[Ag^{I}(tsc)_3]_2Cl_2$	tr	972.8(3)	97.20(1)	AgS_4	S	256.3(2,25)	307.6(1)	not given		194
	$P\bar{1}$	1255.8(3)	102.07(8)		μS	252.7(2)	70.5(1)			
	1	653.9(1)	69.56(2)			278.8(3)	109.5(1)			
$[Ag^{I}(2\text{-Mepy})_2Br]_2$	tr	987.0(8)	109.67(7)	AgN_2Br_2	N	234(2,2)	308.0(5)	N,N	117.4(5)	197
	$P\bar{1}$	924.9(9)	118.38(5)		μBr	273.8(4,3)	68.45(8)	N,Br	107.1(4,7.3)	
	2	918.5(8)	93.23(7)				111.55(8)			
$[Ag^{I}(dppm)(NO_3)]_2$	m	1268.7(4)		AgO_2P_2	O	241.6(5)	308.5(1)	O,O	48.9(2)	198
	C2/*c*	1699.7(3)	100.73(3)			268.9(6)		P,P	138.3(1)	
	4	2262.7(6)			P	242.6(2,10)		O,P	106.7(1,12.6)	
$[Ag^{I}(dppm)(NO_3)]_2$	m	1270.4(1)		AgO_2P_2			308.9			199
	C2	1702.8(2)	100.66(1)							
	4	2263.4(2)								
$[Ag^{I}(C_{19}H_{17}N_7Cl)]_2\cdot(PF_6)_2$	m	2385.4(3)		AgN_4	N	232.2(5,2)	314.1(1)	N,N	70.1(1,1)	200
	C2/*c*	1308.3(1)	98.36(1)			237.1(5)			124.4(1,15.9)	
	8	1550.5(2)				242.8(4)			153.4(1)	
$[Ag^{I}(pch)]_2(CF_3SO_3)_2$	m	1041.2(2)		AgN_4	N	224.6(12,6)	325.4(2)	N,N	116.0(4,1)	201
	$P2_1/c$	3331.0(8)	105.38(2)			243.8(11,17)			146.9(4,2.6)	
	4	1319.7(2)								
$[Ag^{I}(PPh_3)(py)I]_2$	m	1117.6(2)		AgI_2NP	N	241(1)	334.3(2)	I,N	101.5(4,1.4)	195
	$P2_1/c$	1728.5(1)	121.75(1)		P	244.0(6)	71.96(5)	I,P	115.3(1,7.0)	
	2	1634.9(3)			μI	284.4(2,30)	108.04(7)	N,P	113.2(4)	
$[Ag^{I}(Mecyt)(NO_3)]_2$	tr	1047.4(3)	97.33(2)	AgO_3N	N	222.5(2)	337.0(1)			202
	$P\bar{1}$	1114.1(3)	95.82(2)		O	241.8(3,51)	95.1(1)			
	2	364.2(1)	76.76(2)		O_2NO	256.4(2)				
$[Ag^{I}{}_2\{(EtO)_2PS_2\}(PPh_3)_2]$	m	1496.5(13)		AgS_3P	P	240.4(2)	344.1(1)	S,μS	83.7(1,10.0)	203
	$P2_1/c$	975.3(8)	119.0(1)		S	281.0(2)	80.29(5)	S,P	109.66(6)	
	2	1843.8(12)			μS	250.2(2)	99.71(6)	μS,P	128.5(1,14.2)	
						282.1(2)				
$[Ag^{I}(PPh_3)(py)Br]_2$	m	1115.4(2)		$AgBr_2NP$	N	239.1(5)	349.8(1)	Br,N	99.3(1,1.1)	195
	$P2_1/c$	1676.4(2)	122.45(1)		P	241.4(2)	80.14(2)	Br,P	119.6(1,4.2)	
	2	1655.0(2)			μBr	271.7(1,16)	99.86(3)	N,P	114.9(2)	
$[Ag^{I}(PPh_3)(py)Cl]_2$	m	1118.4(1)		$AgCl_2NP$	N	240.3(4)	350.7(1)	Cl,N	97.4(1,1.5)	195
	$P2_1/c$	1649.8(3)	122.87(1)		P	240.0(2)	84.18(4)	Cl,P	122.7(1,9)	
	2	1660.6(3)			μCl	261.7(2,2)	95.82(5)	N,P	115.2(1)	
$[Ag^{I}\{(Ph_2PC_2H_4)_2S\}Cl]_2$	tr	1156.0(4)	95.61(3)	$AgCl_2P_2$	P	247.1(4,11)	370.8(3)	P,P	117.7(1)	204
	$P\bar{1}$	1006.3(2)	101.98(4)		μCl	265.0(4,7)	88.8(1)	P,Cl	111.4(1,7.7)	
	1	1204.5(6)	93.24(3)				91.2(1)			
$[Ag^{I}\{(Ph_2PC_2H_4)_2S\}Br]_2$	tr	1163.1(3)	95.50(3)	AgP_2Br_2						204
	$P\bar{1}$	1007.3(7)	102.06(4)							
	1	1216.3(7)	93.77(5)							

Table 8 *Continued*

$[Ag^{I}(PPh_3)_2Br]_2 \cdot CHCl_3$	m	1431.1(2)		AgP_2Br_2	P	249.6(7,17)	372.0		not given	205
	l2/m	1762.4(3)	96.56(1)		μBr	274.2(3,0)	not given			
	2	1496.1(3)								
$[Ag^{I}(p\text{-tolylCS}_2)(PPh_3)]_2$	tr_	1174.4(3)	106.90(2)	AgS_3P	P	239.2(2)	373.8(2)	S,μS	67.2(1)	206
	P$\bar{1}$	1086.2(2)	96.51(2)		S	265.7(2)	89.2(1)		94.3(1)	
	1	983.1(2)	74.54(2)		μS	266.2(3,31)	90.8(1)	S,P	127.6(1)	
								μS,P	129.9(1,6.3)	
$[Ag^{I}(dbp)_2Cl]_2$	tr_	1083.1(3)	82.73(2)	$AgCl_2P_2$	P	251.5(4,11)	375.0(2)	P,P	111.5(1)	207
	P$\bar{1}$	1168.3(3)	89.39(2)		μCl	263.9(4,5)	90.5(1)	Cl,P	105.6(1,3.0)	
	1	1124.3(3)	78.01(2)				89.4(1)		122.0(1,5)	
$[Ag^{I}(Ettu)_2(SCN)]_2$	tr_	894.6(1)	109.73(1)	AgS_4	S	247.8(2)	379.0(2)	S,S	118.6(2)	208
	P$\bar{1}$	576.9(1)	96.51(2)		NCS	261.8(3)	84.6(1)	S,μS	77.5-	
	2	1253.4(5)	76.78(1)		μS	261.8(2)	95.4(1)		120.7(2)	
						310.5(2)				
$[Ag^{I}(dppp)Cl]_2$	m	1342.8(1)		$AgCl_2P_2$	P	248.9(4,17)	381.2(1)	P,P	126.5(1,2.1)	209
	$P2_1/n$	3326.3(4)	99.30(1)		μCl	268.1(3,37)	90.7(1,5)	P,Cl	109.2(1,17.4)	
	4	1241.4(1)					89.3(1,4)			
$[Ag^{I}(PPh_3)_2Cl]_2$	tr_	1030.8(5)	113.36(4)	$AgCl_2P_2$	P	247.0(2,3)	384.0(2)	P,P	122.91(7)	210
	P$\bar{1}$	1260.8(4)	110.29(3)		μCl	259.6(2)	91.97(7)	P,Cl	109.8(1,6.2)	
	1	1389.3(6)	75.02(3)			274.1(2)	88.03(6)			
$[Ag^{I}\{(Ph_2PC_2H_4)_2S\}I]_2$	tr_	1179.6(2)	96.45(2)	AgP_2I_2	P	246.1(2,0)	385.2(2)	P,P	119.87(7)	211
	P$\bar{1}$	1010.8(2)	102.95(3)		μI	289.6(1,16)	83.41(3)	P,I	101.6(1,7.7)	
	1	1233.2(3)	94.84(2)				96.59(3)			
$[Ag^{I}\{P(OPh)_3\}_2(NO_3)]_2$	or	4050.7(15)		AgO_2P_2	P	240.3(5,1)	405.5(1)	P,P	147.9(1)	212
	Fdd2	2591.7(14)			μO	236.6(8)	108.1(3)	P,O	102.2(4,16.5)	
	8	1335.5(5)				264.1(8)	71.9(3)			
$[Ag^{I}\{P(OMe)_3\}_2(NO_3)]_2$	or	914.6(3)		AgO_2P_2	P	241.2(3,1)	409.5(2)	P,P	133.8(1)	213
	Pbca	1676.9(4)			μO	245.5(8,4)	113.0(3)	P,O	109.1(2,2.7)	
	4	2068.9(6)					67.0(3)			
$[Ag^{I}(C_{10}H_{20}S_5)]_2 \cdot$	tr_	1146.2(3)	78.503(18)	AgS_4	S	256.9(4,40)	422.2(1)		not given	214
$\{B(C_{24}H_{20})\}_2$	P$\bar{1}$	1189.5(3)	84.729(13)		μS	253.7(3)	not given			
	2	2701.9(10)	67.118(18)			290.7(3)				
				AgS_5	S	263.2(5,84)				
					μS	248.6(3)				
						313.1(3)				
$[Ag^{I}{}_2(C_{46}H_{60}N_8O_2)] \cdot (ClO_4)_2$	m	1659.5(16)		AgN_4	N	231.0(26,76)	582.8	N,N	64.3-	191
	$P2_1/a$	1336.3(11)	105.43(8)			245.7(30,2)			160.2(7)	
	4	2395.1(25)								

Table 8 *Continued*

$[Ag^{I}_2(C_{36}H_{42}N_8)]\cdot(CF_3SO_3)_2$	m	1336.2(9)		AgN_4	N	236(2,9)	606	N,N	77.1(-,1.7)	215
	$P2_1/a$	2140.3(2)	109.0(1)						114.7(-,4.4)	
	4	1578.0(4)								
$[Ag^{I}_2(C_{42}H_{55}N_{10})]\cdot$	tr	1227.7(16)	77.30(20)	AgN_4	N	230.2(20,69)	682.4	N,N	64.7-	191
$(ClO_4)_2\cdot O.5H_2O$	$P\bar{1}$	1389.9(14)	70.17(20)			246.6(24,26)			145.2(9)	
	2	1526.0(50)	71.27(9)							
$[Ag^{I}(ClCH_2CH_2Cl)\cdot(OTeF_5)]_2$	or	1337.1(5)		AgO_2Cl_2	Cl	272.2(3,193)		Cl,Cl	83.4(1,7.8)	216
(at 153 K)	Pbca	819.2(2)			μO	233.7(7,29)	101.1(3,1)	Cl,O	100.1(2,7.5)	
	4	3272.0(9)							135.7(2,3.8)	
									166.3(2,1.5)	
$[Ag^{I}_2(dppm)_2(py)_2Cl]\cdot(ClO_4)$	or	1341(7)		AgP_2NCl						217
	$P2_12_12_1$	2010(5)								
	4	2143(5)								
$[Ag^{I}(P_2Ph_4)(py)_6](ClO_4)_2$	m	1403(2)		AgN_3P	N	236.8(6,35)		N,N	102.8(3,6.2)	218
	$P2_1/c$	1037(1)	91.19(9)		P	246.3(2)		N,P	115.2(1,7.4)	
	2	1927(2)								
$[Ag^{I}(C_6H_{10}N_4)_2(NO_3)]_2$	tr	953.1(5)	107.43(4)	AgN_3O	N	223.8(10)		N,N	104(1,1)	219
	$P\bar{1}$	960.5(5)	101.45(4)		(μL)N	221.6(10)			138(1)	
	2	1112.9(6)	108.98(4)			254.1(10)		N,O	80(1)	
					O_2NO	242.2(10)			110(1)	
$[Ag^{I}(PPh_3)(NCS)]_2$	tr	1321.0(4)	88.14(2)	AgP_2NS	P	247.9(4,24)		P,P	124.9(2)	220
	$P\bar{1}$	1347.0(5)	79.37(2)		SCN	234.6(16)		P,N	105.8(4,6.0)	
	2	1034.6(5)	113.10(2)		NCS	258.1(6)		P,S	109.4(2,3.6)	
								N,S	97.1(4)	
$[Ag^{I}_2(I_2C_{16}H_{14}N_2)_3\cdot$	tr	1324.5(5)	89.35(3)	AgN_3O	N	222(3)		N,N	76.6(6,3)	66
$(CF_3SO_3)]CF_3SO_3\cdot$ thf	$P\bar{1}$	1320.7(5)	100.64(3)			236(4)			138.8(4,10.9)	
	2	2049.6(5)	108.20(3)		O	not given		N,O	103.4(8,9)	
$[Ag^{I}(dmpe)_2]_2(BPh_4)_2$	m	1117.3(3)		AgP_4	P	249.6(4,61)			83.5(2)	221
	$P2_1/n$	2181.9(4)	103.85(3)						114.2(2,4.6)	
	4	1656.5(5)							144.4(2)	
$[Ag^{I}_2(dppe)(py)_6](ClO_4)_2$	tr	1053.5(1)	81.25(2)	AgN_3P						222
	$P\bar{1}$	1072.2(3)	81.20(1)							
	2	1294.8(2)	86.45(2)							
$[Ag^{I}_2\{(CH_2S)_3\}_5]\cdot(AsF_6)_2\cdot SO_2$	or	1628.6(3)		AgS_4	S	253.7			64.8-	223
	Pbca	2848.7(5)				276.9(4,75)			125.2(2)	
	8	1811.8(3)								
				AgS_5	S	263.5(3,29)			62.7-	
						289.3(3,37)			156.2(2)	

Table 8 *Continued*

$[Ag^{I}_2(C_{30}H_{44}N_8)](BPh_4)_2$	m	1343.0(11)		AgN_4	N	241(3,17)			64.9-	224
	$P2_1/n$	2188.2(15)	101.2(1)						145.7(9)	
	2	1165.2(15)								
$[Ag^{I}(dppp)(NO_3)]_2$	tr	1105.5(1)	111.65(1)	AgO_2P_2	O	262.8(3,47)		O,O	46.9(1)	225
	$P\bar{1}$	1283.8(1)	112.20(1)		P	241.5(1,11)		P,P	152.2(1)	
	1	1085.8(2)	90.04(1)					O,P	107.2(1,9.4)	
$[Ag^{I}(C_{10}H_{18}OS_4)]_2 \cdot (ClO_4)_2$	m	1001.9(1)		AgS_3O	S	252.8(1,88)		S,S	85.22(5)	79
	$P2_1/n$	947.8(1)	94.88(1)		O	261.2(3)		S,O	70.61(8)	
	4	1756.0(1)							109.51(8)	
$[Ag^{I}_2(C_2O_2S_2)(PPh_3)_4]$	m	1315.9(2)		AgP_2OS	P	247.3(2,15)		P,P	122.2(1)	226
	$P2_1/c$	1189.5(2)	101.35(2)		O	251.0(6)		P,O	88.9(1)	
	4	2093.9(5)			S	251.3(2)		O,S	73.8(1)	
$[Ag^{I}_2(LC)_2(pic)](pic)$	tr	1310.2(3)	99.82(2)	AgO_2N_2						227
	$P\bar{1}$	1431.6(4)	97.56(2)							
	2	1607.0(3)	94.23(2)							
$[Ag^{I}(S_4N_4O_2)_4]AsF_6$	tr	1142.6(6)	66.44(4)	AgN_4	N	255.7(4,49)			87.6(1,3.5)	228
	$P\bar{1}$	1194.9(5)	96.71(4)						156.0(1,3.1)	
	2	1254.8(6)	91.30(4)							
$[Ag^{I}(C_{11}H_8N_4O_2)(NO_3)$	m	1042.4(5)		AgO_2N_2	O	248.4(6)			not given	229
	C2/c	1656.4(8)	116.87(1)		N	229.4(6)				
	8	1626.0(8)								
				AgO_4N_2	O	262.9(6)				
					O_2NO	257.3(9,47)				
					N	282.7(6)				
$[Ag^{I}\{o\text{-}(Me)_2C_6H_4\}_2(ClO_4)$	tr	859.5(1)	86.21(1)	AgO_2C_2	μO	258(3,2)	419.8(5)	O,O	71(1)	230
	$P\bar{1}$	1076.6(1)	103.28(1)		C	247(3,3)	109(1)	O,C	157.5(9)	
	2	1081.7(1)	113.70(1)							
$[Ag^{I}(C_8H_8)(NO_3)$	m	1090		AgC_4	C	232				231
	$P2_1/c$	740	114			255				
	4	1810								

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns.

macrocyclic ligand the two bridging nitrogen atoms bring the silver(I) atoms to within 317.7(1) pm.

In this group silver only occurs in the oxidation state of +1. The ligands range from uni-, bi-, penta-, octa- and decadentate. Tables 6 to 9 cover the binuclear silver derivatives and contain examples only of silver in an oxidation state of +1. There are one hundred and seven of these derivatives consisting of 54 four-coordinate (tetrahedral), 22 tri-coordinate, 10 penta-coordinate, 4 hexa-coordinate and 1 hepta-coordinate complexes.

The shortest Ag–Ag distance for each geometry increases with increasing coordination number in the following manner: 265.4(1) pm (bi-) < 272.6(1) (tri-) < 284.5(1) pm (tetra-) < 287.7(6) pm (penta-) < 317.7 pm (hexanuclear). In the equivalent series of binuclear copper(I) compounds [42] no such tren d was found.

4. TRINUCLEAR SILVER COMPOUNDS

Structural information for the trinuclear silver compounds are summarized in Table 10. There are thirteen examples in which only silver(I) atoms are found. Yellow $[Ag(Ph_2PCHPPh_2)]_3$[245] consists of silver atoms arranged at the vertices of a nearly regular isosceles triangle (Fig. 1) with the basal Ag(I)–Ag(2) length of 293.3(2) pm

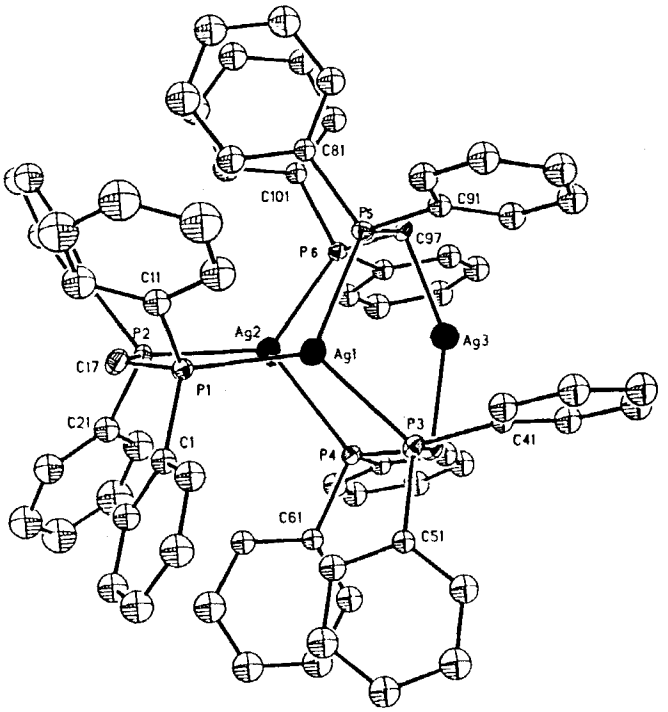

Figure 1

Table 9 Structural data for binuclear silver compounds with coordination number five and higher[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm] M-L-M [°] μL-M-μL [°]		L-M-L [°]	Ref.
$[Ag^{I}(\mu\text{-glyH})(NO_3)]_2$	m $P2_1/a$ 4	545.1(4) 1949.3(10) 554.1(8)		AgO_5	O^b O_2NO	228(2,9) 286(2,1)	287.7(6) 163.1(7)			232
$[Ag^{I}_2(C_{38}H_{46}N_{10})]\cdot(ClO_4)_2$	tg $I4_1cd$ 16	2811(4) 2161.8(16)		AgN_5	N μN	237.8(24,20) 252.0(28) 259.7(21)	306.8(6) 72.0(6)	N,N[b]	66.7- 153.2(8)	191
				AgN_6	N μN	243.2(25,48) 260.2(25,20) 262.0(28)		N,N	65.4- 155.9(7)	
$[Ag^{I}(C_{21}H_{21}N_7O_2)]_2\cdot(BF_4)_2$	m $P2_1/n$ 4	1829.5(3) 976.3(2) 2564.3(5)	105.03(1)	AgN_5	N μN	231.7(8,1) 245.7(8,2) 237.9(9)	347.2(1)	N,N	66.5(3,2.3) 125.0(3,3.0)	233
				AgN_6	N μN	237.5(8,18) 250.4(8,12) 258.5(8)		N,N	65.2(3,3.2) 119.7(3,18.6)	
$[Ag^{I}(C_{12}H_{18}S_5)]_2(ClO_4)_2$	m $P2_1/n$ 2	1088.66(2) 944.19(4) 1496.08(2)	97.132(1)	AgS_5	S μS	256.6(2,2) 275.0(3) 260.0(5) 299.5(2)	408.2(3) 93.45(5) 86.55(5)	S,S	79.9(1,3.5) 114.9(1,15.5) 162.94(5)	234
$[Ag^{I}(2\text{-}SO_3\ py)]_2$	m $P2_1/c$ 4	1057.8(1) 532.9(3) 1263.8(2)	113.44(1)	AgO_4	N O μO	228.2(4) 252.3(4,59) 233.9(3) 263.5(4)	not given not given 81.0(1)	O,O O,N μO,N	85.3(1) 103.7(1,14.9) 71.0(1) 148.4(1) c	235
$[Ag^{I}(bzttcp)]_2\cdot$ $\{2,4,6\text{-}(NO_2)_3C_6H_3O\}_2$	tr $P\bar{1}$ 2	1094.7(2) 1306.7(3) 910.7(1)	96.79(1) 101.54(1) 96.32(1)	AgS_5						236
$[Ag^{I}(C_{15}H_{23}NO_3S_2)]_2\cdot(PF_6)_2$	m $P2_1/n$ 4	2367.8(3) 1872.1(4) 969.0(3)	96.31(1)	AgO_3NS	O N S	248.7(7,117) 236.8(6) 250.1(3)		O,O	66.6(2,1.0) 123.6(3) d_1	237
				AgS_3ON	S O N	258.9(3,44) 288.3(7) 252.8(8)		S,S	108.1(1,7.5) 141.82(9) d_2	

Table 9 *Continued*

$[Ag^{I}(AsPh_3)_2(NO_3)]_2$	tr	1197(1)	102.0(1)	AgO_3As_2	As	252.8(4,7)	not given	As,As	134.2(1)	91
	$P\bar{1}$	1202(1)	113.3(1)		O	268.4(7)	not given	As,O	99.2(3.2.6)	
	2	1368(1)	104.0(1)		μO	240.9(6)	68.7(2)		e	
						273.7(6)				
$[Ag^{I}(PPh_3)(C_2B_9H_{11})]_2 \cdot Me_2CO$	tr	1054.6(1)	122.20(1)	AgB_3PH	B	243.1(5,91)			not given	238
(at 173 K)	$P\bar{1}$	1108.3(1)	108.33(1)		P	241.8(1)				
	1	1265.6(1)	107.10(1)		μH	219(5)				
$[Ag^{I}\{C_5(CO_2Me)_5\} \cdot (PPh_3)]_2$	tr	1459.5(6)	101.91(3)	AgO_2C_2P	O	251.4(3,99)		O,O	70.9(1)	58
	$P\bar{1}$	1104.3(4)	101.79(3)		C	255.2(4,80)		C,C	32.1(1)	
	2	1108.4(5)	105.56(3)		P	239.7(1)			f	
$[Ag^{I}(LN_5)]_2(ClO_4)_2$	m	1215.4(8)		AgN_6	N	244.5(10,81)	317.7(1)		not given	239
	I2/*c*	2065.0(9)	110.11(8)		μN	256.8(10)	not given			
	4	1646.1(8)				274.8(10)				
$[Ag^{I}(C_{34}H_{53}O_8)]_2$	or	2243.9(5)		AgO_6	O	231.0(10)	319.7(2)		64.7-	240
	$C222_1$	1697.6(3)				256.1(11,97)			154.7(4)	
	8	1861.9(4)				282.7(12)				
$[Ag^{I}{}_2(dmpte)_3] \cdot (ClO_4)_2EtOH$	m			AgO_4S_2						241
	C2/*c*									
	4									
$[Ag^{I}(PhMe)_2(OTeF_5)]_2$	m	936.3(2)		AgC_4O_2	C	246.4(5,21)		C,C	30.9(2,1)	242
	$P2_1/c$	1810.9(4)	112.89(2)			266.1(5,36)	101.4(1)		109.4(2,18.7)	
	2	1051.4(2)			O	238.2(3,14)			g	
$[Ag^{I}(C_{34}H_{53}O_8)]_2 \cdot Me_2CO$	m	1225(3)		AgO_5C_2	O	270				243
	$P2_1$	1681(3)	97.39(1)		C	257(2,22)				
	4	1182(4)								

[a]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.d., and the second is the maximum deviation from the mean.[b] The chemical identity of the coordinated atom/ligand is specified in these columns. [c]O-Ag-μO = 97.1(1,4.7) and 137.4(1,1.8)°. [d1]O-Ag-N = 83.4(3), 104.3(2) and 129.6(2)°; O-Ag-S = 77.4(2), 124.9(2) and 158.5(2)°; N-Ag-S = 81.3(2)°. [d2]S-Ag-O = 69.2(2), 89.7(2) and 142.8(2)°; S-Ag-N = 75.1(2,4) and 123.3(2)°; O-Ag-N = 94.0(2)°. [e]O-Ag-μO = 49.5(2) and 117.9(2)°; As-Ag-μO = 103.8(3,9) and 111.9(3,1.8)°. [f]O-Ag-C = 102.5(1,12.2) and 136.45(9)°; O-Ag-P = 88.32(7) and 123.39(8)°; C-Ag-P = 119.94(7) and 146.2(1)°. [g]C-Ag-O = 105.8(1,13.0) and 132.5(2,4.7)°; O-Ag-O = 78.6(1)°.

and sides of length 341.4(1) pm (Ag1–Ag3) and 345.6(1) pm (Ag2–Ag3). Coordination about the basal silver atoms, which are bridged by three $Ph_2PCHPPh$ ligands through phosphorus atoms, is trigonal. The methylene carbon atoms of two ligands are bridged by the Ag3 atom with Ag–C distances of 220(1,1) pm and C-Ag-C angle of 149.8(4)°. The Ag–P distances of a bidentate ligand at 247.6(3,9) pm are significantly shorter than those involving the tridentate phosphines (253.6(3,40) pm).

