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ON THE COORDINATION NUMBER OF THE METAL IN CRYSTALLINE HALOGENOCUPRATES(I) AND HALOGENOARGENTATES(I)

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I. Introduction

The aim of this article is to summarize the various structural motifs documented for halogenocuprate(I) and halogenoargentate(I) ions in the solid state, placing special emphasis on variations in the coordination number of the metal. Unlike the situation for many transition metal complexes, anionic configurations in crystalline halogenocuprates(I) and halogenoargentates(I) appear to be strongly dependent on the nature of the cation, thus permitting, in principle, the preparation of a species containing copper(I) or silver(I) with a desired coordination number by pertinent choice of cation.

The interpretation and correlation of spectroscopic properties, in the context of structure and bonding, for compounds of group IB and group IIB metals, have been covered in a comprehensive review (*1*). It is hoped that the present article may serve as a complement by providing somewhat more detail concerning structures of crystalline halogenocuprates(I) and halogenoargentates(I), with special reference to variations in metal coordination numbers. We have restricted the content to anionic species in which halogenide ions are the sole ligands, and no attempt has been made to provide comprehensive coverage concerning preparative methods or physical properties. By far, the most widespread method of preparation is reaction between the metal(I) halide and the halide salt of the appropriate cation dissolved in an organic solvent. Other methods have, however, been employed, in particular for the preparation of iodocuprates(I). For details the reader is referred to the individual papers cited.

In the following presentation, solid-state structures documented hitherto for halogenocuprate(I) and halogenoargentate(I) ions are described in order of increasing coordination number of the metal. Possible correlations between the coordination number of copper(I) or silver(I) in the anion and properties of the cation with which it is coprecipitated, such as size, shape, and exposure of the positive charge, are then discussed.

II. Structures of Halogenocuprates(I) and Halogenoargentates(I) in the Solid State

A. SPECIES CONTAINING A TWO-COORDINATED METAL CENTER

Two-coordinated species are of two types: discrete monomers, usually linear, and X—M—X linkages as part of infinite chains.

1. Discrete Monomeric Anions

Although frequent in solution in nonaqueous solvents (*1–12*), discrete monomeric dihalogenocuprate(I) ions and dihalogenoargentate(I) ions appear to occur in the solid state solely in combination with relatively large cations with low effective positive charge.

The first crystal structure determination of a compound containing a monomeric dihalogenocuprate(I) ion was that of $[(C_6H_5)_2PO(CH)_2NH(C_2H_5)_2][CuCl_2]$, reported in 1970 (*13*). Monomeric dibromocuprate(I) was inferred in bis(*N*,*N*-di-*n*-butyldithiocarbamato)gold(III)dibromocuprate(I) from isomorphism with the corresponding dibromoaurate(I) (*14*). Tetrabutylammonium dibromocuprate(I) and tetraphenylphosphonium dibromocuprate(I) were shown to contain linear, monomeric anions by means of far-infared and Raman spectroscopy

(*2*), the anionic configurations in these compounds being confirmed later by crystal structure determinations (*15, 16*). Despite many attempts to prepare and characterize a monomeric diiodocuprate(I) in the solid state, this species proved elusive until 1985, when its isolation was finally accomplished using the K(18-crown-6)$^+$ and K(dicyclohexano-18-crown-6)$^+$ cations (*17*). Copper(I) lies on a center of symmetry in both compounds, with Cu—I distances in the two compounds of 2.383(1) and 2.394(2) Å, respectively; the iodide ligands are further involved in ionic interactions with potassium, K$^+$—I distances being 3.598(1) and 3.656(3) Å in the two compounds, respectively (*17*).

The situation regarding documentation of isolated, monomeric dihalogenoargentate(I) ions in the solid state is analogous, with no definitive evidence for the existence of such species until fairly recently. $Cs_2AgAuCl_6$ (*18, 19*) was reported to contain monomeric $[AgCl_2]^-$ (*19*). The structure of the compound can, however, be seen as a somewhat distorted close-packed array of cesium and chloride ions in which alternate octahedral interstices are occupied by silver(I) and gold(III) ions, and a more recent study (*20*) has shown that silver(I), in contrast to gold(I), shows no tendency toward the formation of linear dichloroargentate(I) ions in "$Cs_2AgAuCl_6$." Recently, a discrete, monomeric $[AgCl_2]^-$ anion (Fig. 1) has, however, been isolated with the K(crypt-2,2,2)$^+$ cation (*21*). The anion is well separated from the cation and there are no K$^+$—Cl contacts <4 Å (*21*). Monomeric dibromoargentate(I) has been determined in $[(Bu_2NCS_2)_2Au][AgBr_2]$ (*22*), there being a cation–anion contact (Ag—S) of 3.16(1) Å in this compound; monomeric $[AgI_2]^-$, however, still remains totally unknown in the solid state. Connectivity relationships for discrete monomeric dihalogenocuprate(I) and dihalogenoargentate(I) anions, characterized hitherto by crystallographic determination, are summarized in Table I (*13, 15–17, 22–46*).