The structure of colourless $[Ag_3(dppph)_2(MeCN)_2](ClO_4)_3(Et_2O)_2$[246] consists of non-equivalent silver atoms bridged by a pair of tridentate *trans*-bis(diphenylphosphinophenylphosphine) molecules, with the Ag-Ag-Ag angle of 175.33(7)°. The derivative $[Ag\{(PhMe_2Si)_3CHS\}]_3$[247] consists of a discrete six-membered ring of alternating silver and sulphur atoms, Ag_3S_3. Each silver atom exhibits a coordination number of two, with distorted digonal geometry (Table 10). In the $[Ag_3(dppm)_3X_2]^+$ cation (X = Br[248] or Cl[249,250]) a triangular array of silver atoms is bridged by triple X atoms and by the dppm ligands in a syn-syn arrangement. All three silver atoms are tetra-coordinate in a distorted tetrahedral arrangement of two halogen and two phosphorus atoms.

In a white derivative[251] three silver centres are bridged by three 3,5-diphenylpyrazolate units to form a nine-membered ring of Ag_3N_6. The three silver atoms are in a digonal arrangement with Ag–N distances of 209(1,1) pm and N-Ag-N angles of 175.5(5,8)°. The Ag–Ag distances range from 330.5(2) to 349.6(2) pm. Two of the three silver atoms in another derivative[252] are coordinated to two 2-aminopyridine ligands *via* the heterocyclic N atom and the O atoms of NO_3 groups. The remaining and central silver atom lies on a crystallographic two-fold axis, which rotates one half of the molecule into the other. The 2-aminopyridine ligands are bridging, bidentate through the ring N atom and the exocyclic amino groups (Table 10).

A trinuclear double helix 980 pm wide and 2000 pm long is found in another example.[253] All three silver atoms are tetrahedrally coordinated by the N atoms of the two macrocyclic ligands. Another example[254] has two *pseudo*-tetrahedral silver atoms and one *pseudo*-octahedral silver all sitting within the cavity of a tetradecadentate macrocyclic ligand.

Colourless $[Ag_4(C_6H_{12}S_3)_5](ClO_4)_4$[140] consists of two different cations, one monomeric $[Ag(C_6H_{12}S_3)_2]^+$ with a *pseudo*-octahedral environment and the other trimeric $[Ag(C_6H_{12}S_3)]_3^+$. All three silver atoms in the latter are coordinated to a highly distorted tetrahedral array of four S atoms, one S atom of each nine-membered macrocycle being bound to two Ag centres. The Ag_3S_3 six-membered ring is planar.

An extremely hygroscopic, colourless and crystalline derivative[255] has two crystallographically equivalent silver(I) atoms coordinated by alternate O atoms of the twelve-membered $(CH_2O)_6$ ring. The *pseudo*-octahedral coordination about the third silver atom is by six fluorine atoms of different AsF_6^- anions.

There are uni-, bi-, tri-, tetra- and tetradecadentate ligands. In the series of unidentate ligands, the mean Ag–L distance increases with the covalent radius of the coordinated atom, for example: 245.8 pm (L = O, 73 pm) < 248.9 pm (N, 75 pm). However, in the bidentate series the distances are 220 pm (N) < 244.3 pm (P, 106 pm) < 262.2 pm (F, 72 pm) < 267 pm (O). In the multidentate N-donor ligands the mean Ag–N distance increases in the sequence: 220 pm (bi-) < 234 pm (tetra-) < 239.6 pm (tetradeca-) < 248.9 pm (unidentate). The Ag–X (bridging) distances,

Table 10 Structural data for trinuclear silver compounds[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm]		L-M-L [°]	Ref.
$[Ag^{I}(Ph_2PCHPPh_2)]_3 \cdot$	m	1400.4(2)		AgC_2	C[b]	220(1,1)	293.3(2)	C,C[b]	149.8(4)	245
	$P2_1/n$	2363.2(4)	101.66(1)				341.4(2)			
2 toluene	4	2457.2(4)					345.6(2)			
				AgP_3	P	247.6(3,9)		P,P	120.0(1,14.0)	
				(2x)		253.6(3,40)				
$[Ag^{I}_3(dpph)_2(MeCN)_2 \cdot$	or	1063.9(6)		AgP_2	P	239.7(3,0)	294.3(2)	P,P	169.3(1)	246
$(ClO_4)](ClO_4)_2(Et_2O)_2$	Pbcm	2725.6(6)					301.4(2)			
	4	2838.0(4)		AgP_2N	P	240.2(3,0)		P,P	161.24(12)	
					N	255.2(16)		P,N	not given	
				AgP_2ON	P	244.7(3,0)		P,P	137.91(12)	
					O	276.2(13)		P,O	98.97(14)	
					N	242.5(16)		O,N	86.4(5)	
$[Ag^{I}\{(PhMe_2Si)_3CHS\}]_3 \cdot$	tr	1123.6(2)	92.79(1)	AgS_2	μS	248.1(2,63)	301.5(1)	S,S	155.5(1,7.6)[c]	247
$0.5C_6H_6$	$P\bar{1}$	1644.5(3)	97.52(1)				303.5(1)			
	2	2568.6(4)	108.77(1)				323.7(1)			
$[Ag^{I}_3(dppm)_3Br_2]Br$	or	1909.8(1)		AgP_2Br_2	P	244.1(8,28)		P,P	125.0(3,1)	248
	$Pna2_1$	2146.8(2)			μ_3Br	279.7(4)		Br,Br	95.5(1,1)[d]	
	4	1858.1(2)				284.0(4,18)				
$[Ag^{I}_3(dppm)_3Cl_2] \cdot$	m	3982.2(16)		$AgCl_2P_2$	P	245.5(4,19)	319.8(2)	P,P	126.9(2,7.8)	249
$[Sn(Ph)_2(NO_3)_2Cl]MeOH$	$P2_1/a$	1060.3(2)	91.27(5)		μ_3Cl	268.9(4,20)	329.6(3)	P,Cl	108.4(2,11.5)[e]	
	4	2055.4(14)				282.6(4,12)	354.0(2)			
$[Ag^{I}_3(dppm)_3Cl_2]ClO_4$	m	1155(9)		$AgCl_2P_2$						250
	$P2_1/n$	2752(4)	102.8(1)							
	4	2296(4)								
$[Ag^{I}(3,5\text{-}Ph_2pz)]_3(thf)_2$	m	1406.6(6)		AgN_2	N	209(1,1)	330.5(2)	N,N	175.5(5,8)	251
	$P2_1/n$	1498.7(3)	106.88(3)				336.2(2)			
	4	2330.6(6)					349.6(2)			
$Ag^{I}_3(2\text{-}NH_2py)_4(NO_3)_3$	or	799.2(4)		AgN_4	μN	239(1,2)		N,N	82.5- 130.0(4)	252
	Pccn	1678.8(5)								
	4	2103.4(8)								
				AgO_3N_2	μN	218(1,2)		O,O	77.7(3)	
				(2x)	O	255(1)			120.9(3)	
					O	279(1,1)		N,N	154.0(4)	
								O,N	98.2(2,14.6)	

$[Ag^{I}_3(C_{36}H_{32}N_6O_2)_2]\cdot$	tr	1712.5(6)	102.39(2)	AgN_4	N	226-242(1)		N,N	71.5(4,1.2)	253
$(CF_3SO_3)_3$	$P\bar{1}$	1765.4(6)	98.59(2)						114.8-	
	2	1352.2(4)	91.59(2)						138.7(4)	
$[Ag^{I}_3(C_{48}H_{48}N_{14})](BF_4)_3$	tr	1358.0(1)	106.95(1)	AgN_4	N	233.1(8,115)	490	N,N	77.2(3,1.0)	254
	$P\bar{1}$	1433.3(3)	99.98(1)	(2x)			493		115.0(3,4.5)	
	2	1576.7(7)	82.99(1)							
				AgN_6	N	248.4(6,40)		N,N	66.4(3,1.0)	
									100.0(3,7.9)	
									151.8(3,3.9)	
$[Ag^{I}(C_6H_{12}S_3)]_3\cdot$	hx	1591(2)		AgS_4	S	260.4(4,9)		S,S	84.9(1)	140
$[Ag^{I}(C_6H_{12}S_3)_2](ClO_4)_4$	$P6_3$	—		(3x)	μS	272.4(2,0)		μS,μS	114.0(1)[f]	
	2	1345.9(2)								
				AgS_6	S	see Table 5				
$[Ag^{I}_3(CH_2O)_6(AsF_6)_3$	c	1637.6(2)		AgF_6	F	265.5(6,0)			not given	255
	la3									
	24									
				AgO_3F_3	O	245.8(5,0)				
				(2x)	F	258.9(5,0)				
$[Ag^{I}_3\{PrS(CH_2)_2SPr\}_2]\cdot$	tr	894.5(1)	98.69(2)	AgS_5						256
$(NO_3)_3$	$P\bar{1}$	1235.5(2)	92.74(2)							
	2	1357.2(5)	90.45(1)							

[a]Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number if parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns. [c]Ag–S = Ag = 78.3(1,5.3)° and Ag-Ag-Ag = 60.0(1,4.7)°. [d]Ag-Br-Ag = 70.81(1,2.7)°; P-Ag-Br = 108.0(2,10.6)°. [e]Ag-Cl-Ag = 88.8(1,1.7)°; P-Ag-Cl = 108.4(2,11.5)°. [f]Ag-S-Ag = 126.0(1)°; μS-Ag-S = 81.3(1,5) and 136.2(1,2.4)°.

where X is triply-bridging, increases with the covalent radius of the coordinated atom: 273.4 pm (Cl, 99 pm) < 283.5 pm (Br, 114 pm).

5. TETRANUCLEAR SILVER COMPOUNDS

5.1. Coordination number two

Structural data for these silver compounds are summarized in Table 11. The structure all contain silver(I) in discrete eight-membered rings (Ag_4X_4) with alternating silver and X atoms. The μL-Ag-μL angles range from 165° to 180°. The mean Ag-L(bridge) distance increases with the covalent radius of the X atom in the sequence: 212.7 pm (N, 75 pm) < 220 pm (C, 77 pm) < 238.1 pm (S, 102 pm). The shortest Ag–Ag distance is 273.3(3) pm.[25] There is an interdependence between the mean Ag–Ag distance and the Ag-L-Ag angle. As the distance increases the angle opens (Table 11). The shortest Ag(I)–Ag(I) distance of 273 pm is about 31 pm longer than that of Cu(I)-Cu(I), but shorter by about 19 pm than the corresponding Au(I)–Au(I) distance.[43]

5.2. Coordination number three

The structural data for these compounds are listed in Table 12. There are ten examples, seven of which contain two silver(I) atoms of higher coordination number, and these are cross-listed with the appropriate table.

The structure of $[Ag_2(4\text{-}FC_6H_4OCH_2CO_2)_2(H_2O)_2]_2$[261a] shows a discrete centrosymmetric tetramer with one water molecule on each of the four silver(I) atoms. Carboxylate groups bridge a pair of silver atoms in a syn-syn arrangement, and two of these dimeric units are held together by two bridged oxygen atoms from different

Table 11 Structural data for tetranuclear silver compounds, coordination number two[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm] M-L-M [°] μL-M-μL [°]	Ref.
$[Ag^I(mes)]_4$	rh $R\bar{3}$ 3	1839.5(3)	116.28(2)	AgC_2	μC[b]	220(3,4)	274.4(3,11) 77.1(7,1.0) 167.1(8,1.9)	245, 257
$[Ag^I(FC_6H_4N_3C_6H_4F)]_4$	m C2/*c* 4	1863.0(3) 1270.2(1) 2005.1(2)	103.07(1)	AgN_2	μN	212.8(4,26)	282.0(1,14) not given 177.7(2,2.3)	258
$[Ag^I(mpsa)]_4$	m C2/*c* 4	2867(1) 1149.3(3) 2056.5(8)	126.25(2)	AgN_2	μN	212.6(4,43)	307.7(1,87) not given 169.7(2,1.5)	259
$[Ag^I\{(Bu^tO)_3SiS\}]_4$	tr $P\bar{1}$ 2	1769.7(25) 2012.8(17) 1266.8(6)	119.63(6) 82.22(7) 95.08(9)	AgS_2	μS	238.3(3,6)	313.5(7,18) 82.3(3,5) 172.3(3)	260
$[Ag^I\{(Me_3Si)_3CS\}]_4$	or Pbca 8	1747.8(3) 2831.4(4) 2970.6(4)		AgS_2	μS	237.8(8,18)	331.3(3,18) 88.3(3,1.0) 177.5(3,7)	247

[a] 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.d., and the second is the maximum deviation from the mean.
[b] The chemicaly identity of the coordinated atom/ligand.

Table 12 Structural data for tetranuclear silver compounds, coordination number three[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm] M-L-M [°]		L-M-L [°]	Ref.
$[Ag_2(4\text{-}FC_6H_4OCH_2CO_2)_2 \cdot (H_2O)_2]_2$	tr $P\bar{1}$ 1	804.52(6) 1074.9(1) 1184.8(1)	66.45(1) 81.201(6) 77.826(7)	AgO_3	O^b H_2O	216.5(3,7) 249.9(4)	283.6(2)		94.1(1,5.8) 171.8(1)	261*a*
				AgO_4	O μO H_2O	229.6(3) 227.1(3) 249.8(4) 249.9(4)			78.5(2) 87.1(2,4.6) 116.4(2,2.2) 156.9(1)	
$[Ag^I\{PhN_3C_6H_4N_3(H)Ph\}]_4$	or Pbcn 4	1989.7(8) 1917.5(3) 1767.1(4)		AgN_3	N	219(1,2) 236(1,0)	291.1(2,192)		72.5(5,4) 115.8(5,4.3) 162.9(5,2.7)	261*b*
$(PPh_4)_2[Ag^I_4(SCH_2C_6H_4 \cdot CH_2S)_3] \cdot 6MeOH$ (at 150 K)	tr $P\bar{1}$ 2	1395.9(3) 1427.2(3) 2286.8(5)	76.10(2) 87.68(2) 60.96(2)	AgS_3	μS	250.5(1,83)	304.4(1,46) 74.8(1,1.6)		119.8(1,13.0)	262
$(NEt)_4[Ag^I(Se_4)]_4$	m $P2_1/n$ 2	1622.9(3) 1148.0(5) 1717.1(3)	106.06(1)	$AgSe_3$ (2x)	Se μSe	259.6(1) 260.0(1,17)	304.8(1,131) 73.5(1,10.9)		119.7(1,14.8)	263
				$AgSe_4$ (2x)	μSe	266.4(1,44) 290.1(1)			104.0(1,13.4) 136.47(4)	
$(NPr_4)[Ag^I_4(S_4)_3]$ (at 148K)	m $P2_1/n$ 4	1049.3(2) 2457.3(3) 1749.9(1)	93.84(1)	$AgSe_3$	μSe	260.4(1,106)	305.0(1,143) 72.3(1,1.8)		111.1(1,11.4) 137.6(1,9.0)	263
$[Ag^I_4(dppm)_4(NO_3)_2] \cdot (PF_6)_2$	tr $P\bar{1}$ 1	1370.3(3) 1451.6(2) 1340.2(2)	112.21(1) 96.82(2) 83.56(1)	AgP_2O	P μO	242.8(3,38) 251.0(8,32)	309.9(1)	P,R[b] P,O	146.8(1,5.3) 101.9(2,6.9)	198
$[Ag^I(PPh_3)(MeCO_2)]_4$	m $P2_1/c$ 2	1361.6(11) 1243.6(12) 2348.9(17)	91.28(11)	AgO_2P (2x)	P O	237.6(3) 225.1(9,10)	312.2(1) 101.1(3)	O,O O,P	97.9(3) 128.7(2,1)	264
				AgO_3P (2x)	P O μO	235.4(3) 222.6(12) 239.8(7,78)		O,O O,P	78.9(2) 97.7(4,2.2) 122.1(2,12.7)	

Table 12 *Continued*

$(PPh_4)_4[Ag^I_4I_8]$	tr	1345.3(7)	102.83(4)	AgI_3	I	272.7(2)	321.4(2,43)	I,I	119.96(5,5.6)	179
	$P\bar{1}$	1660.7(9)	103.94(4)	(2x)	μI	276.4(2,1)	68.02(5,1.48)			
	1	1106.8(7)	82.96(4)							
				AgI_4	μI	284.4(2,2)		I,I	109.45(5,3.81)	
				(2x)		294.6(2,45)				
$(AsPh_4)_4[Ag^I_4I_8]$	tr	1344.6(3)	103.36(2)	AgI_3	I	272.1(1)	325.2(2,54)	I,I	119.99(4,6.44)	179
	$P\bar{1}$	1671.2(3)	103.84(2)	(2x)	μI	276.2(1,5)	69.15(3,1.85)			
	1	1129.3(4)	83.43(2)					I,I	109.45(4,4.01)	
				AgI_4	μI	284.7(1,1)				
				(2x)		293.5(1,38)				
$[K(crypt)]_4[Ag^I_{Br_8}]$	m	1655.7(2)		$AgBr_3$	Br	251.8(2)	357.9(1,17)		not given	31
	$P2_1/c$	2386.4(2)	107.45(1)	(2x)	μBr	264.1(2,10)	86.5			
	2	2	1407.0(2)	$AgBr_4$	μBr	274.2(2,57)				
				(2x)						

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns.

dimers. This results in triangular coordination about two silver atoms and tetrahedral coordination about the other two. The brown compound $[Ag\{PhN_3C_6H_4N_3(H)Ph\}]_4$[261] is built up of a rhombus of four silver(I) atoms and four bis-triarsenido units. In another three examples[262,263] the metal rhombus is held together by sulphur[262] or selenium ligands.[263] In a colourless derivative[198] two $[Ag_2(dppm)_2]^{+2}$ subunits are held together by two bridging NO_3 groups. In another example[264] non-equivalent silver(I) atoms are linked together by acetate groups. Tetranuclear $[Ag_4X_8]^{-4}$ anion (X = Br[31] or I[179]) is centrosymmetric and was described in terms of two edge-sharing silver(I) bromide or iodide tetrahedra, each linked by a common edge of an approximately planar silver halide triangle (Table 12).

In general, the mean Ag–L(terminal) are shorter than Ag–L(bridge) distances. For tri-coordinated silver(I) atoms, the mean Ag–L distance increases with the covalent radius of the coordinated atom. For example the bidentate ligands give the order: 220.8 pm (O) < 242.8 pm (P) < 259.6 pm (Se, 116 pm). For the bidentate bridged ligands the order is 251 pm (O) < 260.2 pm (Se). For unidentate terminal and bridging ligands the order is: 251.8 and 264.1 pm (Br) < 272.4 and 276.3 pm (I), respectively. the shortest Ag-Ag distance found in this series of tetranuclear derivatives, 279.9(1) pm, is about 6.6 pm longer than that found in the previous examples with coordination number two (Table 11).

5.3. Coordination number four

The structural data for these derivatives are given in Table 13. There are several distinct types of structures, the distorted "cubane-like" geometry being the most common. From nineteen examples given in Table 13, thirteen belong to the cubane type (Table 13A). The cubane-like structure, for example in a colourless derivative,[271] is composed of four silver and four iodine atoms situated at alternative corners of a highly distorted cube with each silver atom being closer to one of the PPh_3 ligands. In this series (Table 13A) the Ag–Ag distances range from 299 to 420 pm, the mean value being given in the table. The variation of Ag–Ag distances range from 3 pm to 70 pm, which occurs because of a nonsystematic distortion from idealized T_d symmetry.[271] It is evident from the data in Table 13A that there are links between the Ag–Ag distances and the Ag-L-Ag angles. The mean distances increases with an opening of the angle. The mean Ag–L(bridge) distance increases with covalent radius of the triply-bridged atom in the sequence: 266.8 pm (Cl) < 280.6 pm (Br) < 291.0 pm (I). In the corresponding series of Cu(I) cubane-type structures,[42] the mean Cu-L(bridge) distance increases in the same order, viz: 238.3 pm (Cl) < 255.0 pm (Br) < 271.1 pm (I). All are shorter than those found in silver cubane type structures. It is seen that the value of {[Ag-L(bridge)]-[Cu-L(bridge)]} distances decreases with increasing covalent radius of the bridged atom in the sequence: 28.5 pm (Cl) < 25.6 pm (Br) < 19.9 pm (I), suggesting the limiting effect of ligand steric hindrance.

The mean Ag-L(terminal) distance increases in the sequence: 230 pm (pip) < 237 pm (NEt_3) < 240.2 pm (Me_4pip) < 241.3 pm (PEt_3) < 242.0 pm (PPh_3) < 250.2 pm (ppyp), due to both the steric and electronic nature of the ligands. From these correlations it can be seen that the degree of distortion mentioned above follows the degree of steric hindrance. It is interesting to note that while monoclinic $[Ag(PPh_3)I]_4$[271] has a cubane-like structure, the colourless triclinic

Table 13 Structural data for tetranuclear silver compounds, coordination number four[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M M-L-M [°] μL-M-μL [°]		L-M-L [°]	Ref.
A: Cubane-like structure										
$[Ag^{I}(pip)Br]_4$	or	1986(1)		$AgBr_3N$	N[b]	227.0(7)	301.9(2,87)	Br,N[b]	99.4(2,8)	266
	Pcna	798.5(4)			μ_3Br	269.8(2)	65.5(1,9)		127.1(2)	
	8	1018.7(6)				283.5(2,7)	109.8(1,1.6)			
$[Ag^{I}(pip)I]_4$	or	2022.0(40)		AgI_3N	N	232.9(15)	303.2(2,63)	I,N	99.4(4,1)	265
	Pcna	822.6(20)			μ_3I	285.3(2)	62.8(5,8)		122.6(4)	
	8	1024.0(30)				293.9(2,3)	111.3(7,1.6)			
$[Ag^{I}(pip)I]_4$	or	2024.3(6)		AgI_3N	N	229.1(12)	303.9(2,66)	I,N	99.0(2,1)	266
	Pcna	826.0(3)			μ_3I	285.3(2)	62.8(1,8)		123.3(3)	
	8	1028.0(3)				294.8(2,3)	111.4(1,1.5)			
$[Ag^{I}(tht)I]_4$	tr	967.3(3)	91.73(3)	AgI_3S	S	254.6(7,18)	310.8(3,147)	I,S	108.7(1,14.4)	267
	$P\bar{1}$	1068.4(3)	104.07(3)		μ_3I	289.5(3,66)	64.9(1,3.7)			
	2	1657.4(8)	110.62(3)				110.1(1,5.4)			
$[Ag^{I}(NEt_3)I]_4$	tg	1320.2(6)		AgI_3N	N	237(3)	320.2(5,42)	I,N	109.5(6,9)	268
	$P4_2/nmc$	—			μ_3I	290.7(4,10)	66.8(1,9)			
	2	1165.4(8)					108.5(1,1.9)			
$[Ag^{I}(PEt_3)I]_4$	tg	1373.6(1)		AgI_3P	P	243.8(2)	320.8(1,1)	I,P	110.3(1)	269
	$P4_2/nmc$	—			μ_3I	291.9(1)	66.7(1,5)			
	2	1207.3(1)					109.0(1,1.0)			
$[Ag^{I}(Me_4pip)I]_4$	tg	1802.4(8)		AgI_3N	N	240.2(12)	341.7(2,55)	I,N	91.2(3)	266
	$I4_1/amd$	—			μ_3I	286.7(2,0)	71.7(1,2.8)		123.9(1)	
	4	1503.4(9)				302.0(3)	105.4(1,6.0)			
$[Ag^{I}(PEt_3)Br]_4$	c	1316.5(2)		$AgBr_3P$	P	240.2(5)	326.7(1,172)[c]	Br,P	110.3(2)	270
	$I\bar{4}3m$				μ_3Br	242.2(7)	78.5(1,5.3)		129.2(3)	
	2					289.7(5)	100.3(1,7.3)			
$[Ag^{I}(PPh_3)I]_4$	m	2499.1(5)		AgI_3P	P	245.8(4,4)	348.3(2,367)	I,P	112.2(1)	271
	$P2_1/c$	1240.2(3)	113.30(7)		μ_3I	285.9(2,23)	73.6(1,9.0)		134.9(1)	
	4	2507.4(6)				298.8(2,50)	104.1(1,11.3)			
$[Ag^{I}(PEt_3)Cl]_4$	c	1291.9(2)		$AgCl_3P$	P	238.9(2)	354.1(2,398)	Cl,P	112.2(5)	270
	$I\bar{4}3m$				μ_3Cl	230.0(1)	83.7(1,6.5)		134.9(8)	
	2					282.1(1)	95.8(1,7.6)			
$[Ag^{I}(PPh_3)Cl]_4$	or	1792.5(4)		$AgCl_3P$	P	237.9(3,7)	363.3(2,225)	Cl,P	122.3(1,16.4)	271,
	Pbcn	2077.8(15)			μ_3Cl	260.9(1,77)	86.5(9,7.2)			272
	4	1827.9(3)				274.2(1,18)	92.7(9,8.5)			

Table 13 *Continued*

$[Ag^{I}(PPh_3)Br]_4$	rh R3*c* 2	1749.4(5)	56.01(2)	$AgBr_3P$	P μ_3Br	242.2(4,7) 274.5(1,68) 296.2(1)	395.3(2,247) not given		not given	205
$[Ag^{I}(ppyp)Cl]_4$	m C2/*c* 8	2365.0(8) 2354.1(9) 2348.6(9)	90.88(3)	$AgCl_3P$	P μ_3Cl	250.2(5,98) 265.0(5,112) 291.4(5,1)	not given 88.9(1,5.2) 91.1(1,4.3)	Cl,P	115.7(1,9.1) 135.6(1,3.4)	273
B: Different types										
$[Ag^{I}_4(C_3H_4NS_2)_4(PPh_3)_2$	m C2/*c* 4	1465.61(6) 1223.1(6) 2961.3(7)	97.71(3)	AgS_2NP AgS_2N	N P μS N μS	228.7(9) 252.3(3) 267.6(3,52) 227.1(9) 249.0(3,57)	309.4(1,16)[d]		not given	274
$[Ag^{I}_4(PPh_3)_4\cdot$ $\{C_{10}H_6(CO_2)\}_2]2C_6H_6$	tr P$\bar{1}$ 2	1180.4(4) 1839.0(4) 2204.6(1)	103.23(7) 95.81(3) 90.08(7)	AgO_3P (3x) AgO_4P	P O μO P μO	236.1(4,19) 227.8(9) 244.0(9,191) 234.6(5) 247.7(9,151)	380.9(2,152)[e] 101.0(3,7.1)	O,O O,P O,O O,P	51.7- 116.9(3) 120.6(2,8.7) 144.0(2,2) 50.8- 118.1(3) 118.6(3,7) 128.0(2,2.9)	275
$[Ag^{I}_4(dppm)_2Br_4$	m P2$_1$/*c* 4	1136.0(7) 1603.3(12) 1689.1(12)	122.36(4)	$AgBr_3P$	P μBr μ_4Br	238.6(5,6) 258.4(5,5) 283.3(4,139)	302.3(3,59) 65.2(1,7.8)[f] 91.7(1,8.0)	Br,P	107.4(1,5.7) 130.2(2,4.2)	248, 276
$[Ag(PPh_3)I]_4\cdot 1.5CH_2Cl_2$	tr P$\bar{1}$ 1	1210.2(3) 1507.1(2) 1194.8(2)	110.59(1) 96.40(2) 71.64(2)	AgI_3P	P μI μ_3I	244.2(3,13) 278.7(1,63) 282.0(1,14) 299.5(1)	68.0(1,3.4)[g] 110.1(1,5.3)	I,P	111.7(1) 115.6(1,11.8)	270, 271
$[Ag^{I}_4(py)_6\cdot\{1,2\text{-}C_6H_4(CO_2)_2\}_2$	tr P$\bar{1}$ 1	1205.0(2) 1070.1(2) 919.9(2)	84.02(2) 75.02(2) 73.50(2)	AgO_3N (2x) AgO_2N_2 (2x)	N μO μO N O μO	222.0(4) 226.1(4) 252.3(4,96) 226.3(5,36) 232.5(5) 275.8(4)	362.5(1) 95.7(1) 142.7(1)	O,O O,N O,O N,N O,N	88.6(1,9.8) 111.2(1,2) 147.7(1) 50.6(1) 119.4(1) 94.7(1,3.9) 144.3(1,3.0)	277

$[Ag^{I}(pmqu)]_4$; or, Pbca, Z = 8; *a* = 1462.9(3), *b* = 1539.4(3), *c* = 2180.8(5) pm.[278] $[Ag^{I}(\alpha\text{-}C_{10}H_7CS_2)(py)]_4.2py$.[279] $[Ag^{I}(2\text{-}MeC_6H_4CS_2)(py)]$; m, P2$_1$/n, Z = 2.[280] $Ag^{I}_4(dppe)_3(NO_3)_4$; tr, P$\bar{1}$, Z = 1; a = 1274.89, b = 1347.15, c = 1470.15 pm; α = 59.748, β = 63.949 and γ = 70.196°.[281]

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns. [c]Additional Ag...Ag is 431.5(1) pm. [d]Additional Ag...Ag is 427.5(1) pm. [e]Additional Ag...Ag are 475.4 and 538.8 pm. [f]Additional Ag-Br-Ag = 95.7(1,5)°. [g]Additional Ag-I-Ag = 99.82(4)°.

$[Ag(PPh_3)I]_4.1.5CH_2Cl_2$[271] has a chair-like configuration, as shown in Figure 2, which clearly shows two non-equivalent silver(I) atoms. The atoms Ag(1) and Ag(1)' are approximately trigonally coordinated (AgI_2P), while Ag(2) and Ag(2') are tetrahedrally coordinated (AgI_3P). This unprecedented type of isomerism allowed a detailed stereochemical comparison, which has been fully discussed in the original literature.[271]

There are two examples[274,275] where four silver(I) atoms are positioned in a butterfly arrangement with the ligand on the "wing-tip" silver atoms. The shortest Ag–Ag distance in the former compound[274] is between the "body"atoms, about 308–311 pm. In the second case[275] the value is 367–396 pm (Table 13B). A similar structure is found for other silver complexes.[279,280] Unfortunately, the only data obtained for these compounds were from Chemical Abstracts (footnote to Table 13), and therefore a more detailed comparison of this group of derivatives is not possible.

The structure of monoclinic $Ag_4(dppa)_2Br_4$[248,276] is a tetragonal bipyramid with four silver(I) atoms in the equatorial plane and the bromine atoms in axial positions. The Ag–Ag edges are alternatively bridged by bromine atoms and dppa ligands. A colourless derivative[277] has one Ag(I) atom in a distorted tetrahedron of AgO_3N, the other Ag(I) atom forms part of an approximate plane of AgO_2N. Two phthalate groups coordinate two silver atoms in a fourteen-membered

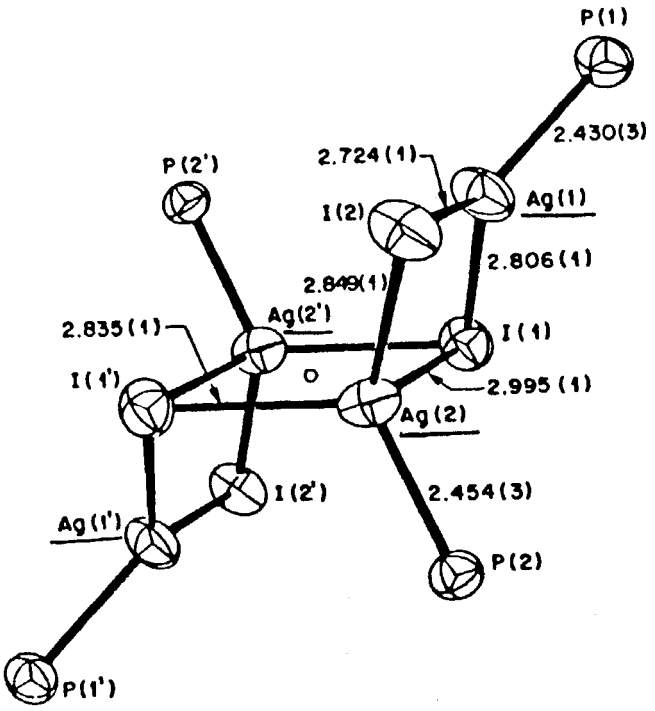

Figure 2

ring. The additional bridging capacity of two of the four oxygen atoms subdivides the fourteen-membered ring into one four- and two seven-membered chelating rings.

The mean Ag-L bond distances for tetrahedrally-coordinated Ag(I) atoms in the tetranuclear species increases in the sequence: 233.2 pm (LN) < 242.3 pm (LP) < 254.6 pm (LS); for μ-bidentate ligands the order is: 239.2 pm (LO) < 274.3 pm (LSe); for μ-*vs* μ_4-Br and I the order is: 266.3 pm vs 283.3 pm < 287.2 vs 287.8 pm, respectively.

The mean Ag-L bond distances found in the trigonal species are shorter than those in the tetrahedral species, for example: 236.1 vs 242.3 pm (LP); 264.1 vs 266.3 pm (μ-Br); 276.2 vs 287.2 pm (μ-I) and 260.2 vs 274.3 pm (μ-bidentate Se-donor ligands). However, for μ-bidentate O-donors the opposite trend is observed, 251.0 and 239.2 pm, respectively.

The shortest single Ag–Ag bond distances found for tetranuclear species increases with increasing coordination number in the order: 237.3(2) pm (digonal) < 279.9(2) (trigonal) < 296.1(2) pm (tetrahedral).

Two orthorhombic derivatives $[Ag(pip)I]_4$[265,266] differ mostly by degree of distortion, an example of distortion isomerism, which is also common both in the copper complexes[42,44] and gold complexes.[43]

Thirty-seven tetranuclear silver(I) compounds have been studied and analyzed (Tables 11–13) which is much less than the one hundred and fifteen copper(I) examples.[42] In general, in the M(I) digonal species an eight-membered ring type is the most common structure. In the M(I) coordinated examples, a rhombus or adamantane-like arrangement is most common, and in the tetrahedral M(I) examples it is the cubane-like structure. The mean M(I)-L(terminal) distances are shorter than the M(I)-(bridge) values, and the general order observed is Cu(I)-L < Au(I)-L < Ag(I)-L.

6. OLIGONUCLEAR SILVER COMPOUNDS

Structural data for the oligonuclear silver compounds are listed in Table 14. Included are pentanuclear,[282] hexanuclear[283–293] octanuclear,[289] nononuclear,[299] decanuclear[289] and tetradecanuclear.[298] In all cases the silver is found in the oxidation state of +1.

In the pale yellow pentanuclear compound,[282] five silver atoms form a trigonal bipyramid with Ag–Ag distance within the same cage of 335.7 pm (trigonal plane) and 401.5 pm (axial axis), and a distance of 318.1 pm between different cages. The molecular cage contains six doubly-bridging thiolate ligands, leading to trigonal planar coordination for the silver atoms related by a two-fold axis, and digonal linear coordination for the three other silver atoms related by a three-fold axis (Table 14).

There are eleven hexanuclear silver(I) derivatives. A white compound[283] reveals the presence of a planar Ag_6 cluster in which three radiating pairs of Ag(I) atoms 305.1(1) pm apart are disposed on the corners of an equilateral triangle. The inner silver atoms are 349.3(1) pm apart, and each silver atom is linearly coordinated by imidazole ligands. The structures of some pale yellow derivatives are identical.[284,285,288] The silver atoms form a distorted octahedron in which each silver is tri-coordinate. The Ag–Ag distance[284] ranges from 290.5(1) to 401.4(1) pm and indicates the highest degree of distortion of the Ag_6 octahedron of this set. The

Table 14 Structural data for oligonuclear silver compounds.[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm] shortest longest M-L-M [°]		L-M-L [°]	Ref.
$[Ag^{I}_5\{Me_2N(CH_2)_3S\}_3\cdot$	hx	1363.0(2)		AgS_2	μS[b]	228.9	318.1		170.7	282
	$P6_322$	—			(3x)			401.5		
$\{Me\}_2NH(CH_2)_3S\}_3](ClO_4)_2$	2	1607.8(3)								
				AgS_3	μS	258.0			119.7	
				(2x)						
$[Ag^{I}(im)_2]_6(ClO_4)_6$	hx	1444.4(10)		AgN_2	N	208.2(3,7)	305.1(7)		not given	283
	$R\bar{3}c$	—					349.3(1)			
	12	5484(4)								
$[Ag^{I}\{(Pr)_2NCS_2\}]_6$	tr	1337.4(5)	96.10(2)	AgS_3	S	244.9(15,31)	290.5(1)		99.6(5,5.5)	284
	$P\bar{1}$	1237.5(5)	116.40(2)		μS	251.2(13,44)	401.4(1)		127.1(5,9.9)	
	1	1299.7(5)	83.24(4)				97.4(4,9.5)			
$[Ag^{I}\{S_2CC(CN_{(2)}\}]_6\cdot$	tr	1659.0(3)	84.84(5)	AgS_3	S	246.9(6)	301(2)		not given	285
$(PhCH_2NEt_3)_6$	$P\bar{1}$	1880(1)	87.06(1)		μS	252.7(7)	374(5)			
	2	1896.9(4)	81.92(6)							
$[Ag^{I}(Et_2NCS_2)]_6$	m	1090(2)		AgS_3	S	250.0(3)	284.1(1)		118.4(9,19.0)	286
	$P2_1/c$	2472(1)	125.8(1)	(4x)	μS	253.0(3,52)	409.1(1)			
	2	1151(2)								
				AgS_4	S	247.1(3)			95.5(9,11.7)	
				(2x)	μS	273.3(2,261)			155.03(9)	
$[Ag^{I}_6(4\text{-}ClC_6H_4S)_6\cdot$	tr	1502.4(5)	82.14(2)	AgS_3	μS	244.4(4,37)	287.5(2)		108.3(1,18.7)	287
	$P\bar{1}$	1848.8(5)	86.19(2)	(2x)	μ_3S	257.6(4,120)	318.9(2)		143.0(1,8.4)	
$(PPh_3)_5](tol)_2$	2	2650.6(10)	66.45(3)				66.7(1,9.5)			
				AgS_2P	μS	250.3(4)	95.0(1,7.8)	S,S[b]	95.8(1)	
					μ_3S	265.6(4)		S,P	126.2(1,5)	
					P	240.5(4)				
				AgS_3P	μ_3S	268.2(4,89)		S,S	101.9(1,10.2)	
				(2x)	P	245.5(4,4)		S,P	116.1(1,12.5)	
				AgS_2P_2	μ_3S	265.6(4,28)		S,S	86.2(1)	
					P	250.4(4,25)		P,P	112.4(1)	
								S,P	116.0(1,4.8)	
$[Ag^{I}\{Pr_2NCOS\}]_6$	m	1331.3(5)		AgS_2O	O	236(4,2)	294.3(5)	S,S	125.(5,1.0)	288
	$P2_1/a$	1990.4(8)	93.28		μS	246(1,3)	328.1(5)	S,O	113.1(9,3.8)	
	2	1190.1(5)					80.2(4,3.3)			

Table 14 *Continued*

$[Ag^I\{3\text{-}(Me_2Ph)Si\text{-}2\text{-}(S)C_6H_3N\}]_6$	or Pbc*a* 4	1757.6(3) 1863.4(3) 2584.5(6)		AgS_2N	N μS	231.7(10,17) 248.0(3,16)	315.7(2)	S,S S,N	124.6(1,1.9) 113.0(3,4.1)	289
$[Ag^I(Me_3SiNC_5H_3S)]_6 \cdot CH_2Cl_2$	m C2/m 2	1720.1(3) 2061.1(3) 1097.7(2)	95.46(1)	AgS_2N	N μS	230.6(3,6) 247.7(2,3)	332.3(1) 80.7(1,3.3)	S,S S,N	124.8(2) 117.8(2,8)	290
$[Ag^I(CNO)]_6$	trg R$\bar{3}$ 6	908.7(3)	115.73(3)	AgO_xC_2	O μC	249.7(4) 278.8(8,57) 216.4(7,13)	281.9(1) 81,3(3)	C,C	166.0(3)	291
$[Ag^I{}_6I_8](Me_6en)$	tr P$\bar{1}$ 1	1047(1) 958(1) 786(1)	101.4(4) 101.8(4) 95.5(4)	AgI_4	μ_3I	287(1,11)			109.3(1,13.8)	292
$[Ag^I{}_6(Ph_3CCS_2)_6(py)] \cdot 6dmf$	c P2/n$\bar{3}$ 4						297.5 351.2			293
$[\{Ag^I(Pr^i{}_3C_6H_2SCS_2)\}_2 \cdot$ $\{Ag^I(Pr^i{}_3C_6H_2S)\}_6]8CHCl_3$	m P2$_1$/n 2	1789.7(7) 2713.1(18) 1911.1(9)	113.59(3)	AgS_2	μS	236.9(8,17)	278.2(3) 335.0(3) 107.9(3,10.6)		156.0(3) 173.4(3,1)	294
$[Ag^I\{(Me_3Si)_2CHS\}]_8$	m C2/*c* 4	1833.9(4) 2462.3(4) 2447.3(4)	96.74(1)	AgS_2	μS	240.1(4,17)	290.4(2) 309.4(2) 77.2(1,3.2)		175.6(1,9)	247
$[\{Ag^I(2\text{-}Me_3SiC_6H_4S)\}_4]_2$	m A2 4	1192.3(2) 1476.1(2) 2661.8(4)	98.30(1)	AgS_2	μS	238.7(9,10)	306.5(4) 332.0(5) 82.2(3,12.7)		79.0(3) 113.4(3) 170.3(3,5.2)	295
$[Ag^I{}_{82}CC(CN)_2\}_6] \cdot (NBu_4)_4$	m P2$_1$/*c* 2	1575.6(2) 2251.6(3) 1807.8(3)	107.50(1)	AgS_3	μS	249.1(4,29)	295.7(2) 308.5(2)		not given	296
$Ag^I{}_8(Et_2MeCS)_8(PPh_3)_2$	m P2$_1$/*c* 4	1473.6(8) 2710.8(4) 2494(2)	99.85(3)	AgS_2 (2x)	μS	237.9(6,18)	not given *c*		172.0(2,1.2)	298
				AgS_2 AgS_3 (2x)	μ_3S μS μ_3S	237.3(5,15) 240.3(6,3) 241.2(5,15) 286.8(5,5)			173.3(2,5) 169.6(2,3.9)	
				AgS_3P (2x)	P μS μ_3S	243.5(5,1) 250.3(6,5) 264.3(5,1) 293.2(5,35)		S,S S,P	102.8(2,1.9) 115.6(2,2.5) 136.9(2,1.6)	

Table 14 *Continued*

$(PPh_4)_3\cdot$	m	1389(4)		AgS_2	μ_3S	247.8	not given		177.4(4)	299
$[Ag^I_9(SCH_2CH_2S)_6]3MeOH$	$P2_1/n$	4005(13)	93.4(3)				*d*			
	4	1678(7)		AgS_3	μS	251.2				
					μ_3S	264.6				
$[Ag_8(SC_5H_3N\text{-}3\text{-}SiMe_2\cdot$	tr	1310.3(3)	63.88(1)	AgS_3	μ_3S	248.9(3,16)	285.6(1)	S,S.	104.5(1)	289
	$P\bar{1}$	1476.6(3)	80.27(2)	(2x)	μS	253.7(2)	386.7(1)		123.3(1,6)	
$Ph)_6\cdot Ag_2(NO_3)_2\cdot(MeOH)_2]$	1	1560.0(3)	72.35(1)							
				AgNS	N	220.0(5)		N,S	150.1(1)	
				(2x)	μ_3S	240.3(2)				
				AgONS	N	220.8(5)		N,S	171.6(2)	
				(2x)	(MeOH)O	262.3(5)				
					μS	241.7(2)				
				AgONS	N	217.9(5)		O,N	84.0	
				(2x)	O_2NO	262.4(5)		O,S	107.6	
					μS	238.2(2)		N,S	167.1(2)	
				AgO_2S	μ_3S	278.4(2)		O,O	139.2(2)	
				(2x)	O_2NO	239.5(8,35)		O,S	107.6(2,13.3)	
$Ag^I_{14}(Bu^tS)_{14}(PPh_3)_4$	tr	1352.3(8)	79.86(4)	AgS_2	μS	237.9(8,37)	309(1)		172.4(3,2.3)	298
	$P\bar{1}$	1385.2(7)	86.08(4)	(10x)			314(1)			
	1	2180.8(12)	85.75(4)				97.9(3,9.7)			
				AgS_2P	P	245.4(8,6)		S,S	118.2(3,1)	
				(4x)	μS	253.9(9,56)		S,P	120.2(3,10.5)	

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns. [c]Ag-S-Ag = 88.8(2,10.4) and 128.4(2)°. [d]Ag-S-Ag = 78.2 and 116.6(3,2.4)°; Ag-μ_3S-Ag = 76.1 and 150.3°.