Bonding in linear dihalogenocuprate(I) (*1, 2, 47–49*) and dihalogenoargentate(I) (*47–49*) ions has been discussed in terms of ds hybridization of the metal atom. A theoretical study of the bonding and nuclear quadrupole coupling in $[CuCl_2]^-$ and $[CuBr_2]^-$ has demon-

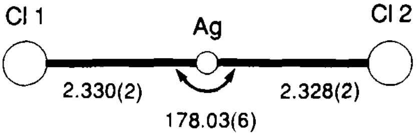

FIG. 1. The anion in [K(crypt-2,2,2)][$AgCl_2$].

TABLE I

CONNECTIVITY RELATIONSHIPS IN MONOMERIC DIHALOGENOCUPRATE(I) AND DIHALOGENOARGENTATE(I) IONS

Compound	M — X distance (Å)	X — M — X angle (°)	Comments	Ref.
Dichlorocuprates(I)				
$[(C_6H_5)_2PO(CH)_2NH(C_2H_5)_2][CuCl_2]$	2.086(4), 2.095(4)	175.8(2)	—	*13*
$[N_6P_6(N(CH_3)_2)_{12}CuCl][CuCl_2]$	2.06(1), 2.11(1)[a]	179.5(2)	Cu on 2	*23*
$[Cu(\mathrm{bipy})_2][CuCl_2]_2$	2.091(2)	180	Cu at $\bar{1}$	*24*
$[Cu_4(C_{24}H_{20}NP_2S_2)_3][CuCl_2]$	1.96(1), 2.06(1)	177	—	*25*
$[Cu(C_{18}H_{15}AsO)_4][CuCl_2]_2$	2.079(2)[b]	178.65(8)	—	*26*
$[CuCl(C_{44}H_{60}N_4)][CuCl_2]$	2.066(7), 2.088(8)	179.0(3)	—	*27*
$[CuCl[C_{44}H_{60}N_4)][CuCl_2] \cdot 3C_2H_6O$	2.046(9), 2.10(2)	169.5(1)	Anion disordered	*28*
$[P(C_6H_5)_4][MoOS_3(CuCl)_3][CuCl_2]$	2.091(2), 2.095(2)	178.1(1)	—	*29*
$[Cu(\mathrm{tmeda})_2][CuCl_2]$[c]	2.084(4)	180	Cu at $\bar{1}$ in both independent anions	*30*
	2.088(4)	180		
$[Cu(\mathrm{tmeda})_2][CuCl_2]$	2.095(4)	180	Cu at $\bar{1}$ in both independent anions	*31*
	2.095(4)	180		
$[N(C_4H_9)_4][CuCl_2]$	2.107(1)	180	Cu at $\bar{1}$	*15*
$[As(C_6H_5)_4)][CuCl_2]$	2.069(3), 2.072(3)	176.4(1)	—	*16*
$[P(C_6H_5)_4][CuCl_2]$	2.088(2), 2.090(2)	174.7(1)	—	*16*
$[N(C_3H_7)_4][CuCl_2]$	2.071(2)	178.5(1)	Cu on 2	*32*
$[N(C_6H_5)(CH_3)_3][CuCl_2]$	2.105(2), 2.117(2)	179.63(7)	—	*33*
$[\mathrm{BEDT\text{-}TTF}][CuCl_2]$[d]	2.108(1)	180	Cu at $\bar{1}$; Cu partly Cu(I), partly Cu(II)	*34*
$[\mathrm{BEDT\text{-}TTF}]_2[CuCl_2]$	2.084(2)	180	Cu at $\bar{1}$	*35*
$[(\mathrm{MeCN})Cu(\mathit{meso}\text{-}L)][CuCl_2]$[e]	2.096(6), 2.083(6)	178.0(3)	—	*36*
	2.053(7), 2.077(8)	178.7(3)		
$[\{(\mathrm{mad})_2Cu\}_2Cl][CuCl_2]$[f]	2.09	177.2	—	*37*
$[Cu(2,4,6\text{-}\mathrm{tmpy})_2][CuCl_2]$[g]	2.084(1)	180	Cu at $\bar{1}$	*38*