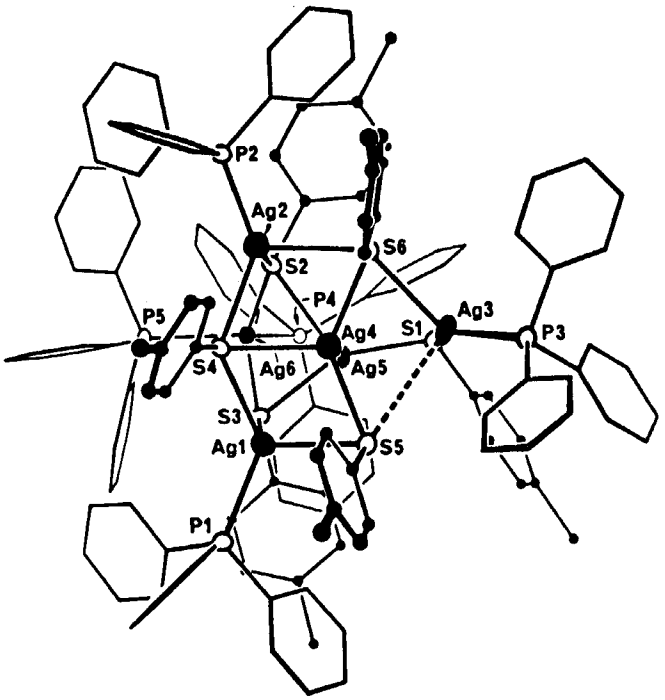

Figure 3

mean Ag-S(terminal) distances (245.9 pm) are shorter than the Ag-S(bridge) value of 250.0 pm. In another example, light yellow $[Ag(Et_2NCS_2)]_6$, six silver atoms form a bent chain.[286] Four silver atoms are connected to three sulphur atoms (AgS_3) and the remaining two have four sulphur donors (AgS_4).

The structure of colourless $Ag_6(4\text{-}ClC_6H_4S)_6(PPh_3)_5$[287] is shown in Figure 3. The structure contains a $Ag_6(SR)_6$ central cage with PPh_3 terminal ligands at three of the silver atoms and a $Ag(PPh_3)_2$ appendage inserted between two bridging thiolates. There are four non-equivalent silver(I) atoms (Table 14). The Ag–Ag distance ranges from 287.5(2) to 318.9(2) pm with a mean value of 301.5 pm.

A yellow derivative[289] possesses a centre of symmetry at the centroid of the Ag_6S_6 "drum", with a *pseudo*-three-fold axis passing through the centroids of the Ag_3S_3 rings. The $-C_5H_5N(SiMe_2Ph)$ fragments of the ligands provide the six links between the rings such that three thiolate and three pyridine donors ligate alternately to each ring. A similar structure was found in another example[290] (Table 14). A colourless hexanuclear derivative[292] has each silver atom tetrahedrally surrounded by iodine atoms with all the tetrahedra doubly edge-shared.

There are five examples of the octanuclear silver cluster. The molecular structure of a pale yellow example[294] consists of eight coplanar silver atoms linked through arenethiolate (RS) and arylthiocarbonate ($RSCS_2$) ligands. The structure of another

two octanuclear clusters[297,295] also consists of a ring of eight units of alternating silver and sulphur atoms.

The structure of a yellow decanuclear cluster[289] is shown in Figure 4. There is a crystallographically imposed centre of symmetry at the midpoint of the Ag(1)...Ag(1a) vector, with five chemically and crystallographically unique silver sites (Table 14). The structure of a colourless tetradecanuclear cluster, shown in Figure 5,[298] consists of a single 28-membered ring of alternating silver and sulphur atoms, with ten linear S-Ag(dig)-S segments and four angular segments in which phosphine ligands are attached to give trigonal-planar coordination of Ag(trig).

The data in Table 14 reveal that the "soft" sulphur donor ligands are by far the most common in this series. The silver atoms are found in digonal, trigonal and tetrahedral arrangements. The mean Ag-L distances increase with increasing coordination number. For example, the μ-S bidentate ligands are in the order: 238.2 pm (digonal) < 248.0 pm (trigonal) < 250.8 pm (tetrahedral); for the unidentate P ligands the order is: 245.4 pm (trigonal) < 247.1 pm (tetrahedral); for the μ_3-S ligands the order is: 261.6 pm (trigonal) < 278.7 pm (tetrahedral).

7. POLYNUCLEAR SILVER COMPOUNDS

7.1. Coordination number two

The structural data for these compounds are given in Table 15. Some of the derivatives contain silver atoms of coordination greater than two and these are

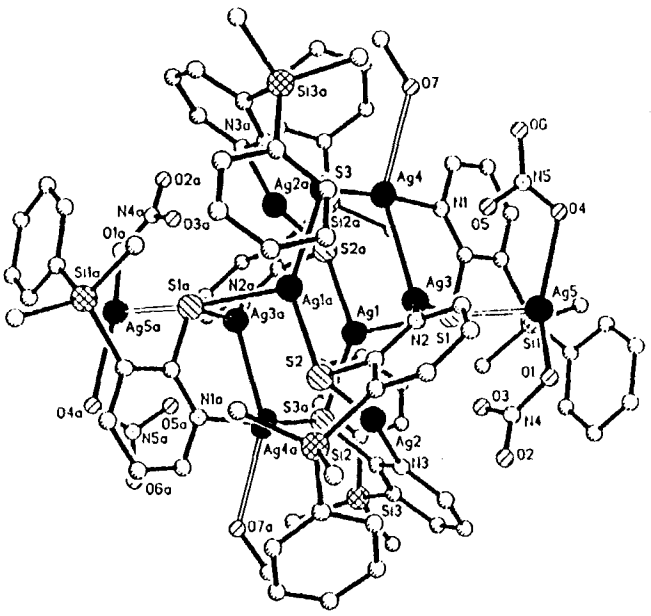

Figure 4

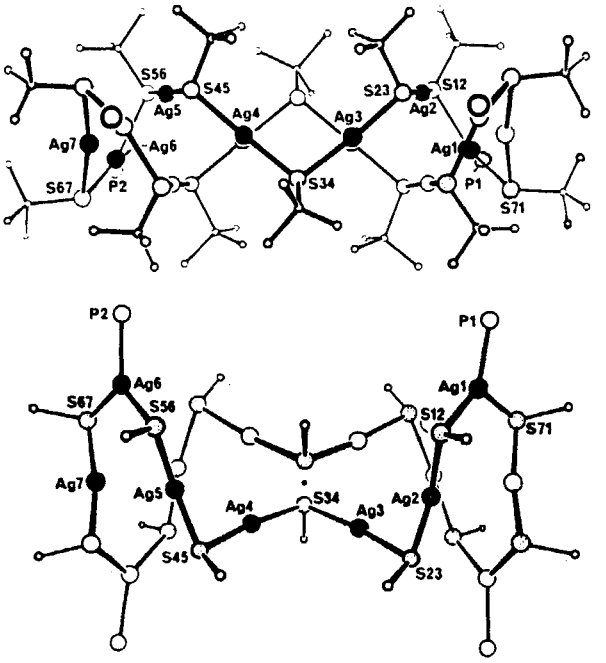

Figure 5

cross-listed to the appropriate table. The structures are arranged in order of increasing covalent radius of the ligand donor atom, and increasing atomic number of the principle coordinating ligand atom. There are fifty polynuclear examples listed in Table 15, and the "soft" nature of the silver(I) atom is reflected in the structures of the polymers. There is no straightforward classification of the structures as in the previous cases. The structure of colourless $[Ag_2(2\text{-}ClC_6H_4OCH_2CO_2)_2\text{-}Ag(ClO_4)]$[300] is shown in Figure 6. It can be seen that this polymer is based on a bis(carboxylato-O,O') bridge with a Ag–Ag distance of 280.9(1) pm, the shortests in this series of compounds. This is an unusual structure for at least two reasons. The first is the bridging of the carboxylate oxygen atom O(11B') through the axial site, with a Ag(2)–O(11B') distance of 237.3(4) pm. The second is the occupation of the other axial site by a perchlorate group (Ag(1)–O(1) = 245.4(4) pm).

In another example[302] triazenide ligands form three-atom bridges bringing the silver atoms within 283.7(1) pm. The associated N-Ag-N angles are 174.7(3)°. The structure of orthorhombic $Ag\{N(CN)_2\}$[310] consists of infinite chains -Ag-N-C-N-C-N-Ag running parallel to the *a* direction. The polymeric structure of $[Ag_{13}(MeHNC_5H_9S)_{16}]^{+13}$ [340] contains $Ag_{10}S_{16}$ units linked by three silver atoms. Each unit contains a central $Ag_6(\mu\text{-}SR)_6$ core and two $Ag_4(\mu\text{-}SR)_4$ rings, comprising digonal, trigonal and tetrahedral silver atoms, with both doubly- and triply-bridging sulphur atoms (Table 15). The $Ag\{N(CN)_2\}$ system exists as a trigonal[309] and

Table 15 Structural data for polynuclear silver compounds, coordination number two[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm] M-L-M [°]	L-M-L [°]	Ref.
$[Ag^{I}_2(2\text{-}ClC_6H_4OCH_2\cdot CO_2)_2\cdot Ag(ClO_4)]$	tr $P\bar{1}$ 2	1024.5(2) 1079.8(2) 1106.7(2)	75.27(2) 68.27(2) 82.70(2)	AgO_2 AgO_3 AgO_3	O^b O O O_3ClO	230.9(4,13) 230.0(4,73) 227.1(4,13) 245.4(4)	280.9(1) 110.6(2)	126.4(4) 76.3(2) 102.1(2,9.4) 158.1(2,1.9)	300
Ag^{I}_2(malonate)	m $P2_1/c$ 4	488.0(1) 972.5(4) 1388.3(2)	104.44(1)	AgO AgO_4	O O	214.9(7) 227.0(7,103) 266.8(7)	285.1(1)	96.6(3,16.2) 162.3(7)	301
$Ag^{I}(F_3CC_6H_4N_3C_6H_4F_3)$	m $P2_1/c$ 8	2943(2) 475.8(5) 2280(1)	111.99(6)	AgN_2	N	210.0(7,30)	283.7(1,3)	174.7(3,2.5)	302
$[Ag^{I}_3(HN_2O_2S)(NH_3)]H_2O$ (at 108 K)	or Pcam 4	1181.3(6) 966.5(5) 657.8(2)		AgN_2	H_3N N	208(1) 211(1)	312(-,22)	173.5(5,2.5)	303
$[Ag^{I}_3(SO_3N)(NH_3)_3]2H_2O$	or $P2_12_12_1$ 4	627.5(1) 1182.6(2) 1429.9(12)		AgN_2	H_3N μ_3N	213.4(15,34) 209.3(15,9)	324.7(3,134)	174.6(7,7.9)	304
$[Ag^{I}(NH_3)_2]\cdot [Ag^{I}_2(SeO_3N)(NH_3)_8]\cdot 2H_2O$	or $P2_12_12_1$ 4	1186.4(3) 1455.0(3) 643.3(2)		AgN_2 AgN_2 AgN_2	H_3N H_3N μ_3N μ_3N	213.3(10,18) 211.0(8) 211.1(8) 210.1(7,5)		170.0(4) 177.4(3) 178.7(3)	10
$[Ag^{I}(H_2NCH_2CH_2NH_2)]\cdot ClO_4$	m $P2_1/c$ 4	883.4(4) 988.5(2) 989.3(4)	125.09(2)	AgN_2 AgN_2	N N	217.1(11,1)	327.7(1)	175.8(3)	305
$[Ag^{I}(NH)]_2\cdot SO_2$	m $P2_1/c$ 4	766.1(1) 571.9(1) 1046.4(1)	93.89(2)	AgN_2	μN	213(2,1) 220(2)		172.3(-,6.9)	306
$Ag_3(Et_2SN_2)NO_3$	or Pbcn 4	681.3(2) 2152.7(6) 683.8(2)		AgN_2	N	215(-,3)		not given	307
$[Ag^{I}(C_8H_6N_2)]ClO_4$	or $Pmc2_1$ 4	721.1(2) 699(2) 2037.5(5)		AgN_2	N	220.6(3,6)		not given	164
$Ag^{I}\{N_3P_2(NH_2)_4SO_2\}$	m $P2_1/n$ 4	990.8(2 930.6(3) 1056.3(5)	108.75(5)	AgN_2	N	221.7(9) 225.5(9)		147.0(3)	308

Table 15 *Continued*

$Ag\{N(CN)_2\}$	trg $P3_12_1$ 3	360.1(2) — 2286.8(22)		AgN_2	N	211(1)	360.1		172.9(9)	309
$Ag\{N(CN)_2\}$	or Pnma 4	1613.3(8) 361.2(2) 598.3(3)		AgN_2	N	211(2,3)	361.2		177(1)	310
$[\{Ag^I(CN)_2\}_2](AsF_6)$ (at 233 K)	m C2/m 2	866.5(-) 836.3(3) 819.8(4)	122.06(3)	AgN_2	N	236.4(7) 239.9(6)			not given	311
$Ag^I(NCO)$	m $P2_1/m$ 2	547.3(9) 637.2(11) 341.6(6)	91.0(5)	AgN_2	N	211.5(8)			not given	312
$[Ag^I(C_{16}H_{14}N_2Cl_2)]\cdot CF_3SO_3$	or $P2_1ca$ 4	1230.5(3) 1273.9(4) 1322.9(9)		AgN_2	N	213.1(15) 216.4(15)			173.3(6)	316
$Li[Ag^I(succinate)_2]4H_2O$	or Pnma 4	1209.1(2) 893.4(1) 1298.1(2)		AgN_2	N	208.8(2,1)			178.48(8)	317
$[Ag^I_2(succinate)_2(H_2O)]$	m $P2_1c$ 4	803.1(4) 1330.6(7) 1034.5(2)	97.16(3)	AgN_2 AgO_4	N O H_2O	207.3(6,6) 239.3(5,55) 236.7(6)			169.0(2) 76.2- 139.3(2)	317
$Ag^I(glycinate)0.5H_2O$	m $P2_1/n$ 2	890(1) 643(1) 1535(2)	97.83(1)	AgN_2 AgO_2	N O	not given 213			172	17
$Ag^I_4(SO_2N_2)$	or $Pna2_1$ 4	1042 578(1) 895(1)		AgN_2 AgON	N O N	216(-,3) 220 214	292(-,12)		167(-,7) 173	318
$[Ag^I(C_6H_{11}N)(H_2O)_{0.5}]\cdot ClO_3$	m $P2_1/n$ 8	1281.0(2) 2471.0(5) 605.1(1)	90.0(1)	AgN_2 AgN_2O	N N H_2O	216(1,0) 227(1,1) 239(1)	89.7(5,2.8) N,N[b] N,O		172.3(5) 144.0(4) 107.6(5,1.4)	319
$Ag^I(NH_3)_2\cdot Ag(NO_2)_2$	tg $P\bar{4}$ 4	963.3(5) — 833.0(5)		AgN_2 AgN_2O	H_3N O_2N ONO	211.5(6,3) 226.7(6,42) 263.9(8,198)			178.3(3) not given	320
$Ag^I(3\text{-}SO_3py)$	tg $I\bar{4}$ 8	1231.6(2) — 900.7(3)		AgN_2 AgO_4	N O	213.9(3) 237.3(3,4)	299.7(7,15)		172.4(2) 90.10(1) 112.0(2,7.1)	321

Table 15 *Continued*

$[Ag^{I}_4\{S(NSO)_2\}_9]\cdot(AsF_6)_4\cdot SO_2$	rh R3*c* 6	1824.9(5) — 3595(2)		AgN_2 AgO_6	N O	238.1(20,60) 251.7(18,13)		154.5(7) 75.4-168.6(6)	322
$Ag^{I}(CNO)$	trg $R\bar{3}$ 6	910.9(15)	115.44	AgC_2	C	217(3,2)	282	163	323
$Ag^{I}(CNO)$	or Cmcm 4	386.4(6) 1072.2(18) 585.1(10)		AgC_2	C	223(2)	293	180	323
$Ag^{I}(CNO)$	or Cmcm 4	388.0(2) 1075.2(5) 580.4(2)		AgC_2	C	218.3(5)	290.2(1) 83.3(1)	180.0	324
$Ag^{I}_2C_2O$	tg $P\bar{4}$ 1	402.8(1) — 584.6(4)		AgC_2	C	not given	284		326
$[Ag^{I}(tmb)]BF_4$	m C2/*c* 8	2730.7(4) 803.2(2) 1570.7(5)	122.53(2)	AgC_2	C	207.3(8,2)		167.8(3)	327
$[Ag^{I}(CN)_2](ttf)$	or Pnmn 2	879.4(3) 2033.3(7) 424.7(2)		AgC_2	C	210.3(5,0)		not given	328
$Na[Ag^{I}(CN)_2]$	m C2/*c* 4	657.2(1) 371.0(1) 1734.6(2)	92.05(1)	AgC_2	C	200.9(16,0)	374.2(-,32)	180	329
$Ca[Ag^{I}(CN)_2]_2\cdot 2H_2O$	or Pbcm 4	843.5(1) 639.85(6) 1858.4(2)		AgC_2	C	206.(2,1)		180.0	330
$Sr[Ag^{I}(CN)_2]_2\cdot 2H_2O$	or Pbcm 4	800.32(8) 686.88(8) 1887.0(1)		AgC_2	C	207(2,0)		176.9(7,3.1)	330
$Ag^{I}(PhCC)(PMe_3)$	m C2/*c* 8	1150(2) 2058(3) 1212(2)	123.25(10)	AgC_2 AgC_2P_2	C C P	204.0(13,0) 255.2(14,0) 249.0(4,0)		180 C,C 107.4(6) P,P 118.4(2)	331
$[Ag^{I}\{cy(mt)_2\}ClO_4\cdot 2H_2O$	or $P2_12_12_1$ 4	2938.0(7) 1042.9(2) 602.6(2)		AgS_2	μS	239.8(7,5)		171.1(3)	332
$Ag^{I}(ET_2MeCS)$	tr $P\bar{1}$ 2	1210.5(2) 1428.9(2) 1953.9(3)	85.77(1) 87.77(1) 86.30(1)	AgS_2	μS	237(1,3)	323.2(5,346)[c] 95.0(5,9.7)	173.2(4,4.5)	333

Table 15 *Continued*

$Ag^{I}(C_6H_{11}S)$	tr	1482.7(3)	103.68(1)	AgS_2	μ_3S	240(1,4)	306.1(5,223)[d]		168(-,1)	334,
	$P\bar{1}$	1574.7(3)	107.71(1)							335
	12	1121.8(1)	91.79(1)	AgS_3	μ_3S	257(1,30)			90–154	
$[Ag_4\{(Me_3Si)_3CH_2S)_3 \cdot$	m	1702.3(3)		AgS_2	μS	247(2,17)	314.3(8,251)[e]		117.5(6,7.2)	247
$(MeO)^2]$	C2/c	2947.0(5)	104.21(1)						165.5(6,7.1)	
	16	2337.2(4)		AgS_2O	μ_3S	241(2,4)		S,S	166.1(7,2.3)	
					O	272(5,5)		S,O	not given	
Ag^{I}(glycinate)	tr	524(1)	84.21	AgON	O	211			177	17
	$P\bar{1}$	571(1)	71.33		N	214				
	2	690(1)	84.44							
α-Ag_3NSeO_3	rh	846.2(4)		AgON	O	222.9(12)			174.5(5)	336
	R3c	—			μN	216.4(8)	107.3(6)			
	2	1137.2(6)								
$NaAg^{I}(SO_3)2H_2O$	tr	594.9(5)	101.06(8)	AgOS	O	219.4(9)			169.5(2)	337
	$P\bar{1}$	927.7(9)	90.65(6)		S	247.4(4)				
	2	546.5(3)	117.29(6)							
$Ag^{I}\{CF\{CF_3)_2\}(MeCN)$	or	629.7(3)		AgNC	N	208.3(7)	320.6(1)		180	30
(at 203 K)	P2na	689.0(3)			C	210.4(11)				
	2	1993.0(10)								
Ag^{I}(SCN)	m	874		AgNS	N	222.3(28)			164.50	338
	C2/c	796	138.6		S	242.8(11)				
	8	1232								
$Ag(CN)\{Ag(NO_3)\}_2$	m	620.2		AgNC	N	not given	530		not given	339
	$P2_1/c$	1134.3	45.55		C	205.8(8)				
	2	727.4								
				AgO_7C	O	262(-,26)				
					C	258				
$[Ag^{I}_{13}(Me(H)NC_5H_9S)_{16}]$	tr	2112.9(4)	121.59(3)	AgS_2	S	240(8)	300		not given	340
$\cdot(ClO_4)_{13}$	$P\bar{1}$	2038.3(4)	114.53(4)							
	1	1517.2(3)	96.21(3)	AgS_3	S	250(7)				
				AgS_4	S	261(9)				

$Ag^{I}(2,4\text{-}Cl_2C_6H_3OCH_2CO_2)$; m, $P2_1/n$, Z = 8; a = 893(2), b = 1332.1(3), c = 1594(4) pm; β = 97.7(1)°.[300] $Ag^{I}\{4\text{-}Cl\text{-}(2\text{-}Me)C_6H_3OCH_2CO_2\}$; m, $P2_1/n$, Z = 8; a = 910.0(2), b = 1350.3(6), c = 1570.2(5) pm; β = 100.12(2)°.[300] $Ag^{I}{}_2(CN_2)$; m, $P2_1/c$, Z = 4; a = 726, b = 592, c = 661 pm; β = 102.21°.[313] Ag^{I}(NCO); m, P2/m, Z = 1; a = 552(5), b = 318(3), c = 342 pm; β = 91.7°.[314] Ag^{I}(NCO); or, lmcb, Z = 4; a = 548, b = 637, c = 682 pm.[315] Ag^{I}(CNO); or, lmca, Z = 4; a = 604, b = 388, c = 1120 pm.[325]

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns. [c]Ag-Ag range 288.6(4)–335.9(5) pm. [d]Ag-Ag range 291.1(5)-328.6(5) pm. [e]Ag-Ag range 289.2(8)-335.0(8) pm.

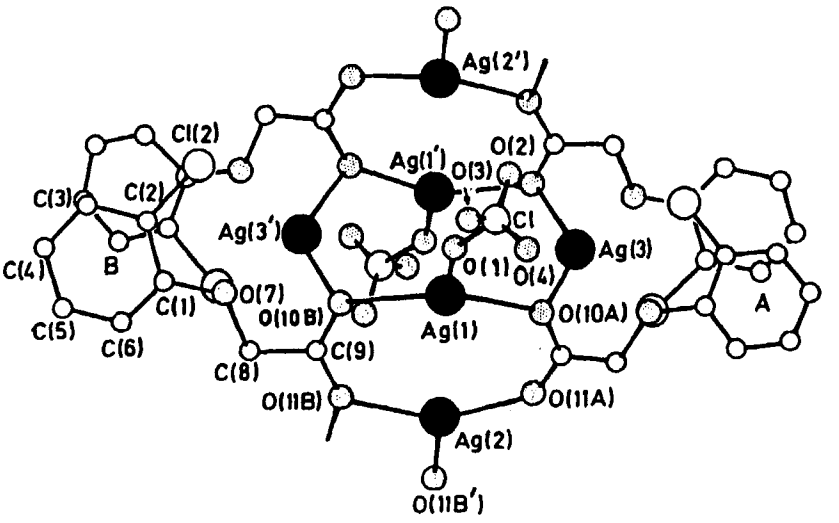

Figure 6

orthorhombic[310] modification, differing by degree of distortion. Similarly, Ag(CNO) exists in two isomeric forms[323,324] as does Ag(NCO).[312,314,315]

Bidentate ligands are by far the most common in this series. The mean Ag-L distance for the bidentate ligands increases with decreasing covalent radius of the coordinated atom in the order: 210.4 pm (C, 77 pm) < 214.5 pm (N, 75 pm) < 222.0 pm (O, 73 pm), indicating that ligand size is an important factor.

7.2. Coordination number three

These compounds are listed in Table 16 together with their structural data. Silver(I) carboxylates, based on a variation of the bis(carboxylato-O,O')-bridged dimer, were previously classified into four types.[342] Three have been found as a polymeric derivative in this survey. There are six examples of silver(I) carboxylates[261a,341,342,343] and five of them contain bis(carboxylate-bridged Ag_2) dimeric units.[261a,341,342] In some examples the dimeric units are extended stepwise into polymeric forms *via* the adjacent carboxyl oxygen atoms.[261a,341] In one of two derivatives[341] water occupies an axial coordination site. In another[342] a centrosymmetric dimer is extended into an infinite zig-zag polymer through the axial positions *via* the carbamoyl oxygens of adjacent ligands. In another[343] two different carboxylato groups of pyridinioacetate ligands bond to two different silver atoms with a third linked to a nitrate group. Each pair of adjacent silver(I) atoms are bridged in the syn-syn mode by the carboxylato group of a single pyca ligand, resulting in a zig-zag polymeric chain as shown in Figure 7. This arrangement differs substantially from all other known silver(I) carboxylates.

The shortest Ag–Ag distance of 284.2(1) pm[341] found in this trigonal silver(I) polymeric series is about 3.3 pm longer than that found in digonal derivatives

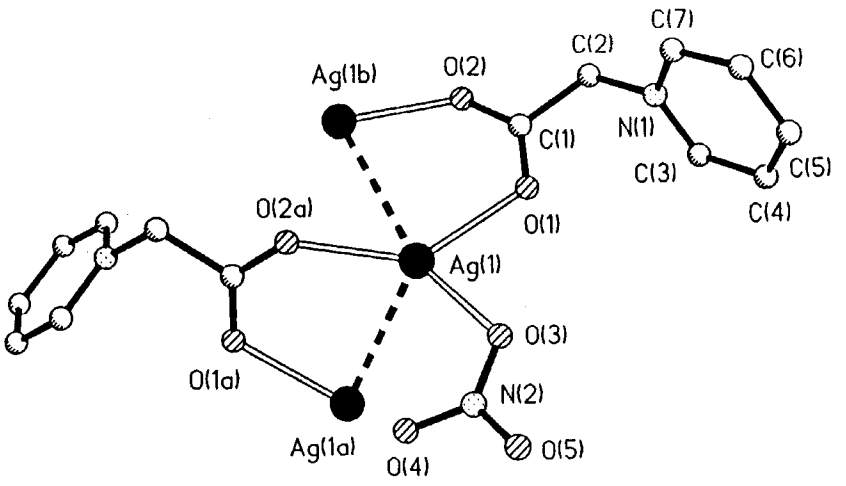

Figure 7

(Table 15). It is noted that the mean Ag-L distance in the series of bidentate ligands increases with decreasing covalent radius of the coordinated atom, as found in the digonal derivatives. The order of Ag-L is: 215.9 pm (C) < 227 pm (N) < 228.1 (O). In general, thses distances are longer than those of the digonal series above.

7.3. Coordination number four

There are over one hundred polynuclear examples, and only silver in the oxidation state of + 1 is involved. There are a few examples in which silver is found with both four and higher coordination numbers. From a bridging point of view, this series is very complex. There are four examples[341a,356] which are structurally similar, being composed of centrosymmetric syn-syn carboxylato-bridged $Ag_2(RCO_2)_2$ dimers extended into a carboxylate oxygen atom linked polymer resembling a flight of stairs. In addition, the primary coordination sphere about the silver(I) atom is completed by a nitrate oxygen atom in some cases,[241a,356] and by a perchlorate oxygen atom, and by an aquo ligand.[356] The Ag–Ag distance in this series ranges from 280.0(2) to 290.1(2) pm, indicating the existence of Ag–Ag bonds. The mean Ag-O(carboxylate) distance of 221.6 pm is shorter than that of Ag-O(bridge carboxylate) of 238.4 pm. However, the Ag–O distance of the remaining additional O-donor ligands ranges from 241.5(9) to 255.4(3) pm, respectively.

The $[AgX_2]^-$ anion (X = Cl[364] or I[371]) forms a one dimensional infinite polymeric chain composed of edge-sharing AgX_4 tetrahedra with a mean Ag-X(bridge) distance of 260.9 pm (Cl) and 278.1 pm (I), respectively. On the other hand, the $[Ag_2X_3]^-$ anion (X = Cl or Br[365a,370] or I[373,374]) contains infinite double-chains composed of edge-sharing AgX_4 tetrahedra with mean Ag-X(bridge) and Ag-X(μ_4-bridge) distances of 252.6 and 271.8 pm for Cl, 263.0 and 285.0 pm for Br and 279.7 and 296.3 pm for I, respectively.

Table 16 Structural data for polynuclear silver compound, coordination number three[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromophore		M-L [pm]	M-M [pm] M-L-M [°]	L-M-L [°]	Ref.
$[Ag^{I}_2(Me_3apr)_2$	m	570.0(1)		AgO_3	O[b]	220.6(7,12)	284.2(1)	78.3(2)	341*a*
$(H^2O)]\cdot(ClO_4)_2$	$P2_1/c$	2492.3(8)	93.25(4)		μO	257.3(6)	101.3(2,1.8)	115.2(2)	
	4	1695.2(4)						166.4(2)	
				AgO_4	O	222.6(6)		85.0(4,6.9)	
					μO	226.4(6)		120.4(2)	
						250.0(6)		160.1(2)	
					H_2O	259(1)			
$[Ag^{I}(pypr)]_2$	m	2928.8(6)		AgO_3	O	218.5(2)	285.4(1)	78.0(1)	341*a*
$(ClO_4)_2$	C2/*c*	554.76(8)	107.47(1)		μO	221.7(2)	102.0(1)	112.2(1)	
	4	1443.9(2)				249.7(2)		161.8(1)	
$Ag^{I}_2(PhOCH_2$	m	1396.2(1)		AgO_3	O	219.8(9,20)	286.6(2)	76.0(3,9)	261*a*
$CO_2)_2$	$P2_1/c$	565.2(1)	91.41(1)		μO	225.5(8,32)		120.2(3,6)	
	4	1982.7(2)				243.0(9,13)		160.2(3)	
$Ag^{I}_2(F_3CCOO)_2\cdot$	m	1525.3(5)		AgO_3	O	225(1,3)	289.3(3)	81.8,116.0(5)	341*b*
C_6H_6	A2/m	967.4(1)	95.66(1)		μO	238(1)		161.6(5)	
	8	1688.2(6)							
				AgO_3C	O	223(1)	285.1(3)	78.1	
					μO	242(1,1)		102.0(5,3.7)	
					C	242			
$Ag_2(sa)_2$	m	2078.9(6)		AgO_3	O	224.7(3,19)	300.1(1)	84.5(1)	342
	C2/*c*	520.2(1)	105.89(2)			249.4(3)		116.8(1)	
	4	1731.8(6)						155.8(1)	
$Ag^{I}(pyac)(NO_3)$	m	1284.9(2)		AgO_3	O	231.2(3,23)	301.1(1)	86.0(1)	343
	$P2_1/c$	499.9(1)	113.91(1)		O_2NO	243.4(3)		118.3(1)	
	4	1504.7(3)						139.8(1)	
$Ag^{I}(NH_3)_3(NO_3)$	tg	805.7(2)		AgN_3	H_3N	228.1(7)	292.0	not given	8
	$P\bar{6}2c$	—							
	2	584.0(6)							
$Ag\{C(CN)_3\}$	or	621(1)		AgN_3	N	211(6)		99.7(2.3)	344
	I2cm	1019(2)				225(4,0)		123.9(1.6)	
	4	798(1)							
$[Ag^{I}_2(tmb)_3]$	tr	889.6(5)	97.61(4)	AgC_3	C	215.4(5,32)		119.7(2,9.3)	327
$(PF_6)_2\cdot 2MeCN$	$P\bar{1}$	909.9(7)	92.14(4)						
	1	1646.2(6)	116.71(5)						
$[Ag^{I}(tht)_2]BF_4$	or	749.7(2)		AgS_3	S	250.6(2,61)		119.9(1,4.8)	345a
	$P2_12_12_1$	1143.2(3)							
	4	1524.9(3)							
$[Ag^{I}\{(SCH_2)_3\}_2]$	m	857.9(2)		AgS_3	S	252.4(3,9)		102.2(1,1.6)	141
AsF_6	$P2_1/c$	2061.8(4)	107.95(2)			276.4(3)		153.4(1)	
	4	986.1(2)							
$(PPh_4)[Ag(Se_4)]$	m	1414.5(3)		$AgSe_3$	Se	255.3(2)	451.8(3)	110.4(2,3.8)	263
	$P2_1/c$	707.6(2)	105.23(2)		μSe	260.9(2,64)	119.71(1)	138.80(2)	
	4	2493.9(5)							
$Ag^{I}(B_{11}CH_{12})$	or	1021.1(3)		AgH_2C	H	197		not given	345b
$(C_6H_6)_2$	$Pb2_1a$	2080.6(3)			C	240.0(3)			
	4	914.6(1)							
Ag(saca)	m	584.9(2)		AgO_2N	O	237.2(5,36)	310.2(1)	not given	346
	$P2_1/n$	772.0(5)	83.16(1)		N	221.8(5)			
	4	2257.3(5)							
$NaAg^{I}(NO_2)_2$	or	760.7(1)		AgO_2N	O	240.6(3)		not given	347
(at 118(1) K)[c]	Fd2d	1066.5(1)				270(1)			
	8	1094.5(1)			N	223.9(5)			

Table 16 *Continued*

$(bet)_2[Ag^I$	m	1259.3(3)		AgC_2N	C	208.6(5,2)	C,O[b]	157.3(2)	348
$(CN)_2]H_2O$	$P2_1$	864.2(1)	109.32(2)		N	256.4(6)	C,N	101.4(2,3.7)	
	2	1608.0(3)							
Ag^I(Mead)	m	1440.5(14)		AgN_2O	O	258(1)	N,N	94.4(-,8.7)	353
$(NO_3)H_2O$	$P2_1/c$	739.7(8)	122.13(5)		N	216.3(9,20)	N,O	171.1	
	8	2336(2)							
Ag^I(2,6-Me_2py)	m	848.1(3)		AgN_2S	N	227.5(1)		not given	354
(SCN)	$P2_1/c$	810.2(2)	97.41(3)						
	4	1367.6(7)			SCN	228(1)			
					NCS	247.4(3)			
Ag^I(tsc)$_2$(NCS)	or	1149.5(7)		AgS_2N	S	243.9(3)	S,S	123.3(1)	194
	$Pna2_1$	1504.9(7)			μS	245.6(3)	S,N	118.3(3,1.0)	
	4	660.1(4)			SCN	231.2(12)			

α-$(bet)_2Ag(CN)_2$; m, $P2_1/n$, 2; a = 795.6(2), b = 673.2(3), c = 3073.8(8) pm; β = 90.05(1)°.[349] $(bet)_2Ag(CN)_2$; or, $P2_12_12_1$, 2; a = 951.9(2), b = 495.2(1), c = 3392.7(7) pm.[350] $(bet)_2Ag(CN)_2$; m, $P2_1/n$, 2; a = 1099.6(1), b = 428.1(1), c = 3409.3(5) pm; β = 93.13(2)°.[350] $(bet)_2Ag_4(CN)_5$; or, Fddd, 8; a = 1324(1), b = 1948(2), c = 1962(2) pm.[351] $(bet)_2Cu(NCS)_2$; m, $P2_1$, 2; a = 1624.8(5), b = 844.0(2), c = 1312.4(5) pm; β = 110.30(3)°.[352] Ag^I(tu)(SCN); m, C2/c, 8; a = 1032(2), b = 1388(2), c = 1411(2) pm; β = 111.48°.[355] [a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns. [c]X-ray analysis was taken also at 218, 268, 297, 308, 323, 334 and 343 K. [d]The Ag-Ag distance ranges from 306.0(3) to 340.2(3) pm.

The chain in the $[Ag_3I_4]^-$ anion[179,375,376] and $[Ag_3I_3X]$ (X = Cl or Br[376] is built up from AgX_4 tetrahedra sharing one edge, and these units are joined to other similar units *via* the free corners. Every tetrahedron contains one Ag(I) atom, but the octahedral sites defined by adjacent pairs of double tetrahedra are only occupied alternately by Ag(I) atoms. The mean Ag-X(μ-bridged) distance increases with the covalent radius of X in the sequence: 262.3 pm (Cl, 99 pm) < 271.6 pm (Br, 114 pm) < 279.5 pm (I, 133 pm). There are only μ_3- and μ_4-bridged iodine atoms with mean Ag–I distances of 285.3 and 293.8 pm respectively. It can be seen that the mean Ag–I distance elongates with the degree of multiple bridging as might be expected.

A "stair" type polymer was found in fifteen derivatives of the composition AgLX, where L is unidentate N donor ligands and X is Cl, Br or I.[197,266,268,402,403] This represents the largest series of structurally related derivatives in the silver(I) polynuclear complexes. The Ag(I) atoms are tetrahedrally coordinated (AgX_3N), with the mean Ag-X(μ_3-bridge) distances increasing with the covalent radius of X, in the order: 267.5 pm (Cl) < 274.8 pm (Br) < 287.4 pm (I), respectively. The mean Ag–N distance increases with the increase in covalent radius of the X atom, in the order: 223.5 pm ($AgCl_3N$) < 225.4 pm ($AgBr_3N$) < 234.2 pm (AgI_3N), which reflects the increase in steric crowding. There is an interdependence between the mean Ag–Ag distance and the Ag-X-Ag bridge angle, the former elongating as the latter opens (Table 17).

There are three derivatives of the type Ag(dea)X (X = Cl, Br or I)[266] which are tube-like polymers. The structures of the "stair" type Ag(2-Mepy)I[266] and the "tube" type Ag(dea) I polymers are shown in Figures 8 and 9 for comparison. The mean Ag-X(μ_3-bridge) distance expands with covalent radius of X in the order: 270.0 pm (Cl) < 276.6 pm (Br) < 287.4 pm (I). It is noted that while the mean values for the Cl and Br bonds are longer than those found in the "stair"-type

Table 17 Structural data for polynuclear silver compounds, coordination number four[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]	M-M [pm] M-L-M [°] μL-M-μL [°]		L-M-L [°]	Ref.
$[Ag^{I}(Me_3apr)(NO_3)]_2$	m	1831.9(6)		AgO_4	O[b]	221.8(4)	280.0(2)	O,μO[b]	87.7(2,8.5)	341*a*
	C2/*c*	1244.0(4)	119.83(2)		μO	223.5(3)	92.1(2)		153.6(2)	
	4	1047.9(2)				258.8(5)	87.9(2)	O,O	118.0(2)	
					O_2NO	249.9(7)				
$[Ag^{I}(PhNCH_2CO_2)(ClO_4)]_2$	m	536.6(1)		AgO_4	O	221.1(6)	281.4(2)	O,μO	100.8(3,7.2)	356
	$P2_1/c$	1513.3(3)	99.54(2)		μO	222.0(6)	96.9(2)		159.5(2)	
	2	1304.1(4)				244.6(7)	83.1(2)	O,O	92.9(3)	
					O_3ClO	241.5(9)				
$[Ag^{I}(Me_3aca)(H_2O)]_2 \cdot (NO_3)_2$	m	565.9(1)		AgO_4	O	224.1(3)	289.8(1)	O,μO	85.3(1,1)	356
	$P2_1/c$	1581.3(2)	98.10		μO	233.4(3)	96.0(1)		115.8(1)	
	2	1154.9(2)				249.7(3)	84.0(1)		154.7(1)	
					H_2O	255.4(3)		O,O	110.6(1)	
$[Ag^{I}(pypr)(NO_3)]_2$	m	2943(2)		AgO_4	O	219.4(4)	290.1(2)	O,μO	102.2(1,6.2)	341*a*
	C2/*c*	537.1(3)	107.83(1)		μO	221.6(4)	98.4(2)		161.0(1)	
	4	1381.3(6)				255.2(4)	81.6(2)	O,O	99.6(2)	
					O_2NO	251.1(5)				
$[Ag^{I}(pycac)]H_2O$	m	1223.3(6)		AgO_4	O	232.1(5,37)	312.4	O,μO	82.7(2,4.5)	357
	$P2_1/c$	504.9(1)	94.96(4)		μO	237.4(5)	78.3(1)		133.3(2)	
	4	1441.8(7)				257.0(5)	122.1(2)	O,O	128.9(2)	
$Ag^{I}\{PO_2(OEt)_2\}$	or	2019(1)		AgO_4	O	219.1(8)			103.9(2,13.0)	358
	Pccn	1435(4)				230.3(5)			130.4(3)	
	2	586(1)				246.7(-,8)				
$[Ag^{I}\{NC(CH_2)_4CN\}_2]ClO_4$	tg	907(3)	—	AgN_4	N	228(3)			110.1(5,2.1)	359
	$P42_1c$	—								
	2	1027(4)								
$[Ag^{I}\{S_3(CN)_2\}_2]AsF_6$	tg	1051.0(5)	—	AgN_4	N	228.8(11,14)			109.5(5,7.0)	360
	$P4_2/mnm$	—								
	4	1527.0(2)								
$[Ag^{I}\{S_4(CN)_2\}_2]AsF_6$	tg	838.1(2)	—	AgN_4	N	228.8(7,0)			not given	360
	P4									
	1	666.1(2)								
$[Ag^{I}(dmb)_2]PF_6$ (at 183 K)	or	930.3(3)		AgC_4	C	not given	496.4(1)		not given	361
	$P2_12_12_1$	1410.6(1)								
	4	2226.5(1)								

Table 17 *Continued*

$[Ag^I(C_{10}H_{12})(SO_3CF_3)]$	m	1017.7(9)		AgC_4	C	241		C,C	55.6(1)	362
	$P2_1/n$	976.3(4)	91.20(6)					O,O	71.2(1)	
	4	1322.1(9)		AgC_4O_2	O	231–237		C,O	131.2(1)	
$[Ag^I(C_{12}H_{16})(SO_3CF_3)]$	or	903.8(4)		AgC_4	C	241		C,C	30.4(3)	362
	$P2_12_12_1$	999.1(4)						O,O	80.7(3)	
		1673.1(8)		AgC_4O_2	O	231-237		C,O	138.8(3)	
$[Ag^I(C_{14}H_{20})(SO_3CF_3)]$	or	920.6(4)		AgC_4	C	241		C,C	not given	362
	$Pna2_1$	1041.8(5)						O,O	82.3(1)	
	4	1855.8(9)		AgC_4O_2	O	231-237		C,O	146.5(1)	
$(NEt_4)[Ag^I_2Cl_3]$	or	2077.3(5)		$AgCl_4$	μCl	252.6(2,16)	343.4(2,86)			363
	Pnma	1189.5(3)			μ_4Cl	271.8(2,6)	80.2(1,6.5)[c]			
	12	1668.3(3)					109.5(7,13.4)			
$(NMe_4)[Ag^ICl_2]$	or	882.5(3)		$AgCl_4$	μCl	260.9(1,10)	328.5(1,148)			364
(at 170 K)	Immm	1452.6(4)					78.1(1,3.9)			
	4	657.0(2)					109.5(1,3.8)			
$[Ag^I(qu)Cl]0.25(qu)$	m	3050.8(5)		$AgCl_4$	μ_3Cl	261.5(4,15)	344.9(3,319)			365
	C2/c	721.6(1)	122.11(7)				95.1(3,3.0)			
	4	2269.8(5)		AgN_2Cl_2	N	228(1,1)	105.7(1,19.3)	N,N	125.0(5)	
					μ_3Cl	272.9(4,5)		Cl,Cl	109.8(1,14.8)	
								N,Cl	106.6(3,7.7)	
$Ag^I_2(PhCS_2)_2$	m	782.3(7)		AgS_4			289.0			366
		632.4(7)	95.18(9)							
		1470.7(19)								
β-$Ag^I(Et_2tsc)$	m	1840.6(3)		AgS_4	S	253.6(3,25)	313.3(2,302)		65.5(1,1.1)	367
	C2/c	972.6(2)	104.79(3)		μS	269.8(3,40)	84.5(1,25.9)		116.1(1,13.6)	
	12	1430.(4)				295.1(3)				
$[Ag^I_2(htcod)(pic)](picH)$	m	1457.9(7)		AgS_4	S	253.2(2,93)	347.9(2)	S,μS	93.2(1,8.9)	368*a*
	$P2_1/c$	1603.0(5)	110.67(3)		μS	261.7(2,54)	76.88(3)[d]		132.4(1,2.9)	
	4	1598.5(8)					81.33(4)	S,S	112.99(4)	
				AgS_4O	O	248.1(3)		S,μS	95.0(1,15.9)	
					S	254.9(1,9)		S,S	132.74(5)	
					μS	289.0(2,115)	149.25(4)	μS,O	82.0(1,8)	
								S,O	92.25(7)	
									134.99(7)	
$(NH_4)[Ag^I(SCN)_2]$	m	402		AgS_4	S	247.4(20)			not given	368*b*
	$P2_1/n$	2386	96.08							
	4	723								