Dichloroargentates(I)				
$[K(crypt\text{-}2,2,2)][AgCl_2]$	2.328(2), 2.330(2)	178.03(6)	—	*21*
Dibromocuprates(I)				
$[N(C_4H_9)_4][CuBr_2]$	2.226(1)	180	Cu at $\bar{1}$	*15*
$[TSeT][CuBr_2]^h$	2.267(2), 2.282(3)	153.8(1)	Additional Cu — Br of 2.829(2) Å	*39*
$[\{CH_3C(CH_2P(C_6H_5)_2)_3IrP_3\}_3Cu_5Br_4][CuBr_2]$	2.221(10)	178.4(3)	—	*40*
$[Cu(phen)_2][CuBr_2]^i$	2.209(2), 2.223(2)	180	Cu and Br (1,2) all lie on 2	*41*
$[P(C_6H_5)_4][CuBr_2]$	2.211(2), 2.216(2)	173.62(7)	—	*16*
$[P(C_4H_9)(C_6H_5)_3][CuBr_2]$	2.213(2), 2.220(1)	177.67(6)	—	*42*
$[P(C_3H_7)(C_6H_5)_3][CuBr_2]$	2.225(1), 2.232(1)	173.18(4)	—	*43*
$[P(C_2H_5)(C_6H_5)_3][CuBr_2]$	2.207(2), 2.224(2)	175.0(1)	—	*44*
$[N(C_3H_7)_4][CuBr_2]$	2.194(3)	178.4(1)	Cu on 2	*45*
$[P(CH_3)(C_6H_5)_3][CuBr_2][Br]$	2.228(1), 2.233(1)	175.29(4)	—	*46*
Dibromoargentates(I)				
$[Au(S_2CN(n\text{-}C_4H_9)_2)_2][AgBr_2]$	2.450(4)	179.3(2)	Ag on 2; additional Ag — S of 3.16(1) Å	*22*
Diiodocuprates(I)				
$[K(dicyclohexano\text{-}18\text{-}crown\text{-}6)][CuI_2]$	2.394(2)	180	Cu at $\bar{1}$	*17*
$[K(18\text{-}crown\text{-}6)][CuI_2]$	2.383(1)	180	Cu at $\bar{1}$	*17*

[a] Corrected for libration.

[b] Mean Cu — Cl.

[c] tmeda, Tetramethylethylenediamine.

[d] BEDT-TTF, 3,4;3′,4′bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene.

[e] L, 2,6-bis[1-phenyl-1-(pyridin-2-yl)-ethyl]pyridine.

[f] mad, $C_6H_5CH = CH - CH = N - C_6H_4 - p - CH_3$.

[g] 2,4,6-tmpy, 2,4,6-Trimethylpyridine.

[h] TSeT, Tetraselenotetracene.

[i] phen, 1,10-Phenanthroline.

strated involvement of Cu 4p$_z$, which undergoes contraction relative to the free-atom orbital on bond formation (*50*).

A mixed bromochlorocuprate(I) monomer has been prepared by dissolving copper(I) chloride in molten tetrabutylammonium bromide, and recrystallizing the product from ethyl acetate. The crystalline phase thus obtained contains the $[CuCl_2]^-$, $[CuBr_2]^-$, and $[CuBrCl]^-$ ions in the statistically most favorable ratio, i.e., 1 : 1 : 2 (*51*).

2. *X—M—X Linkages*

A linear Cl—Cu—Cl linkage as part of an infinite chain of copper(I) chloride tetrahedra occurs in bis(2,2′-bipyridyl)copper(II) bis(dichlorocuprate(I) (*24*). The Cu—Cl distance in the $CuCl_2$ group embedded in the infinite chain, 2.140(2) Å, differs little from that in the isolated $[CuCl_2]^-$ ion in the same compound or from distances determined for other discrete dichlorocuprate(I) anions (cf. Table I). Tris[bis(1,2-diaminoethane)platinum(II)dichlorobis(1,2-diaminoethane)platinum(IV)] tetrakis[tetrachlorocuprate(I)] contains chlorocuprate(I) chains in which linear Cl—Cu—Cl groups, with Cu—Cl = 2.16(1) Å, and Cl—Cu—Cl groups, with Cu—Cl = 3.10(1) Å, alternate (*52*). The latter copper(I) atom is trigonally coordinated by three chloride ligands at 2.291(9) Å, whereas the former has three equivalent chloride neighbors at 3.48(1) Å (*52*). The disordered structure of $(S_4C_6H_4)(Cu_{2/5}Cl_{4/5})$ has been interpreted in terms of three models; the model giving the most satisfactory agreement with the experimental data (R = 0.052) contains a linear $[Cu_2Cl_3]^-$ ion. In the other models (R = 0.054 and R = 0.055), linear Cl—Cu—Cl linkages in which Cu—Cl distances are of the order of 2.4 Å are present (*53*).