Table 17 *Continued*

$(C_{18}H_{24}N_3O_3)[Ag^I_5Br_8]$	m	2884(1)		$AgBr_4$	μBr	271.0(7,43)	327.8(6,198)			369
	C2/*c*	635.0(2)	108.25(3)		μ_3Br	271.8(7,21)	84.5(2,33.1)			
	8	3648(1)					109.5(2,8.7)			
$(NMe_4)[Ag^I_2Br_3]$	or	1703.6(3)		$AgBr_4$	μBr	262.5(2,13)	337.1(3,293)			370
	Pnma	703.5(1)			μ_4Br	289.8(2,14)	83.5(1,28.6)			
	4	970.2(1)					109.6(8,12.7)			
$(NEt_4)[Ag^I_2Br_3]$	or	2116.1(7)		$AgBr_4$	μBr	263.6(2,6)	343.4(2,184)			365a
	Pnma	1220.7(3)			μ_4Br	280.3(2,41)	77.1(1,7.5)[e]			
	12	1720.8(4)					109.5(1,11.9)			
$(NMe_4)[Ag^I(Se_5)]$	m	1135.0(2)		$AgSe_4$	Se	270.2(2,54)	378.6(4)	Se,Se	94.03(7)	263
	Cc	1876.4(3)	124.59(1)		μSe	265.2(3,19)	91.11(7)	Se,μSe	111.1(1,11.2)	
	4	743.4(1)					115.40(7)			
$(NEt_4)[Ag^I(Se_5)]$	m	1135.0(2)		$AgSe_4$	Se	270.2(2,54)				263
	C*c*	1876.4(3)	124.59(1)		μSe	265.2(3,19)				
	4	743.4(1)								
$(NMe_4)[Ag^I I_2]$	or	922.8(3)		AgI_4	μI	278.1(3,25)	not given			371
	Immm	1535.3(6)					—			
	4	689.9(3)					109.7(-,10.4)			
$Sr[Ag^I_2I_4]\cdot 8H_2O$	tg	1286(3)		AgI_4	μI	287.9(2)	278(1)		not given	372
	1422	—								
	2	556(2)								
$(NH_4)_2[Ag^I I_3]$	or	2120(2)		AgI_4	I	284.6(3,19)	not given	I,μI	105.86(6)	373
	Pbnm	1084(1)			μI	285.9(2)	105.86(6)	I,I	110.7(1,1.1)	
	4	462.9(3)					108.08(7)			
$(NMe_4)[Ag^I_2I_3]$	or	1776.0(7)		AgI_4	μI	279.4(2,14)	not given			373
	Pnam	1007.7(4)			μ_4I	296.6(2)	76.8(1,15.0)[f]			
	4	743.1(2)					109.7(1,10.8)			
$(NMe_4)[Ag^I_2I_3]$	or	1777(1)		AgI_4	μI	280(-,3)	303			374
	Pnam	1007(3)			μ_4I	296(-,4)	not given			
	4	743.7(5)					109.7(-,10.4)			
$(NBu_4)[Ag^I_3I_4]$	m	945(1)		AgI_4	μI	276.7(8,5)	334.2(9,329)			375
	$P2_1/c$	1577(2)	101.08(15)		μ_3I	284.6(8,63)	59.2(2,1.6)			
	4	1888(2)			μ_4I	303.2(8,77)	112.0(2,27.3)			
$(PPh_4)[Ag^I_3I_4]$	m	1338.0(5)		AgI_4	μI	279.9(2,3)	322.7(3,136)			179
	$P2_1/c$	2653.6(5)	108.09(4)		μ_3I	287.5(2,97)	67.8(6,6.0)[g]			
	4	850.4(4)			μ_4I	294.2(2,18)	107.3(1,1.3)			
$(AsPh_4)[Ag^I_3I_4]$	m	1344.8(7)		AgI_4	μI	280.3(4,5)	324.8(5,133)			179
	$P2_1/c$	2672.3(4)	107.99(4)		μ_3I	287.8(4,88)	68.2(1,6.0)[h]			
	4	854.6(4			μ_4I	294.7(4,17)	107.1(1,1.5)			

Table 17 *Continued*

$(AsPh_3Me)[Ag^I_3I_4]$	m	1278.3(4)		AgI_4	μI	281.2(2,12)				376
	$P2_1/c$	2580(1)	108.36(5)	$(2x)_n$	μ_3I	289.4(2,57)	66.5(1,5.0)[l]			
	4	838.8(7)			μ_4I	291.7(2,1)	109.5(1,8.8)			
				AgI_4	μ_3I	282.0(2,12)		I,I	108.8(1,18.2)	
				$(1x)_n$	μ_4I	294.2(3,12)				
$(AsPh_3Me)[Ag^I_3I_3Cl]$	m	1244.8(2)		AgI_3Cl	μCl	262.3(9,32)		I,I	109.9(1,4.3)	376
	$P2_1/c$	2533.9(6)	109.96(1)	$(2x)_n$	μ_3I	286.8(4,57)	67.0(1,2.5)[l]	I,Cl	109.0(2,11.1)	
	4	837.2(1)			μ_4I	288.7(4,12)				
				AgI_4	μ_3I	280.6(4,15)		I,I	108.6(1,17.6)	
				$(1x)_n$	μ_4I	293.3(4,19)				
$(AsPh_3Me)[Ag^I_3I_3Br]$	m	1255.1(3)		AgI_3Br	μBr	271.6(2,17)		I,I	110.3(1,2.4)	376
	$P2_1/c$	2563.1(9)	108.75(2)	$(2x)_n$	μ_3I	287.7(2,56)	66.6(1,2.7)[k]	I,Br	108.7(1,9.8)	
	4	839.0(2)			μ_4I	289.8(2,4)				
				AgI_4	μ_3I	281.5(2,14)		I,I	108.7(1,17.8)	
				$(1x)_n$	μ_4I	294.3(2,18)				
$(TeEt_3)[Ag^I_4I_5]$	m	1233.4(5)		AgI_4	μ_3I	285.4(4,137)	335.8(4,2.18)			377
	$P2_1/c$	2131.5(7)	104.0(3)		μ_4I	292.0(3,110)	70.0(1,4.6)[l]			
	4	833.3(3)					110.2(1,12.7)			
$(pip)[Ag_4I_6](dmso)_4$	tr	1296(2)	93.8(2)	AgI_4	μ_nI	287(2,9)	327			378
	$P\bar{1}$	1154(2)	100.7(3)				not given			
	1	654(1)	104.2(3)				109.4(2,5.9)			
$(pip)[Ag_{10}I_{12}](dmf)_4$	m	1452(7)		AgI_4	μ_nI	287(1,13)	325(2,10)			379
	$P2_1/c$	2506(9)	100.3(4)				not given			
	2	784(4)					109.2(3,14.0)			
$(C_9H_{24}N_2)_2[Ag_{21}I_{25}]$	m	2246(2)		AgI_4	μ_nI	285(-,46)				380
	C2/c	1297(2)	104.15(5)							
	4	3059(2)								
$(C_{11}H_{30}N_3)_3[Ag_{44}I_{53}]$	m	614.0(4)		AgI_4	μ_nI	287(9,49)				381
	C2/c	1369(2)	108.71(5)							
	4	2223(2)		AgI_5	μ_nI	322(6,43)				
$(pyH)[Ag^I_5I_6]^m$	or	1703(2)		AgI_4	μ_nI	282(1,17)				382
	P6/mcc	—								
	2	743(1)		AgI_6	μ_nI	314.0(1)				
$Ag^I_2(PhCO_2)_2(py)_2{}^n$	m	2433.7(6)		AgO_3N	N	237(1)	285.6(2)	O,O	83.7(3)	383
	$P2_1/c$	573.3(1)	110.54(2)		O	226(1,3)	96.3(4)		114.3(4)	
	4	1028.7(6)			μO	250(1)			141.6(4)	
								O,N	101.2(5,11.4)	
				AgO_3N	N	233(1)	290.2(2)	O,O	86.0(4)	
					O	229(1,2)	94.0(4)		113.2(3)	
					μO	253(1)			135.5(5)	
								O,N	103.2(4,13.6)	

Table 17 *Continued*

$[Ag^{I}(pef)(H_2O)]3H_2O$	tr	871.5(1)	69.17(1)	AgO_3N	N	243.1(3)	290.1(1)	O,O	140.8(2)	384
	$P\bar{1}$	988.5(1)	67.54(1)		O	230.7(3,22)		H_2O,O	95.4(1,9.5)	
	2	1381.2(1)	84.69(1)		H_2O	245.4(4)		O,N	108.1(2,10.7)	
								H_2O,N	93.8(2)	
$Ag^{I}_3(NSO_2)_3 \cdot 3H_2O$	trg	1056.3(5)		AgO_3N	N	237.6(5,52)	303.2(1)		not given	385
	P31*c*	—			O	250.0(6,17)				
	2	536.8(5)				266.0(6)				
$Ag^{I}(Mecy)(NO_3)$	tr	1047.4(3)	97.33(2)	AgO_3N	N	222.5(2)	350.6(1,136)	O,O	95.1(2)	386
	$P\bar{1}$	1114.1(3)	95.82(2)		O	236.7(2)			160	
	2	364.2(1)	76.76(2)		O	256.4(3)		O,N	136.2(2)	
					O_2NO	246.4(3)				
$Ag^{I}(pta)$	or	2677.2(8)		AgO_3S	O	223.0(4)	342.5(1)	O,μO	87.9(1)	387
	Pccn	1047.9(3)			μO	248.1(3,27)	not given		133.3(1)	
	8	600.7(1)			S	251.3(2)	79.0(1)	μO,S	75.2(1)	
									118.7(1)	
								O,S	146.6(1)	
$Ag^{I}(PPh_3)(NO_3)$	m	1065.9(2)		AgO_3P	P	236.9(2)		O,O	48.3(2,1.4)	388
	$P2_1/c$	1855.8(4)	100.39(1)		O	240.0(7,38)			89.1(2,7.1)	
	4	904.5(1)				262.8(7)			118.8(2,8.8)	
$Ag^{I}_2(dpae)(NO_3)_2$	m	1994.2(20)		AgO_3As	O	233(3)		O,O	50.6(8)	103
	$P2_1/c$	815.9(5)	109.8(1)			256(3.3)			81.4(9,6)	
	4	1806.5(23)			As	244.4(6)		O,As	103.9(7)	
									135.7(7,2.1)	
				AgO_4As	O	247(3,1)		O,O	47.1-	
						268(3,5)			155.5(1)	
					As	250.2(6)		O,As	105.2(7,8.7)	
									134.2(9)	
$Ag^{I}(C_{10}H_9N_4O_2S)$	m	617.2(5)		AgN_3O	N	224(1,0)	291.6(2)	N,N	106.5(2,7.2)	389
	$P2_1/c$	960.5(8)	96.60(8)			245(1)		N,O	80(1,6)	
	4	2033(2)			O	254(1)			128(1)	
$Ag^{I}(C_{10}H_9N_4O_2S)$	m	617.3(2)		AgN_3O	N	224.1(6,36)	291.6(1)	N,N	106.5(2,7.2)	390
	$P2_1/c$	960.0(5)	96.22(8)			245.9(6)			137.6(2)	
	4	2030(2)			O	257.1(6)		N,O	78.9(2,5.2)	
									129.3(2)	
$Ag^{I}\{C(CN)_2\}NO$	or	1172.9(14)		AgN_3O	N	216(3)		N,N	103.2(1.0,8.1)	391
	Pbca	1029.9(4)				233(3,3)			128.2(1.5)	
	8	786.8(5)			O	243(3)		N,O	107.7(2.0,10.2)	

Table 17 *Continued*

$Ag^I(qu)_2(SCN)$	or	1597.7(4)		AgN_3S	quN	236.3(4,2)			119.6(1)	354
	$P2_12_12_1$	1354.4(4)			SCN	233.2(5)				
	4	800.9(2)			NCS	249.5(1)				
$Ag^I{}_2(tmb)_3(ClO_4)_2$	tr	895.1(5)	93.54(7)	AgC_3O	C	213.9(12,23)		C,C	118.7(4,9.9)	392
	$P\bar{1}$	901.8(9)	90.73(5)		O_3ClO	273.3(13)		C,O	96.9(4,8.6)	
	1	1550.0(10)	115.86(6)							
$Ag^I(C_3H_6S_3)_2(NO_3)$	or	1252(1)		AgS_3O	S	255(2,9)		S,S	118.2(5,17.8)	393
	$Pca2_1$	911(1)			O	271(5)		S,O	97.8(1.1,8.4)	
	4	1283(1)								
$[Ag^I(C_3H_6S_3)(NO_3)]H_2O$	or	1145(3)		AgS_3O	S	262(1,7)		S,S	119.3(2,28.9)	394
	Pacb	963(3)			O_2NO	248(2)		S,O	94.8(5,16.6)	
	8	696(4)								
$Ag^I(C_3H_6S_3)(NO_3)$	m	2381(6)	97.8(3)	AgS_3O	S	265(2,5)		S,S	118.0(2,13.2)	394
	$P2_1/n$	1283(4)			O	279(5)		S,O	81.4(1.1,6.4)	
	8	583(3)								
				AgO_3S_2	S	265(2,2)				
					O	262(6,11)				
$[Ag^I(C_3H_6S_3)(H_2O)]\cdot$	m	602(2)		AgS_3O	S	258(1,6)		S,S	113.7(3,1.8)	394
ClO_4	$P2_1/m$	1082(3)	80.4(3)		H_2O	248(2)		S,O	104.1(5,22.8)	
	4	1624(4)								
$NaAg^IS_2O_3(H_2O)$	m	778(1)		AgS_3O	S	255(1,10)		S,S	115.3(5,11.6)	395
	Pc	907(1)	96.3(2)		H_2O	269(2,7)		S,O	92.2(8,13.3)	
	4	771(1)								
$[Ag^I(C_9H_{18}S_3)$	or	860.1(1)		AgS_3O	S	247.0(2,7)		S,S	104.5(1,5.9)	96
$(CF_3SO_3)]\cdot MeCN$	$P2_12_12_1$	1422.4(3)				262.1(2)			140.92(6)	
	4	1609.8(2)			O	248.3(6)		S,O	98.6(2,8.6)	
$\{Ag^I{}_2(SCN)_4\}$	m	1203.2(3)		AgS_3N	N	230.7(5)		S,S	115.0(1,7.9)0	396
$C_{18}H_{36}N_4$	$P2_1/n$	728.8(4)	90.44(4)		S	250.1(1,25)		S,N	79.5(4)	
	2	1693.3(4)				287.1(1)			112.0(1,1.8)	
$Ag^I(tsc)_2(SCN)$	or	1144(1)		AgS_3N	S	246(1,3)			not given	397
	$Pna2_1$	1496(3)			NCS	299(1)				
	4	657(1)			SCN	224(3)				
β-$Ag^I(SCN)$	or	408.3(1)		AgS_3N	S	266.4(15,23)	not given	μS,S	100.0(4,1.2)	398
	Pmnn	704.3(1)			N	200(5)	116.3(4,15.1)	S,N	98.4(1,12.0)	
	4	1121.9(1)								
$Ag^I(tu)_2Cl$	m	3670(4)		AgS_3Cl	S	247(5,4)	313.4(2)	μS,S	112.0(1,16.5)	399
	$P2_1/a$	824(1)	92.50(15)		μS	253.6(5,52)	77.3(2)°	μS,Cl	102.0(1,4.1)	
	8	587(1)			Cl	294.5(5,91)	110.3(11,3)	S,Cl	94.9(1,10.7)	

Table 17 *Continued*

$Ag^{I}_2(tsc)_3Br_2$	m	857(5)		AgS_3Br	S	237(-,1)	320		not given	400
	$P2_1$	2227(4)	92.5(3)		μS	278(-,32)				
	2	430(1)			Br	267(-,1)				
$Ag^{I}_2(tsc)_3Br_2$	m	431.9(1)		AgS_3Br	S	243.7(9,1)	325.2(7)	S,μS	100.9(3,1.2)	194
	$P2_1$	2247(4)	96.62(4)		μS	252.7(9,2)	72.1(3,8.0)			
	2	870.7(4)				306.2(8,45)				
					Br	267.0(6,37)				
$Ag^{I}(C_{12}H_{24}S_6)Br$	tr	1035.9(1)	115.72(1)	AgS_3Br	S	257.4(1,62)		S,S	85.7(1)	96
	$P\bar{1}$	1042.0(1)	115.56(1)		Br	263.6(1)			122.4(1,5.5)	
	2	1131.1(2)	82.62(1)					S,Br	107.9(1,2.3)	
$Ag^{I}(tsc)Cl$	or	1193(1)		AgS_3Cl	S	250(1,2)		S,S	98.5(2,2.8)	401
	$P2_12_12_1$	2486(5)			μS	277(1)			132.3(3)	
	8	407.8(5)			Cl	266(1)		S,Cl	107.0(3,5.8)	
				AgS_2Cl_2	μS	251(1,1)		S,S	114.6(2)	
					Cl	270(1,5)		Cl,Cl	98.0(3)	
								S,Cl	110.8(2,8.7)	
$Ag^{I}(qu)Cl$	m	414.4(6)		$AgCl_3N$	N	220(8)	345(1,31)	Cl,N	117(2,7)	266
	$P2_1/c$	1548(5)	99.5(1)		μ_3Cl	271(2,7)	78.4(6,8.2)			
	4	1559(3)					101.4(7,8.4)			
$Ag^{I}(Me_3py)Cl$	m	416.3(4)		$AgCl_3N$	N	227(3)	347.5(5,241)	Cl,N	116.8(7,3.6)	266
	$P2_1/c$	1542.6(16)	92.91(8)		μ_3Cl	264(1,10)	81.5(3,6.8)			
	4	1435.1(4)					101.2(3,9.5)			
$Ag^{I}(py)Br$	m	423.5(2)		$AgBr_3N$	N	228.6(6)	316.4(1,60)	Br,N	100.1(2,1.0)	266
	$P2_1/n$	1445.2(5)	93.51(3)		μ_3Br	273.9(1,112)	70.0(1,2.5)		132.2(2)	
	4	923.1(4)					107.8(1,4.7)			
$Ag^{I}(3\text{-}Mepy)Br$	or	1471.8(4)		$AgBr_3N$	N	230.5(8)		Br,N	100.1(2,5)	197
	Pccn	1440.7(4)			μ_3Br	274.9(1,73)	66.80(4)		129.8(2)	
	8	730.1(2)					110.2(4,17.7)			
$Ag^{I}(4\text{-}Mepy)Br$	m	1028.6(5)		$AgBr_3N$	N	228(3)	316.5(6,3)	Br,N	102.9(9,4.7)	197
	$P2_1/n$	1806.6(9)	104.31(5)		μ_3Br	274.1(6,120)	69.6(1,6)		119.4(8)	
	4	439.0(3)					110.3(2,7)			
$Ag^{I}(qu)Br$	m	421.0(4)		$AgBr_3N$	N	209(7)	345(1,34)	Br,N	116(2,5)	266
	$P2_1/c$	1556(2)	100.22(9)		μ_3Br	276(2,4)	77.4(4,8.9)			
	4	1563(2)					101.8(5,9.7)			
$Ag^{I}(Me_3Py)Br$	m	433.4(3)		$AgBr_3N$	N	231(1)	356.7(2,240)	Br,N	116.5(3,8.6)	266
	$P2_1/c$	1583(1)	90.92(7)		μ_3Br	275.2(2,78)	80.3(1,6.8)			
	4	1374(1)					101.8(1,8.8)			
$Ag^{I}(pip)I$	or	2022.0(40)		AgI_3N	N	232.9(15)	303.2(2,63)	I,N	107.1(1,15.5)	402
	Pcna	822.6(20)			μ_3I	291.0(2,57)	62.3(5,1.2)			
	8	1024.0(30)					111.3(7,1.6)			

Table 17 *Continued*

$Ag^{I}(Me_3py)I$	m	451.2(5)		AgI_3N	N	230(1)	308.5(4,79)	I,N	106.0(3,5.7)	266
	$P2_1/c$	1619(3)	91.8(2)		μ_3I	288.1(3,87)	64.8(1,3.3)			
	4	1366(4)					112.7(1,2.5)			
Ag^{I}(3-Mepy)I	m	1957(2)		AgI_3N	N	232.4(7)	309.0(2)	I,N	105.7(2,2.4)	268
	$P2_1/n$	463.3(3)	90.85(7)		μ_3I	285.8(2,37)	65.33(3)			
	4	935.5(7)					112.9(1,3.7)			
Ag^{I}(py)I	m	951.8(4)		AgI_3N	N	239(2)	312.4(4,118)	I,N	106.3(1,7.8)	266
	$P2_1/n$	1705.6(5)	106.37(3)		μ_3I	285.4(3,60)	66.1(1,2.0)			
	8	928.8(3)					112.4(1,6.2)			
Ag^{I}(2-Mepy)I	or	1663(1)		AgI_3N	N	235.2(9)	320.0(3)	I,N	108.8(3,9.3)	268
	$P2_12_12_1$	1079.7(9)			μ_3I	287.3(2,23)	67.89(4)			
	4	457.0(4)					109.7(1,4.9)			
Ag^{I}(qu)I	m	1296.4(9)		AgI_3N	N	232(2)	323.1(3,171)	I,N	109.8(3,20.0)	268
	$P2_1/n$	1684(2)	97.10(7)		μ_3I	288.6(3,89)	72.4(1)			
	4	445.4(4)					109.1(1,8.0)			
Ag^{I}(mor)I	m	1814(3)		AgI_3N	N	237.6(24)	330.4(9)	I,N	110.0(6,20.8)	403
	C2	452.8(10)	95.9(1)		μ_3I	285.9(6,49)	70.2(2,1)			
	4	918.0(20)					108.5(2,2.5)			
Ag^{I}(dea)Cl	or	1948.2(4)		$AgCl_3N$	N	228(3)	307(2)[p]	Cl,N	81(2)	266
	Iba2	1221.8(3)			μ_3Cl	263(2,3)	72(1)		126(1,2)	
	8	643.2(2)				284(4)	106(1,1)			
Ag^{I}(dea)Br	or	1902.2(6)		$AgBr_3N$	N	235(4)	310.1(9)[q]	Br,N	110.6(9,8.6)	266
	Iba2	1206.7(4)			μ_3Br	273.1(8,3)	69.2(2)			
	8	662.8(2)				283.5(14)	108.4(3,4.3)			
Ag^{I}(dea)I	or	3843.0(9)		AgI_3N	N	237(2)	308.7(5)[r]	I,N	106.0(6,1.2)	266
	Ccca	2245.9(5)			μ_3I	279.5(4)	64.0(1)			
	32	745.0(2)				291.3(5,14)	112.5(1,11.4)			
Ag^{I}_4(hmta)Cl_4	or	859.4(1)		$AgCl_3N$	N	238.0(4,31)		Cl,N	86.2(2,2.1)	404
	Pnam	956.7(1)			μCl	270.9(1,131)	72.7(1,3.3)		163.4(2)	
	8	1640.3(2)			μ_3Cl	280.7(1,130)	104.6(2,43.1)			
				$AgCl_2N$	N	238.0(4)		Cl,N	105.5(2,1.5)	
					μ_3Cl	255.6(1,11)		Cl,Cl	113.1(2,2.0)	
α-Ag^{I}(pysa)	or	1433(1)		AgO_2N_2	O	291(1,12)		O,O	141(1)	405
	Pbca	1025(1)			N	228(1,3)		N,N	163(1)	
	8	1713(2)						O,N	55-121(1)	
β-Ag^{I}(pysa)	m	751.8(7)		AgO_2N_2	O	290(1,7)		O,O	134(1)	406
	$P2_1/c$	671.3(6)	103.1(1)		N	218(1,2)		N,N	175(1)	
	4	2619(2)						O,N	55-125(1)	