In tris(tetraethylammonium) *catena*-μ-chloro-ennea-μ-chloro-heptacuprate(I) (cf. Section II,B,5), six vertex-sharing copper(I) chloride triangles are joined to form an infinite chain via a bent Cl—Cu—Cl linkage in which the Cl—Cu—Cl angle is 153.9(1)° and Cu—Cl = 2.165(2) Å (*54*). The two-coordinated copper(I) atom has two additional intrachain Cu—Cl contacts of 2.896(2) Å, so that it is also possible to regard the coordination polyhedron of this copper(I) atom as being a very distorted tetrahedron (*54*). Two two-coordinated copper(I) centers are present in the $[Cu_6Br_9]^{3-}$ cluster, which is described in more detail in Section II,C,6, the remaining copper(I) atoms being four coordinated (*55*).

There would seem to be no analogous examples of digonal X—Ag—X linkages in halogenoargentates(I).

B. SPECIES CONTAINING THREE-COORDINATED METAL CENTERS

The structures of halogenocuprates(I) and halogenoargentates(I), in which the metal is three coordinated, can be described in terms of discrete or of vertex- or edge-sharing metal(I) halide triangles. In all subsequent structural illustrations, halide ligands and metal(I) centers are represented as large circles and small circles, respectively.

1. *Mononuclear Anions*

The simplest species is the discrete $[MX_3]^{2-}$ triangle (Fig. 2), the first example of which to be isolated and characterized crystallographically being $[CuI_3]^{2-}$ in bis(methyltriphenylphosphonium) triiodocuprate(I) (*56*). Since then, a further triiodocuprate(I) ion has been determined in $[Co(Cp)_2]_2[CuI_3]$, Cp = η^5-C_5H_5 (*57*); the bromocuprate(I) analog has been determined in $Cu_4Br_7L_3 \cdot 3H_2O$ [L = tris(1-pyrazolylethylamine)] (*58*) and in the bis(methyltriphenylphosphonium) (*46*) and tetramethylphosphonium salts (*59*), whereas the chlorocuprate(I) analog has been isolated with the tetramethylphosphonium cation (*60*). The triiodocuprate(I) ion does not possess strict threefold symmetry in $[P(CH_3)(C_6H_5)_3]_2[CuI_3]$ and the copper(I) atom lies 0.015(1) Å from the plane through the three iodide ligands (*56*). In $[P(CH_3)_4]_2[CuBr_3]$ (*59*), the tribromocuprate(I) anion has perfect D_{3h} symmetry, whereas the anions in bis(tetramethylphosphonium) trichlorocuprate(I) (*60*) and bis(methyltriphenylphosphonium) tribromocuprate(I) (*46*) both have C_{2v} symmetry, the former with the copper atom and one chloride ligand situated on a crystallographic mirror plane (*60*) and the latter with a twofold axis through the copper atom and one bromide ligand (*46*). $[P(CH_3)(C_6H_5)_3]_2[CuBr_3]$ can be prepared in an additional crystalline form: $[P(CH_3)(C_6H_5)_3]_2[CuBr_2]Br$, containing a monomeric dibromocuprate(I) anion (*46*). A novel environment has been observed for the mononuclear $[CuCl_3]^{2-}$ species in tetrakis(*N*-methylimidazole-*N*′) copper(II) trichlorocuprate(I) hydrate in that, in this compound, it

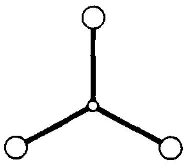

FIG. 2. The discrete $[MX_3]^{2-}$ monomer.

bridges two copper(II) centers to give a Cu(II)—Cu(I)—Cu(II) chain structure (*61*).

For halogenoargentates(I), again, the first mononuclear species to be isolated and fully characterized was the triiodoargentate(I) anion in $[P(CH_3)(C_6H_5)_3]_2[AgI_3]$ (*46*). The $[AgI_3]^{2-}$ anion is not constrained to planarity by crystallographic symmetry, but it is very nearly planar with silver(I) displaced 0.036 Å from the plane through the three iodide ligands (*46*). Recently, mononuclear trichloroargentate(I) and tribromoargentate(I) anions have been isolated with the [Rb(dibenzo-18-crown-6)]$^+$ and [K(dibenzo-18-crown-6)]$^+$ cations (*62*). In all three cases, the anions exhibit perfect D_{3h} symmetry. In Rb(dibenzo-18-crown-6)]$_3$[AgCl$_3$]Cl, the rubidium ions appear to be somewhat too large for the crown cavity and are displaced toward the anion, such that each Rb^+ is involved in two short Rb^+—Cl contacts (Fig. 3). In the potassium analog, however, K^+ is accommodated in the cavity of the crown and the $[AgCl_3]^{2-}$ ion is rotated about the threefold axis, relative to the cations, so that there is only one short K^+—Cl contact per chloride ligand (Fig. 3). As expected, the stronger outer-sphere coordination in the latter complex results in a slight lengthening of the Ag—Cl bond [2.463(2) Å as compared with 2.447(2) Å in the rubidium complex] (*62*). The tribromoargentate(I) isolated with [K(dibenzo-18-crown-6)]$^+$ is completely analogous to [K(dibenzo-18-crown-6)]$_3$[AgCl$_3$]Cl, each bromide ligand being involved in one short K^+—Br contact of 3.199(5) Å (*62*). Comparison with [Rb(dibenzo-18-crown-6)]$_3$[AgBr$_3$]Br (isostructural with [Rb(dibenzo-18-crown-6)]$_3$[AgCl$_3$]Cl) indicates a similar trend toward a longer Ag—Br bond in the potassium compound relative to the rubidium compound. Bond distances and angles determined hitherto for mononuclear $[CuX_3]^{2-}$ and $[AgX_3]^{2-}$ ions are compiled in Table II.

2. *Dinuclear Anions*

By linking two metal(I) halide triangles through a common vertex, planar or folded $[M_2X_5]^{3-}$ anions (Fig. 4) are obtained, only one example of each type of ion being known. The planar ion is a halogenoargentate(I), the μ-chloro-bis[dichloroargentate(I)] ion, determined in $(NH_4)_6[AuCl_4]_3[Ag_2Cl_5]$ (*63*), in which the Cl—Ag—Cl angle involving the terminal chloride ligands is 152.5° and the bridging Ag—Cl distance is 2.69 Å, as opposed to the terminal distance of 2.46 Å (*63*). A description in terms of "chlorine-bridged $AgCl_2^-$" was suggested as being appropriate for this ion (*63*). The folded $[M_2X_5]^{3-}$ species is exemplified by $[Cu_2Br_5]^{3-}$, determined in tris(tetramethylammonium)

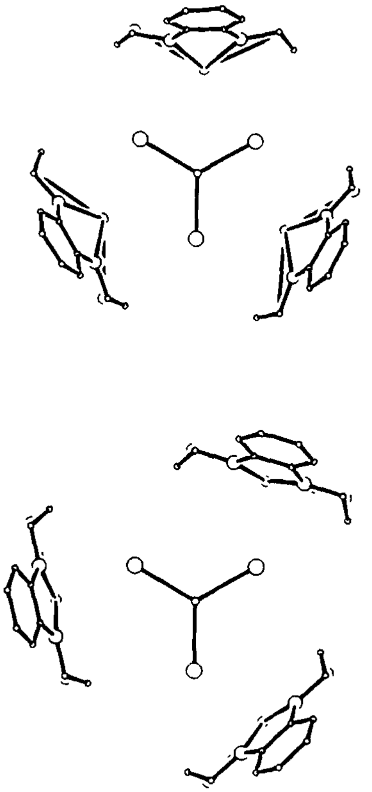

FIG. 3. The packing of $[AgCl_3]^{2-}$ anions and $[Rb(dibenzo\text{-}18\text{-}crown\text{-}6)]^+$ and $[K(dibenzo\text{-}18\text{-}crown\text{-}6)]^+$ cations in $[Rb(dibenzo\text{-}18\text{-}crown\text{-}6)]_3[AgCl_3]Cl$ (top) and $[K(dibenzo\text{-}18\text{-}crown\text{-}6)]_3[AgCl_3]Cl$ (bottom), respectively.

μ-bromo-bis[dibromocuprate(I)] (*64*). In this ion, the angle subtended by the copper(I) atoms at the bridging bromide ligand is 72.8(1)° (*64*), i.e., of the same magnitude as in the doubly bridged $[Cu_2Br_4]^{2-}$ ions (see below). The bridging ligand lies on a crystallographic twofold axis and copper(I) is displaced 0.123(2) Å from the trigonal plane toward its symmetry-related equivalent, affording a Cu—Cu separation of 2.837(4) Å; terminal [2.381(3) and 2.397(2) Å] and bridging [2.392(3) Å] Cu—Br distances do not differ (*64*).