Table 17 *Continued*

$Ag^{I}(Bu^{t}dab)(CF_3SO_3)$	tr	902.0(1)	111.96(1)	AgO_2N_2	O	243.4(3,10)	O,O	not given	407
	$P\bar{1}$	1006.5(2)	96.48(1)		N	232.2(4,9)	N,N	123.9(1)	
	2	1137.4(1)	114.19(1)						
$Ag^{I}(CN)_2(NO_2)\}$	m	2957(20)		AgO_2N_2	O	237.9(10,100)		not given	406
	C2/*c*	781.8(8)	116.69(5)		O	274.3(10,28)			
	32	1958.1(14)			CN	219.6(11,102)			
				AgO_3N_2	O	256.3(10,114)			
					CN	224.4(11)			
						267.1(13)			
				AgN_3O_2	CN	231.0(11,29)			
					O	272.7(10,36)			
$Ag^{I}(ttof)(NO_3)$	or	691.8(1)		AgO_2N_2	O	247.7(4,42)			418
	$P2_12_12_1$	1257.6(2)			N	239.0(2,34)			
	4	1342.2(2)							
$Ag^{I}(tmb)(NO_3)$	or	859.0(7)		AgO_2C_2	O	258.3(5,64)	O,O	48.8(1)	327
	Pbca	1512.5(2)			C	210.7(5,16)	C,C,	144.9(2)	
	8	2107.5(3)					O,C	105.6(2,14.5)	
$Ag^{I}_2(C_7H_8)(NO_3)_2$	or	1767.0(3)		AgO_2C_2	O	233(2)	O,O	84.6(6)	408
	Cmcm	606.5(2)			C	235(2)	C,C	34.1(6)	
	4	1013.5(14)					O,C	122.3(2,2)	
$Ag^{I}(1,2\text{-}Me_2C_6H_4)_2 \cdot (ClO_4)$	or	1659.4(8)		AgO_2C_2	O	249(1)	O,O	125.0(7)	409
	$P2_12_12_1$	886.1(5)			C	245(2)	C,C	161.7(8)	
	2	579.5(3)				261(2)	O,C	95.8(5)	
$[Ag^{I}(p\text{-}MeOacp)_2]BF_4$	m	776.3(1)		AgO_2C_2	O	236(1)	O,O	140.0(5)	410
	C2/*c*	1977.1(4)	103.32(2)		C	255(1)	C,C	126.0	
	4	1277(2)				272(1)	O,C	99.2(4,10.3)	
$Ag^{I}(C_7H_8)_2(NO_3)$	m	1755.4(9)		AgO_2C_2	O	237(1)			411
	$P2_1/c$	690.8(4)	103.10(3)			262(1)			
	4	1103.1(5)			C	232(1,1)			
				AgO_4C_2	O	239(1,2)			
						270(1,8)			
					C	232(1,1)			
$Ag^{I}_2(C_{12}H_{18})(NO_3)_2$	m	1217(2)		AgO_2C_2	O	231(4)	O,O	70(2)	412
	$P2_1/n$	1934(2)	93.0(3)			248(4)	C,C	35(2)	
	4	655(2)			C	232(6,2)	O,C	125(2,1)	
								157(2,3)	
				AgC_4O_2	C	239(6)	O,O	81(1)	
						256(6,3)	C,C	75-125(1)	
					O	246(4,4)	O,C	92-151(2)	

Table 17 *Continued*

Ag^I(2-Mepy)(SCN)	or	1835.0(5)		AgN_2S_2	N	234(1)			not given	354
	$Pn2_1a$	1120.9(3)			SCN	227(1)	107.3(1)			
	4	418.0(1)			μS	259.5(3,43)				
Ag^I(3-Mepy)(SCN)	or	1805.5(8)		AgN_2S_2	N	233.1(5)			not given	354
	Pbca	1138.5(5)			SCN	229.3(5)	132.32(7)			
	8	840.4(4)			μS	259.7(2,19)				
$Ag^I(pip)_2Cl$	m	2076(4)		AgN_2Cl_2	N	236.6(10,19)		N,N	106.9(3)	413
	C2/*c*	642.2(7)	96.9(1)		μCl	252.4(3)	102.62(9)	N,Cl	100.5(3,1.5)	
	8	2069(2)				266.7(3)	107.33(8)		119.2(2,1.2)	
$[Ag^I(adpo)(MeCN)_2]SbF_6$	or	736.0(2)		AgN_2P_2	N	not given		P,P	106.1(1)	414
(at 203 K)	$P2_12_12_1$	1464.4(3)			μP	243.4(5)	131.5(2)			
	4	2284.4(4)				257.4(5)				
$[Ag^I(C_{14}H_{28}S_2)]ClO_4$	or	822.9(3)		AgC_2S_2	C	254.0(15,47)		C,C	30.2(6)	149
	$P2_12_12_1$	1064.5(3)			S	252.3(3,23)		S,S	149.3(3)	
	4	1391.7(3)						C,S	89.8(4,11.7)	
$[Ag^I(C_{16}H_{22}N_4S_2)]\cdot$	or	1133.9(1)		AgN_2OS	N	229.9(5,80)		N,N	115.3(2)	415
	$P2_12_12_1$	1312.2(1)			O	256.8(4)		N,O	80.7(2,10.9)	
$(CF_3SO_3)\cdot MeOH$	4	1745.1(1)			S	250.9(2)		N,S	106.7(1)	
									137.3(1)	
								O,S	110.6(1)	
Ag^I(bdtp)(NO_3)	m	1871.0(4)		AgN_2OS	N	221.6(4)		N,N	118.8(2)	416
	$P2_1/n$	882.8(2)	103.13(3)			248.3(5)		N,O	100.7(2,23.0)	
	4	1116.2(5)			O_2NO	250.3(5)		N,S	77.1(1,4.4)	
					μS	257.1(2)			147.7(1,8.4)	
								O,S	88.2(1)	
$Ag^I(PPh_3)$(SCN)	m	632(2)		AgS_2NP	P	248(3)		S,N	108.0	417
	$P2_1/c$	1400(5)	114.0(1)		SCN	210(1)	86.40	S,P	104.5	
	4	1824(7)			μS	286(2,3)	93.30	N,P	130.0	

Ag^I(tosco)(NO_3); m, $P2_1/n$, 2; a = 1373.8(4), b = 944.7(4), c = 815.1(3) pm; γ = 98.90(4)°; $[AgO_3S]$.[419] $Ag^I(C_3H_6S_3)(NO_3)$; m, $P2_1/b$, 8; a = 1313(3), b = 2370(1), c = 573(1) pm; β = 107.0(1)°; $[AgS_3O]$.[420] $Ag^I(C_3H_6S_3)(NO_3)H_2O$; or, Pcam, 8; a = 1130(2), b = 1687(3), c = 964(2) pm; $[AgS_3O]$-.[420] $Ag^I(C_3H_6S_3)(H_2O)BF_4$; or, $P2_12_12_1$, 4; a = 1072(2), b = 1561(3), c = 591(1) pm; $[AgS_3O]$.[420] $Ag^I(CH_2\text{-}CHCH_2CN)(ClO_4)$; or, $Pma2_1$, 4; a = 993.9(4), b = 1279.8(6), c = 577.6(3) pm; $[AgO_2NC]$.[421] $[Ag^I(bpy)(SCN)]0.25bpy$; m, $P2_1/n$, 4; a = 769.5(2), b = 1846.3(5), c = 1877.7(5) pm; β = 96.27(2)°.[422] Ag^I(acetylide)(NO_3); rh, $R\bar{3}$, 1; a = 794.5(2) pm; α = 106.08(2)°.[423] $Ag^I(C_8H_{14})(NO_3)$; or, Pbca, 8; a = 738.3(2), b = 982.5(2), c = 2698.6(5) pm.[424] Ag^I(sulfadiminate); or, 2; a = 950.0(5), b = 1163.5(6), c = 953.0(5) pm.[425] [a]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.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom/ligand is specified in these columns. [c] Ag-Cl-Ag = 126.6(1,1.6)°. [d] Ag-S-Ag = 127.13(5)°. [e]Ag-Br-Ag = 120.1(1,1.7)°, [f]Ag-I-Ag = 108.48(5)°. [g]Ag-I-Ag = 100.03(8,4.87) and 127.60(7)°. [h]Ag-I-Ag = 100.74(12,5.25) and 128.20(12)°. [i]Ag-I-Ag = 98.38(6,4.83) and 126.55(6)°. [j]Ag-I-Ag = 100.2(1,6.4) and 128.0(1)°; Ag-Cl-Ag = 77.4(2)°. [k]Ag-I-Ag = 100.74(5,7.02) and 127.36(6)°; Ag-Br-Ag = 77.92(6)°. [l]Ag-I-Ag = 102.9(1,19.1) and 161.9(1)°. [m]X-ray analysis was taken also at 243, 313, 328, 353 and 398 K. [n]There are two crystallographically independent molecules. [o]Ag-S-Ag = 133°. [p]Ag-Ag = 388(1,2) pm and Ag-Cl-Ag = 91(1,1)°. [q]Ag-Ag = 405.8(5,4) pm and Ag-Br-Ag = 93.6(3,1)°. [r]Ag-Ag = 431.7(5,2) pm and Ag-I-Ag = 98.3(1,3)°.

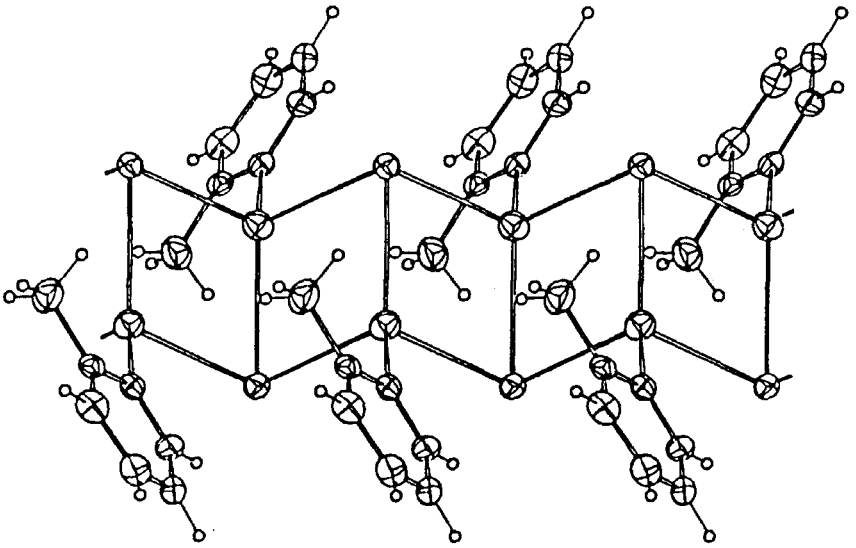

Figure 8

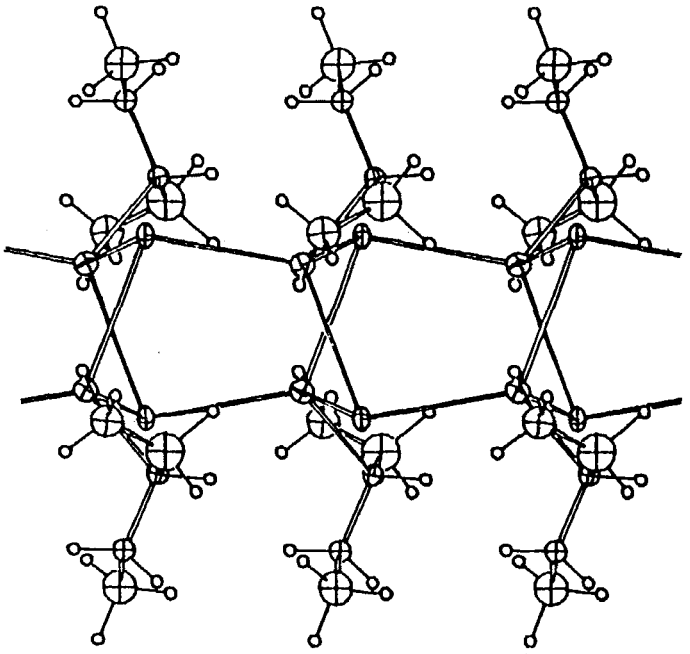

Figure 9

polymers, the mean Ag-I value is almost invariant. The Ag–N distance also increases with the steric effect of the overall AgX_3N chromophore, for example: 228 pm (X = Cl) < 235 pm (Br) < 237 pm (I).

The data in Table 17 show that $Ag_2(tsc)_3Br_2$[194,400] and Ag(Pysa)[405,406] exist in two isomeric forms differing by degree of distortion. In $Ag_2(PhCO_2)_2$[383] two crystallographically independent molecules coexist, again differing by degree of distortion. The mean Ag-L distance in the unidentate ligand series increases in the order: 231.6 pm (LN) < 242.5 pm (LP) < 245.2 pm (LS) < 254.1 pm (LO) < 265.9 pm (Br) < 276.8 pm (Cl) < 284.6 pm (I). In the series of bidentate ligands, the distances increase in the following order: 228.5 pm (LN) < 242.3 pm (LO) < 242.8 pm (LC) < 270.2 pm (LSe). The mean Ag-L distance for the NCS ligand is longer when binding *via* the softer atom, with values of 218.3 and 274.7 pm for Ag-NCS and Ag-SCN, respectively.

The mean Ag-X(bridge) distance increases with covalent radius of X as well as the degree of multiplicity of the bridging of X (Table 17A). In general, the mean Ag-L distances found in this series of Ag(I) derivatives are longer than those of Cu(I) derivatives, as might be expected. This series of derivatives is the richest in terms of variety for the Ag(I) complexes. The most common ligand is the soft iodine atom.

7.4. Coordination number five

Structural data for penta-coordinated polynuclear silver(I) compounds are given in Table 18. There are examples with the Ag(I) atom in a trigonal bipyramidal environment.[426–428,431,442] In the remaining examples, the silver atom is coordinated in an irregular fashion[91] or in a distorted coordination polyhedron, due to the presence of multidentate ligands. Penta-coordinated Ag(I) atoms are found forming chains of differing types of bridges. For example, in $Ag(C_{14}H_{28}S_2)(F_3CCO_2)$[149] a

Table 17A Summary of the mean M(I)-L distances for polynuclear four-coordinated derivatives (Cu(I)-L;[42] M[covalent radius])

Coord. atom/ligand	Covalent radius [pm]	Cu-L [pm] [138 pm]	Ag-L [pm] [153 pm]
LN	75	202.0	231.6
		204.3[a]	228.5[a]
Cl	99	228.6	276.8
		234.3[b]	261.0[b]
		238.5[c]	271.0[c]
LS	102	235.6[b]	269.7[b]
Br	114	234.3	265.9
		245.7[b]	267.2[b]
		250.8°[c]	275.3[c]
		258.5[d]	285.1[d]
I	133	265.1[b]	279.0[b]
		266.8[c]	286.1[c]
		271.5[d]	294.1[d]

[a]Bidentate ligands. [b]Doubly bridged atom/ligand.[c]Triply bridged atom/ligand. [d]Quadruply bridged atom/ligand.

Table 18 Structural data for polynuclear silver compounds, coordination number five[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]		L-M-L [°]	Ref.
$Ag^I(MeSO_3)$[c]	m	869.86(6)		AgO_5	O_e[b]	242.5(5)	O_e,O_e[b]	119.4(2,18.5)	426
	$P2_1/c$	577.76(5)	100.21(3)		O_e	262.7(5,1)	O_eO_a	90.5(2,21.6)	
	4	826.65(6)			O_a	235.2(5,11)	O_a,O_a	162.7(2)	
$Ag^I(dmso)_2(ClO_4)$	m	1033.6(1)		AgO_5	O_e	249.7(7,8)	O_e,O_e	120.0(7,16.6)	427
	$P2_1/n$	1818.8(2)	98.56(1)		O_3ClO_e	241.1(29)	O_e,O_a	89.8(5,13.9)	
	4	652.3(1)			O_a	235.8(7,4)	O_a,O_a	158.1(3)	
$Ag^I_2\{SO_3(CH_2)_4$	m	869.9(3)		AgO_5	O_e	247.5(5,102)	O_e,O_e	119.4(2,20.9)	428
$SO_3\}$	$P2_1/c$	586.6(1)	91.75(1)		O_a	242.3(5,22)	O_e,O_a	89.8(2,14.9)	
	2	894.9(1)					O_a,O_a	169.4(1)	
$Ag^I_2(SO_3CH_2SO_3)$	or	857.8(3)		AgO_5	O	243.5(8,78)		not given	429
	$Pnc2_1$	738.7(2)		AgO_6	O	253.8(8,78)		not given	
	4	995.4(2)							
$Ag^I(OPPh_3)(NO_3)$	or	1345.2(1)		AgO_5	O_e	233.3(8,72)	O_e,O_e	49.8(3,8)	430
	$P2_12_12_1$	1508.6(2)			μO_e	250.8(8,95)		120.8(3,25.3)	
	4	865.0(2)			Ph_3PO_a	226.1(6)	O_e,O_a	107.0(3,17.0)	
$Ag^I(SO_3NH_2)$	or	780.9(2)		AgO_4N	N_e	231.21(8)	O_e,O_e	115.6(3)	431
	Pcab	806.7(2)			μO_e	241.8(8,9)	O_e,N_e	121.3(3,4.1)	
	8	1168.2(3)			μO_a	253.8(8,54)	O_e,O_a	87.2(3,4.2)	
							O_a,N_e	95.5(3,14.1)	
							O_a,O_a	167.3(3)	
$Ag^I(AsPh_3)(NO_3)$	m	1040.5(5)		AgO_4As	O	251.1(7,156)	O,O	48.0-146.5(4)	91
	$P2_1/c$	1889.5(12)	98.35(8)		O	282.9(6)	O,As	110.0(3,14.7)	
	4	913.8(6)			As	247.1(2)		141.9(2)	
$Ag^I_2(C_{11}H_{15}As)$	or	717		AgO_4As	O	267(3,22)		not given	438
$(NO_3)_2$	$P2_12_12_1$	1016			As	248.8(6)			
	4	2202		AgO_4C_2	O	260(3,25)			
					C	240(5,6)			
$[Ag^I(C_{10}H_{10})$	m	849(2)		AgC_4O	O	237(2,5)		not given	432
$(H_2O)]BF_4$[d]	$P2_1/c$	1484(3)	103.4(2)		C	250(3,10)			
	8	1874(4)							
$[Ag^I(C_{11}H_{15}NS_3)]$	or	861.6(1)		AgS_4N	N_e	237.0(4)	S,S	77.3(1,7)	433
(NO_3)	$Pca2_1$	1030.3(2)			S_e	270.6(2,5)		138.6(1)	
	4	1683.9(2)			μS_e	285.6(1)	S,N	76.5(2,1.1)	
					μSa	249.8(1)		100.0(1)	
Ag^I(dmpto)	or	634.5(5)		AgO_3N_2	O	237.8(11)	O,O	99.1(2,11.0)	434
(dmptoH)	$P2_12_12_1$	1401(2)				258.8(11,40)		129.7(2)	
	4	1792(2)			N	227.0(11)	N,N	153.8(2)	
						249.0(11)	O,N	63.2-134.3(2)	
$Ag^I_3(C_9H_{12})(NO_3)_3$	hx	1625.8		AgO_3C_2	O	246.5(11,27)	O,O	98.5(3,13.0)	435
(at 148 K)	R3*c*	—			C	239.5(15,16)			
	6	955.6							
$Ag^I_4(C_{10}H_8)$	tr¯	1187.0(1)	88.93(1)	AgO_3C_2	O	260.5(11,299)	O,O	84.1(3,8.5)	436
$(H_2O)_4(ClO_4)_4$	$P\bar{1}$	924.7(1)	96.88(1)		C	261.6(11,17)	C,C	30.6(4,4)	
	1	1112.3(1)	101.21(1)				O,C	73.5-157.7(4)	
$Ag^I_4(C_{14}H_{10})$	m	2418.9(6)		AgO_3C_2	O	249.0(7,142)	O,O	45.3(2)	437
$(H_2O)(ClO_4)_4$	$P2_1/n$	932.5(2)	90.35(5)		C	251.3(8,59)		80.2(2,11.0)	
	2	530.4(1)					C,C	31.5(3,1)	
							O,C	58.4-156.9(3)	
$Ag^I(C_{20}H_{18})$	m	1249.5(2)		AgO_3C_2	O	256.7(3)	O,O	50.6(1)	439
$(ClO_4)]$	$P2_1/n$	854.6(1)	101.27(1)			271.5(4,62)		66.4	
	?	1619.6(2)			C	248.3(4,125)			
$Ag^I(dtl)(NO_3)$	tr¯	1174.6(1)	90.90(4)	AgO_3S_2	O	not given		not given	440
	$P\bar{1}$	893.1(3)	97.38(3)		S	257.3(-,29)			
	4	2004.1(4)	88.67(4)						

Table 18 *Continued*

$Ag^{I}(hmta)(NO_3)$	or	1383.2(7)		AgN_3O_2	N	238.2(5,47)	N,N	153.8(6)	441
	Pnma	653.5(4)			O	261(1,2)	O,O	88.1-129.7(6)	
	4	1033.7(6)					N,O	63.2-134.3(6)	
$[Ag^{I}(bqtp)](NO_3)^{e}$	m	2701.1(8)		AgS_3N_2	S_e	269.0(2,111)	S,S	112.8(1,4.2)	442
	$P2_1/c$	796.2(1)	110.41(3)		Na	237.7(4,8)		133.6(1)	
	8	2027.0(5)					N,N	148.7(1)	
							N,S	72.9(1,2.7)	
								100.2(1,11.2)	
				AgS_3N_2	S_e	271.4(2,146)	S,S	104.2(1)	
					N_a	234.3(4,7)		130.1(1)	
							N,N	142.0(1)	
							N,S	72.3(1,1.8)	
								99.8(1,13.7)	
$Ag^{I}(C_{14}H_{28}S_2)$	m	1019.4(3)		AgC_2S_2O	O	229(2)	C,C	30.8(8)[f]	149
(F_3CCO_2)	$P2_1/b$	1578.4(5)			C	253(3)	S,S	123.2(4)	
	4	812.5(4)	95.49(2)		S	258.2(6)	C,S	92.3(6,11.9)	
					μS	263.2(6)	S,O	122.8(6)	

[a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns. [c]Ag-Ag = 316.3(2) pm. [d]Ag-Ag = 240(-,6) pm. [e]There are two crystallographically independent molecules. [f]Ag-S-Ag = 126.4(4)°.

polymeric chain is developed *via* S'-Ag-S-Ag' linkages about a two-fold axis, with a five-membered -Ag-S-C(1)-C(2)-C(3)-ring adopting a C(2) envelope conformation (Table 18).

In $Ag(OPPh_3)(NO_3)$[430] a square-pyramidal arrangement about the Ag(I) atom is built up by a triphenylphosphine oxygen, two oxygen atoms of one nitrate group, and two oxygen atoms of a symmetry related nitrate group.

In colourless $[Ag(C_{11}H_{15}NS_3)](NO_3)$,[433] the Ag(I) atom sits in the cavity of the macrocyclic ligand, coordinating to three S atoms and one N atom, and linked to an adjacent ligand by a sulphur atom, forming a chair configuration. The nitrate group does not interact with the Ag(I) atom. In another derivative[434] the Ag(I) atom is coordinated with two organic bidentate ligands of the same asymmetric unit, and with one O atom of a neighbouring molecule to form a chain structure with no Ag–Ag interaction.

The pentacoordinated polynuclear silver(I) compounds utilize uni-, bi_ and multidentate ligands. The mean Ag-L distance of the unidentate ligands are shorter than those of the bidentate ones. For example: 244 pm (uni-) vs 252.5 pm (bidentate: O-donor ligands); and 248 pm (uni-) vs 250 pm (bidentate As ligands).

In the multidentate ligand series, the mean Ag-L distance increases in the order: 238.4 pm (LN) < 247.5 pm (LO) < 250.6 pm (LC) < 263.5 pm (LS). The mean Ag-L(bridge) distance of the multidentate ligands are longer than the terminal bond lengths, and increases with the covalent radius of the bridged atom, 255.9 pm (LO) < 274.8 pm (LS).