The $[M_2X_4]^{2-}$ dimer can be envisaged as two metal(I) halide triangles with a common edge (Fig. 5), this species being unknown until 1981, when the $[Cu_2Br_4]^{2-}$ ion was prepared and characterized in the salt of the tetrathiotetracene cation radical (*65*). The anion in tetraethylam-

TABLE II

BOND DISTANCES AND ANGLES IN MONONUCLEAR MX_3^{2-} IONS

Compound	M—X distance (Å)	X—M—X angle (°)	Comments	Ref.
Trichlorocuprates(I)				
$[P(CH_3)_4]_2[CuCl_3]$	2.215(2)	118.90(5)	C_{2v}; Cu, one Cl in *m*	*60*
	2.232(3)	121.94(10)		
$[Cu(C_4H_6N_2)_4][CuCl_3] \cdot H_2O$	2.224(1)	121.8(1)	Bridges two Cu(II) centers	*61*
	2.246(1)	121.7(1)	Cu(II) — Cl = 2.922(2), 3.007(2) Å	
	2.259(1)	116.4(1)	—	
Trichloroargentates(I)				
[Rb(dibenzo-18-crown-6)]$_3$[AgCl$_3$][Cl]	2.447(2)	120	D_{3h}; Ag at $\bar{6}$, Cl in *m*; Rb$^+$ — Cl = 3.272(2), 3.487(2) Å	*62*
[K(dibenzo-18-crown-6)]$_3$[AgCl$_3$][Cl]	2.463(2)	120	D_{3h}; Ag at $\bar{6}$, Cl in *m* K$^+$ — Cl = 3.019(3) Å	*62*
Tribromocuprates(I)				
[CuBr(TPyEA)]$_3$[CuBr$_3$]Br $\cdot$ 3H$_2$O^a	2.374(2)	116.1(1)	—	*58*
	2.388(2)	121.0(1)	—	
	2.394(2)	122.9(1)	—	

$[P(CH_3)_4]_2[CuBr_3]$	2.365(3)	120	D_{3h}; Cu site symmetry 32	*59*
$[P(CH_3)(C_6H_5)_3]_2[CuBr_3]$	2.353(3)	118.9(1)	C_{2v}; Cu, one Br on 2	*46*
	2.358(6)	122.2(2)	—	
Tribromoargentates(I)				
[Rb(dibenzo-18-crown-6)]$_3$[$AgBr_3$][Br]	2.550(1)	120	D_{3h}; Ag at $\bar{6}$, Br in *m*; Rb^+ — Br = 3.420(2), 3.597(2) Å	*62*
[K(dibenzo-18-crown-6)]$_3$[$AgBr_3$][Br]	2.561(2)	120	D_{3h}; Ag at $\bar{6}$, Br in *m*; K^+ — Br = 3.199(5) Å	*62*
Triiodocuprates(I)				
$[P(CH_3)(C_6H_5)_3]_2[CuI_3]$	2.537(2)	116.55(7)	Cu 0.015(1) Å from ligand plane	*56*
	2.559(2)	120.54(6)	—	
	2.566(2)	122.90(7)	—	
$[Co(C_5H_5)_2]_2[CuI_3]$	2.535(2)	123.53(8)	—	*57*
	2.543(2)	118.74(8)	—	
	2.557(2)	117.61(8)	—	
Triiodoargentates(I)				
$[P(CH_3)(C_6H_5)_3]_2[AgI_3]$	2.742(1)	115.90(3)	Ag 0.036 Å from ligand plane	*46*
	2.746(1)	119.38(4)	—	
	2.755(1)	124.67(3)	—	

[a] TpyEA, Tris (1-pyrazolylethylamine).

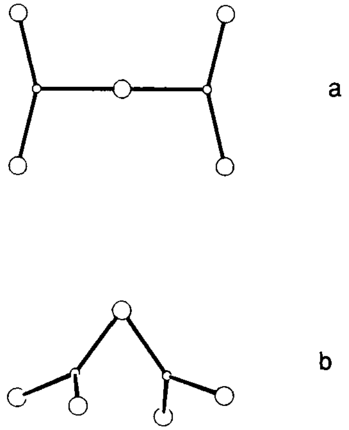

FIG. 4. Planar (a) and folded (b) dinuclear $[M_2X_5]^{3-}$ species.