Two crystallographically independent molecules are found in one example.[442] The structure of one such molecule is shown in Figure 10. These two independent molecules are similar to each other except for the degree of distortion (Table 18).

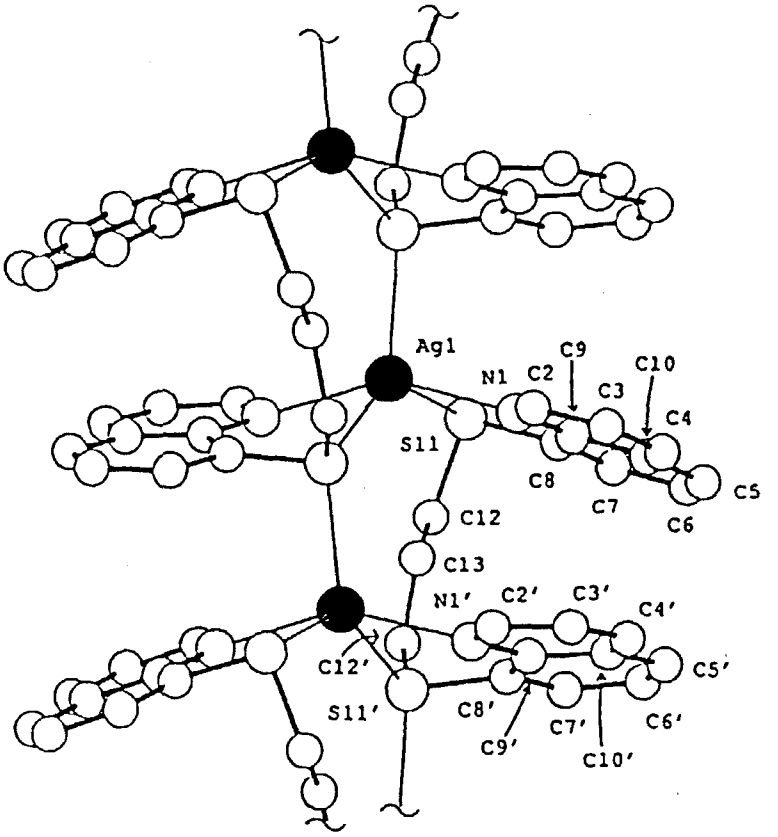

Figure 10

7.5. Coordination numbers six and higher

Structural data for these thirty-two derivatives are gathered in Table 19, with the coordination number of the silver atom varying from six to ten, irregular geometry six coordination being the most common. The soft coordination characteristics of silver(I) are underlined by the structures of the polymers, and as in the previous series (Section 7.4), there are no straightforward ways to classify these. With the exception of two examples[450,456] where silver is in the oxidation state + 2, all of the other examples have silver in the +1 oxidation state. The Ag-L distances cover a wide range of values, especially for O- and C- donor ligands, the most common in the hexa-coordinate series. The mean bond distances for these two donors in multidentate ligands are 256.0(420,383) pm and 255.4(211,254) pm, respectively. These values are smaller than those found for the hepta- and higher coordinated derivatives (259.8(357,625) pm and 264.3(233,327) pm respectively). All of these are larger than those found in the penta-coordinated derivatives (247.5 and 250.6 pm), as might be expected.

Table 19 Structural data for polynuclear silver compounds, coordination number six and higher[a]

Compound	Cryst. cl. Space gr. Z	*a* [pm] *b* [pm] *c* [pm]	α [°] β [°] γ [°]	Chromo-phore		M-L [pm]		L-M-L [°]	Ref.
$Ag^{I}_2(C_2O_4)$[c]	m $P2_1/c$ 2	346(2) 616(2) 947(4)	 76(1) 	AgO_6	O[b]	260(-,43)		not given	443
$Ag^{I}(C_4H_8O_2)_3(ClO_4)$	c Pmcm 1	767(1)		AgO_6	O	246		not given	444
$Ag^{I}(C_4H_8O_2)_3(ClO_4)$ (at 245K)	m	1093 1081 768	 94.40 	AgO_6					445
$Ag^{I}_2\{SO_3(CH_2)_2SO_3\}$	tr $P\bar{1}$ 1	511.35(7) 529.32(4) 790.8(1)	73.99(1) 93.64(1) 119.49(1)	AgO_6	O	243.5(3,67) 261.5(3,83)		74.9-160.8(1)	428
$Ag^{I}(C_6H_{10}N_2O_2)_{0.5}(NO_3)$	tr $P\bar{1}$ 2	541.0(4) 756.2(4) 802.0(6)	92.00(4) 105.07(4) 104.60(4)	AgO_6	O O_2NO	238.0(7,26) 262.4(8,56) 259.5(9,17)		48.8-170.1(2)	446
$Ag^{I}(C_4H_8O_2)_3(AsF_6)$	m $P2_1/n$ 4	939.9(2) 1814.0(3) 1147.6(3)	 	AgO_5F	O F	245.0(6,39) 269.7(7)	O,O[b] O,F	92.7(3,6.6) 168.3(2,6.1) 84.2(3,8.2) 175.6(3)	447
$Ag^{I}_2(C_4H_8OS)(NO_3)_2$	m $P2_1/c$ 4	1206.5(2) 625.9(3) 1352.7(2)	 82.42(2) 	AgO_5S	O μO μS	249.3(6,117) 281.3(7,11) 277.6(6,19) 250.0(2,8)	O,O O,S 	not given 76.2-155.5(2)[d]	448
$Ag^{I}(pz)(NO_3)$	m P2/*a* 2	1421(4) 647(2) 356(1)	 95.15(10) 	AgO_4N_2	O N	272.0(21) 294.3(17) 221.3(14)	O,O N,N 	95.2(6,14.0) 159.2(9)	449
$Ag^{II}(bpy)(NO_3)_2$	tr $P\bar{1}$ 2	697.5(2) 999.4(2) 1032.2(2)	113.46(2) 100.71(2) 95.28(2)	AgO_4N_2	O N	214.2(15,6) 275.8(15,5) 216.6(16,42)	O,O N,N O,N	69.8-160.2(4) 75.9(7) 77.2-166.3(6)	450
$Ag^{I}_3(cry)(NO_3)_3$[e]	m C2/*c* 4	2494.2(4) 1013.4(2) 1588.2(2)	 121.86(2) 	AgO_4N_2	O μO N	244.2(3,60) 260.4(2) 244.6(2,113)		not given	451
$[Ag^{I}\{C_5(CO_2Me)_5\}(H_2O)]\cdot 1.5H_2O$	tr $P\bar{1}$ 2	1245(1) 1077.6(9) 762.4(8)	94.91(7) 91.50(7) 99.90(7)	AgO_4C_2	O H_2O C	240.4(6,13) 244.4(5,7) 269.7(7,111)	O,O 	85.6(2,11.2) 127.3(2) 156.8(2)[f]	58
$Ag^{I}(mgly)(NO_3)$	m $P2_1$ 2	1363.4(6) 622.5(4) 678.4(4)	 104.8(7) 	AgO_4S_2	O S	253.6(9,38) 285.5(9) 254.4(2,33)		not given	452
$Ag^{I}(BrCH_2SO_3)$	or Pnma 4	1342.0(2) 756.9(2) 499.6(1)	 	AgO_4Br_2	O Br	235.4(4) 248.6(4) 297.09(5)	O,O O,Br 	86.9(2) 89.9(1,4.4)	453
$Ag^{I}(C_{16}H_{16})(ClO_4)$[f]	m C2 2	2083.9(4) 699.0(2) 595.6(3)	 95.07(4) 	AgC_4O_2	C O	252.2(7,51) 246.9(9)	C,C O,O C,O	31.9(3) 125.0(5) 97.0(5,3.6)	454
$Ag^{I}(C_6H_6)(ClO_4)$	or Cmcm 4	835 802 1168	 	AgC_4O_2	C O	256.5(7,69) 268.0(14,22)		not given	455
$Ag^{I}(C_8H_8)(NO_3)$	m $P2_1/a$ 4	1684(4) 894(2) 586(1)	 91.7(1) 	AgC_4O_2	C O	265(3,19) 240(2,4)		not given	456
$Ag^{I}(C_8H_8)(NO_3)$[g]	m $P2_1/a$ 4	1679.6(3) 893.2(2) 586.0(1)	 90.72(1) 	AgC_4O_2	C O	263.8(5,167) 240.0(4,32)		not given	457

Table 19 *Continued*

$Ag^{I}(dmcn)(NO_3)$	m	1130.9(6)		AgC_4O_2	C	243.1(1,88)		not given	458
(at 153 K)	Cc	1031.5(12)	95.46(6)		O	243.1(6,50)			
	4	974.0(9)							
$Ag^{I}(anph)(ClO_4)$	or	1853.1(2)		AgC_4O_2	C	249(1,5)	C,C	32.5(5,1)	459
	Pmnb	1558.6(5)			μO	241(2,7)		101.3(8,1)	
	8	787.7(3)						140.1(9,3.3)[h]	
$Ag^{I}(C_{14}H_{28}S_2)$	m	1104.9(1)		$AgO_2C_2S_2$	O	259.2(9,55)	O,O	47.2(2)	149
(NO_3)	$P2_1/c$	782.3(1)	118.39(1)		C	249.4(7,28)	C,C	30.7(3)	
	4	1435.2(3)			μS	256.5(2,7)	S,S	123.0(2)[j]	
$Ag^{I}(C_{12}H_{24}O_5S)$	m	985.6(4)		AgO_5S_2	O	272.0(10,238)		not given	460
$(NO_3)H_2O$	$P2_1/c$	1992.3(6)	92.11(3)		S	261.8(17,55)			
	4	931.0(2)							
$Ag^{I}(C_8H_{10})$	or	2554(5)		AgO_6C_2	O	273(5,30)	O,O	112(-,12)[k]	461
(NO_3)	$P2_12_12_1$	628(1)			C	242(5,1)	O,C	107(-,12)	
	4	560(3)							
$Ag^{I}{}_3(C_8H_8)_2$	or	2602.6(5)		AgC_4O_3	C	250.2(8,2)			462
$(NO_3)_3$	Pbcn	1075.6(2)				295.0(8,20)			
	8	1437.9(2)			O	242.6(8,52)			
				AgC_8O	C	256.8(9,64)			
						280.2(9,42)			
					O	238.9(5)			
				AgO_5C_4	O	268.4(7,215)			
					C	260.6(8,1)			
						275.8(10,15)			
$Ag^{I}(C_{12}O_{10})$	m	804.5(2)		AgC_6O_3	C	262.2(6,111)	O,O	88.5(4,2.1)	463
(ClO_4)	$P2_1/c$	1741.2(4)	91.13(2)		O	241.1(10,170)	C,C	70.0-151.3(2)	
	4	850.1(1)					O,C	75.6-158.2(3)	
$Ag^{I}(C_{15}H_{24})$	or	903.6(4)		AgO_4C_4	O	261(1,23)	O,O	47,75	464
$(NO_3)^{l}$	$P2_12_12_1$	2178.6(7)			C	256(1,12)	C,C	30	
	4	800.8(5)					O,C	86(-,2)	
$Ag^{I}{}_6(C_4H_8OS)$	tr	1073.47(9)	91.556(5)	AgO_xS_y[m]	O	239.7-	O,O	45.3-143.4(3)	448
$(NO_3)_6$	$P\bar{1}$	1313.67(13)	92.668(5)			322.3(15)	S,S	166.4(2)	
	2	724.88(3)	89.141(8)		μS	246.5(2,58)	O,S	68.0-169.8(2)	

$Ag^{I}(amphy)(ClO)_4$; or, $P2_12_12_1$, 4; a = 641.6(1), b = 1028.6(2), c = 1805.6(2) pm $[AgC_4O_2]$.[459] Ag^{I}(cap); tr, $P\bar{1}$, 2; a = 458.8, b = 401.6, c = 2041 pm; α = 101.12, β = 122.28, γ = 80.4°.[465] Ag^{I}(ste); tr, $P\bar{1}$, 2; a = 469.3, b = 412.0, c = 5035 pm; α = 104.35, β = 93.59, γ = 76.1°.[465] $Ag^{II}(C_6H_4NO_2)_2$; tg, 2; a = 698, c = 1268 pm.[466] Ag^{I}(dbp); m, $P2_1$, 2; a = 1450, b = 577, c = 903 pm; β = 112.50°.[467] Ag^{I}(dep); or, Pccn, 8; a = 2030, b = 1440, c = 588 pm.[467] [a]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.d., and the second is the maximum deviation from the mean. [b]The chemical identity of the coordinated atom/ligand is specified in these columns. [c]Ag-Ag = 342(-,16) pm. [d]Ag-O-Ag = 111.1(1)°; Ag-S-Ag = 95.9(2)°; Ag-Ag = 408.8(1,36) pm. [e]Ag-Ag = 387.6(1) pm. [f]Ag-Ag = 242.5(7) pm. [g]Ag-Ag = 263.8 (-,159) pm. [h]O-Ag-O = 99.8(5)°; Ag-O-Ag = 111.5(5)°. [i]C-Ag-C = 30.7(2)°; O-Ag-C = 92.8(2,7.7), 113.6(2,5.3) and 133.1(2)°. [j]O-Ag-S = 91.4(2) and 120.1(2)°; C-Ag-S = 77.5(2) and 106.2(2)°; Ag-S-Ag = 121.2(2)°. [k]values are of mid-point (O...O) and (C = C); Ag-Ag = 234 pm. [l]Ag-Ag = 247(1,1) pm. [m]There are chromophores: AgO_5, AgO_6, AgO_6S_2, AgO_{10} (2x), AgO_9S (2x); Ag-S-Ag = 102.7(1) and 112.5(1)°.

8. CONCLUSIONS

Almost six hundred silver coordination and organometallic compounds are surveyed in this review. The silver atom is found in oxidation states of +1, +2, and +3. There are only two examples of Ag(III)[75,76] and these are in square-planar environments. Silver(II) atoms are found in digonal,[17] square-planar,[64,68–73] tetrahedral[83,106] and hexa-coordinated[143,144,450,466] environments. By far the most

common is the Ag(I) atom, and the number of examples of various geometries increases in the order: 4-coordinate (mostly tetrahedral) < two-coordinate < three-coordinate < six-coordinate < five-coordinate < seven-coordinate. Higher coordination numbers are rare. From a nuclearity point of view all possibilities from mono- to decanuclear are found, with tetradeca- and polynuclear completing the range. The latter are more common than the mono- and binuclear derivatives.

There are several examples[27,49,120,121,130,131,179,180,194,195,265,266,309,310,400,405,406] which exhibit distortion isomerism.[44] In another group of examples[8,9,19,20,24,28,33,36,37,49,61,72,93,110,126,-164,383,442] there are two crystallographically independent molecules, and in one case[63] three such molecules, differing by degree of distortion. It is noted that this type of isomerism is more common in the Ag series than in the Cu[42] and Au[43] series. There is an example of *cis-trans* isomerism,[53,54] and Ag(CNO)[291] exists as a polymerisation isomer,[44] being found both as a hexamer and a polymer.

The mean Ag(I)-L distances are summarized in Table 20 from which the values of hetero-coordinated ligands have been excluded. The biggest variety of donor atoms are found in the three- and four-coordinated derivatives. Higher coordination number silver(I) (five and higher), and two-coordinate derivatives prefer O, N, C, and S donor ligands, with multidentate varieties prevailing for the higher coordination. In the series of four-coordinate silver(I) atoms, there is a very wide range of coordination atoms (ligands) and single atoms bound as unidentate, doubly- triply-, and quadruply-bridged ligands, iodine being the most common. Amongst the unidentate ligands, triphenylphosphine is the most common.

There is a trend for the Ag-L distance to increase with the covalent radius of the coordinated atom and also increasing coordination number. There are some exceptions, especially for Ag-O which covers a wide range of values. Other trends have been discussed in the separate sections. The mean Ag(II)-N bond distances, 212(1,1) pm (2-coordinate) and 215(8,4) pm (4-coordinate), and the Ag(III)-N value of 198(1,1) pm, are all shorter than those of the Ag(I)-N value. The Ag(II)-S value of 255(2,5) pm (4-coordinate) is shorter than the Ag(I)-S distance.

A summary of the M(I)-L distances (M = Cu, Ag or Au) is given in Table 21, which contains the analysis of almost two thousand derivatives (about one thousand Cu(I)[42] and three hundred Au(I)[43] examples). In general it can be seen that the mean M(I)-L bond distance increases with covalent radius of M in the order Cu (138 pm) < Au (143 pm) < Ag (153 pm). The coordination sphere about the M(I) atom is most expanded in the case of Ag(I) and least in the case of Au(I). In general, the M-L distances with O, N, C, and S donor ligands cover the widest range. Whereas 4-coordination prevails in the chemistry of Cu(I) and Ag(I), 2-coordination prevails in the chemistry of Au(I).

Table 22 shows the shortest observed M(I)–M(I) distances found in homobi-, -tri-, -tetra- and -polynuclear derivatives. In general, the shortest M(I)–M(I) distances increase in the order Cu(I) < Ag(I) < Au(I). It is noted that all these distances are within the range acceptable for a direct metal-metal bond.

This review, together with its precursors for copper(I)[42] and gold,[43] represents the first overview of structural data for the M(I) atoms of the copper subgroup. Previous studies have covered other subgroups, titanium,[468–472] vanadium[473–478] and manganese.[479–482] There is also a separate review on the structures of heterometallic silver compounds.[483] During the collection of this data it has become apparent that despite the increasing availability of data retrieval systems, the tracing of

Table 20 Summary of Ag(I)-L distances [pm][a]

Coord. atom (ligand) [b]	Covalent radius [pm]	Coordination number				
		two	three	four	five	six
H	37			176(7,7)		
F	71		255(1,1)[c]			
LO	73		240(31,38)	250(18,26) 250(19,14)[c]	266(40,34)	244(1,1)
L^2O		222(9,10)	230(15,20)	244(25,35)	252(32,16)	245(14,25)
L^nO					247(47,33)	259(45,41)
LN	75	211(9,11) 213(4,4)	236(16,10)	232(30,9)		
L^2N		215(8,11)	226(6,13)	233(11,22)		219(7,4)
L^nN				238(14,17)	242(17,13)	251(18,10)
LC	77	215(14,10) 220(4,4)[c]				
L^2C		211(10,12)	243(30,7)	246(36,15)		219(7,4)
L^nC				238(14,17)	242(17,13)	251(18,10)
Cl	99	234	236 262(18,19)[c]	260(21,40) 264(13,17)[c] 271(18,23)[d] 272[e]		
LS	102	240 238(9,10)[c] 244(11,43)[d]	253(5,7) 252(12,16)[c]	253(16,26) 270(20,40)[c] 271(18,13)[d] 272[e]	251(1,1)[c] 279(15,18)[d]	
L^2S		237	254(12,13)	267(19,13)		
L^nS			262(22,26)	257(17,11)	265(10,21)	255(8,4)
LP	110	241(3,6)	246(5,17) 247[c]	252(16,18) 243[c]	243(3,10)	
L^2P		238	244(5,3)	246(13,10)		
L^nP				253		
Br	114	245	250(2,2) 267(5,8)[c]	265(35,39) 270(12,10)[c] 277(14,19)[d] 284(15,13)[e]		
L^2Se	117		259(10,12) 264(9,7)[c]	270 274(12,16)[c]		
LAs	122	248		266(4,4)	255(7,13)	
L^2As					250	
I	133		270(2,3) 278(2,2)[c]	280(11,7) 285(12,15)[c] 289(13,14)[d] 291(10,20)[e]	287[d]	

[a]The first number in parenthesis is the maximum deviation from the shortest and the second from the longest distances. [b]L^2 bidentate and L^n multidentate ligand. [c]Doubly bridged atom/ligand. [d]Triply bridged atom/ligand. [e]Quadruply bridged atom/ligand.

relevant material is not always straightforward. One of the problems appears to be associated with the choice of key words for indices, resulting in the effective invisibility of the material from a particular point of view. Some of the data is only available as supplemental material, and this can lead to the bypassing relevant structural features for comparative purposes. Some manuscripts do not even show adequate data, names of ligands and other information important for a comparative study. In several cases the same derivatives has been studied by several different groups without cross referencing. Even when results have differed substantially there

Table 21 Summary of the M(I)-L distances [pm] for Cu (cov. radius, 138 pm), Ag (153 pm) and Au (143 pm) compounds[a]

Coord. atom (ligand)	Covalent radius [pm]	M(I) atom	Coordination number				
			two	three	four	five	six
H	37	Cu			173(52,56)		
		Ag			176(6,6)		
		Au		172			
F	71	Cu			222(16,12)		
		Ag		255(1,1)			
O	73	Cu	186(6,14)	203(33,48)	217(23,38)	223(19,42)	228(23,31)
		Ag	222(9,10)	235(26,43)	243(23,36)	255(55,41)	249(35,51)
		Au	202				
N	75	Cu	191(9,21)	194(10,47)	205(15,66)	210(12,43)	212(13,13)
		Ag	213(12,13)	230(10,16)	235(33,20)	242(17,13)	235(23,65)
		Au	202	228			
C	77	Cu	200(12,19)	197(25,45)	191(18,44)	202(24,18)	214(22,20)
		Ag	216(15,10)	243(30,7)	249(39,32)	251(13,13)	258(23,23)
		Au	205	221	247		
Cl	99	Cu	210(4,19)	229(17,27)	236(27,39)	237(19,40)	
		Ag	234	249(13,32)	267(28,33)		
		Au	226	262	277		
S	102	Cu	216(3,12)	235(43,14)	235(16,42)	257(18,15)	
		Ag	240(11,43)	255(15,32)	262(25,48)	262(12,31)	255(8,4)
		Au	229	243	228		
P	110	Cu	219(1,1)	224(11,13)	228(13,29)	223(2,3)	215(2,1)
		Ag	240(3,7)	246(7,17)	248(15,22)	243(3,10)	
		Au	227	231	239		
Br	114	Cu	226(5,6)	239(13,20)	253(32,32)		
		Ag	245	258(10,17)	274(44,23)		
Se	117	Cu		252(26,22)			
		Ag		262(13,9)	272(10,18)		
		Au	244				
As	122	Cu			239(7,29)		
		Ag			266(4,4)	252(5,16)	
I	133	Cu	239	256(11,19)	268(22,30)		
		Ag		274(6,6)	286(17,25)	287	
		Au	258	277	307		

[a]Data for Cu(I) compounds,[42] and for Au(I) compounds.[43] The first number in parenthesis is the maximum deviation from the lowest and the second from the highest values.

Table 22 Summary of the shortest M(I)-M(I) distances (pm)

Coord. number	M	Binuclear	Trinuclear	Tetranuclear	Polynuclear
2	Cu	241.2(1)	246.6	241.8	
	Ag	265.4(1)	293.3(2)	273.3(2)	280.9(1)
	Au	276(1)		274.8(1)	
3	Cu	243.3	234.8	237.7	242.5
	Ag	272.6(1)		279.9(2)	284.2(1)
	Au	296.2(1)		282.1(1)	
4	Cu	237.1	251.9		239.4
	Ag	284.5(1)	319.8(2)	296.1(2)	280.0(2)

is often no explanation offered. It is hoped that this review will serve to bring together the overall picture and serve to stimulate interest in areas of particular interest.

Acknowledgements

The authors wish to thank those who gave permission for reproduction of original figures, the Chemical Faculty of the Slovak Technical University for their cooperation in allowing M.M. to participate, and the Faculty of Pure and Applied Science of York University and the Ministry of Education of the Slovak Republic for financial support.

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