monium dibromocuprate(I) was shown, by means of far-infrared and low-frequency Raman spectroscopy, to have a polymeric structure that breaks down on dissolution of the solid to yield monomeric $[CuBr_2]^-$ ions (*2*). Subsequent crystal structure determination of the compound showed that it contained a centrosymmetric $[Cu_2Br_4]^{2-}$ dimer (*66*). Iodo- and chlorocuprate(I) counterparts have also been prepared and characterized (cf. Table III). The majority of such ions are approximately planar, but $[Cu_2I_4]^{2-}$ ions folded 147° about the bridging I—I contact (cf Fig. 5) have been found in the tetraphenylarsonium (*67*) and tetraphenylphosphonium (*68*) compounds, the latter cation also crystallizing with a planar, centrosymmetric $[Cu_2I_4]^{2-}$ dimer (*68*). As is seen in Table III, bridging copper(I) halide bonds are invariably longer than terminal Cu—X. There is also considerable variation in the geometry of the four-membered $(Cu—X)_2$ ring, particularly with respect to the magnitude of the Cu—Cu separation, both within a given halogeno-

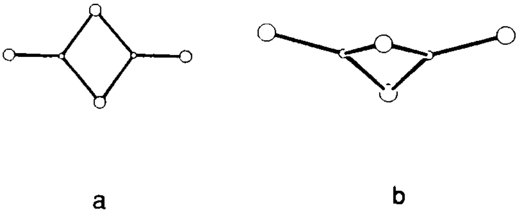

FIG. 5. Planar (a) and folded (b) dinuclear $[M_2X_4]^{2-}$ species.

TABLE III

CONNECTIVITY RELATIONSHIPS REPORTED FOR DI-μ-HALOGENO–DIHALOGENOCUPRATE(I) AND DI-μ-HALOGENO-DIHALOGENOARGENTATE(I) ANIONS $[M_2X_4]^{2-}$ [a]

Compound	$M—X_t$ (Å)	$M—X_b$ (Å)	$M—M$ (Å)	$M—X_b—M$ (°)	$X_b—M—X_b$ (°)	$X_b—M—X_t$ (°)	*d* (Å)	$X_b—X_b$ (Å)	Ref.
Di-μ-chloro-dichlorodicuprates(I)									
$[VO(SALen)(H_2O)]_2[Cu_2Cl_4]$[b]	2.161(2)	2.224(3) 2.427(3)	—	—	96.8(2)	143.9(2)	—	—	*73*
$[Cu_4(dmtp)_4Cl][Cu_2Cl_4]$[c]	2.116(5)	2.369(4)	2.433	61.8(1)	118.2(1)	120.90(8)	—	—	*74*
$[P(C_2H_5)_4]_2[Cu_2Cl_4]$	2.112(2)	2.135(3) 2.924(3)	3.516(2)	86.58(8)	93.42(8)	165.77(11) 100.68(9)	0.032	3.722(5)	*72*
Di-μ-chloro-dichlorodiargentates(I)									
$[As(C_6H_5)_4]_2[Ag_2Cl_4]$	2.359(2)	2.446(2) 2.809(2)	3.659(2)	87.97(6)	92.03(6)	149.06(6) 118.91(6)	0.004(1)	3.789(3)	*70*
$[P(C_6H_5)_4]_2[Ag_2Cl_4]$	2.358(2)	2.447(1) 2.792(2)	3.657(2)	88.27(5)	91.73(5)	149.53(5) 118.74(5)	0.0014(8)	3.768(3)	*69*
Di-μ-bromo-dibromodicuprates(I)									
$(TTT)_2[Cu_2Br_4]$[d]	2.328(2)	2.472(3) 2.490(2)	2.660(3)	64.7(1)	115.4(1)	125.0(1) 117.9(1)	0.196	—	*65*
$[N(C_2H_5)_4]_2[Cu_2Br_4]$	2.319(2)	2.441(2) 2.454(2)	2.937(3)	73.7(1)	106.3(1)	125.7(1) 127.9(1)	0.06(1)	3.916(3)	*66*
$[N(C_6H_5)(CH_3)_3]_2[Cu_2Br_4]$	2.310(1)	2.417(1) 2.421(1)	2.738(2)	68.95(4)	111.05(4)	124.70(4) 124.12(4)	0.049(1)	3.988(2)	*75*

(*continued*)

TABLE III (*Continued*)

Compound	$M-X_t$ (Å)	$M-X_b$ (Å)	$M-M$ (Å)	$M-X_b-M$ (°)	X_b-M-X_b (°)	X_b-M-X_t (°)	*d* (Å)	X_b-X_b (Å)	Ref.
$[P(CH_3)(C_6H_5)_3]_2[Cu_2Br_4]$	2.337(2)	2.426(2) 2.455(1)	2.697(2)	67.09(5)	112.91(5)	124.60(6) 122.47(5)	0.012(1)	4.068(2)	*76*
$[P(C_2H_5)_4]_2[Cu_2Br_4]$	2.263(4)	2.423(4) 2.436(3)	2.870(5)	72.4(1)	107.6(1)	128.2(1) 124.1(1)	0.032(3)	3.921(5)	*59*
$[(MeCN)CuL]_2[Cu_2Br_4]^e$	2.267(4)	2.435(4) 2.439(4)	2.768(5)	69.2(1)	110.8(2)	124.2(2) 125.0(2)	—	4.011(3)	*36*
Di-μ-bromo-dibromodiargentates(I) and heteronuclear (Cu/Ag) counterparts									
$[As(C_6H_5)_4]_2[Ag_2Br_4]$	2.481(1)	2.614(1) 2.741(1)	3.549(2)	82.96(3)	97.04(3)	139.16(4) 123.69(4)	0.048(1)	4.013(2)	*70*
$[P(C_6H_5)_4]_2[Ag_2Br_4]$	2.491(1)	2.617(1) 2.752(2)	3.578(2)	83.53(4)	96.47(4)	140.38(3) 122.99(4)	0.0587(6)	4.006(2)	*69*
$[P(C_6H_5)_4]_2[AgCuBr_4]$	2.401(2)	2.543(2) 2.688(2)	3.449(2)	82.48(5)	97.55(5)	139.06(5) 123.25(5)	0.057(1)	3.934(2)	*71*
Di-μ-iodo-diiododicuprates(I)									
$[As(C_6H_5)_4]_2[Cu_2I_4]^f$	2.490(3) 2.491(3)	2.578(3) 2.584(3) 2.609(3) 2.610(3)	2.663(4)	61.4(1) 62.1(1)	114.2(1) 114.4(1)	120.9(1) 124.6(1) 120.3(1) 125.3(1)	0.04(1) 0.07(1)	4.360(3)	*67*
$[P(C_6H_5)_4]_2[Cu_2I_4] - B^g$	2.471(2) 2.480(2)	2.562(2) 2.588(2) 2.562(2) 2.585(2)	2.647(2)	61.55(6) 62.20(6)	113.81(6) 113.95(6)	121.40(8) 124.71(8) 121.25(8) 124.42(8)	0.04 0.09	—	*68*

$[P(C_6H_5)_4]_2[Cu_2I_4]$ − A	2.497(0)	2.580(0) 2.595(1)	2.957(1)	55.40(3) 54.90(3)	110.29(3)	122.35(4) 127.05(4)	0.08	—	*68*
$[N(C_4H_9)_4]_2[Cu_2I_4]$	2.514(2)	2.566(2) 2.592(2)	2.726(4)	63.8(1)	116.2(1)	117.9(1) 125.8(1)	0.03(3)	4.380(3)	*77*
$[N(C_3H_7)_4]_2[Cu_2I_4]$	2.499(1)	2.571(1) 2.582(1)	2.698(2)	63.14(3)	116.86(3)	120.15(4) 122.98(4)	0.013(1)	4.390(1)	*78*
$[(MeCN)CuL]_2[Cu_2I_4]^{e}$	2.52(1)	2.55(1) 2.56(1)	2.78(1)	66.0(3)	114.0(4)	122.1(4) 124.0(3)	—	4.282(5)	*36*
$[(MeCN)CuL]_2[Cu_2I_4] \cdot MeCN^{e}$	2.518(1)	2.566(1) 2.579(1)	2.721(2)	63.85(4)	116.15(5)	121.11(4) 122.64(5)	—	4.367(1)	*36*
Di-μ-iodo-diiododiargentates(I)									
$[K(crypt\text{-}2,2,2)]_2[Ag_2I_4]$	2.672(1)	2.789(1) 2.801(1)	3.557(2)	79.02(3)	100.98(3)	127.65(4) 130.75(4)	0.123	4.313(2)	*21*

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[a] X_t is a terminal halide ligand and X_b is a bridging halide ligand; *d* is the displacement (Å) of the metal atom from the plane through the three ligand atoms.

[b] $VO(SALen)^+$, *N,N'*-ethylene-bis(salicylideneiminato)oxovanadium(V).

[c] dmtp, 5,7-Dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine.

[d] TTT, Tetrathiotetracene.

[e] L, 2,6-Bis[1-phenyl-1-(pyridin-2-yl)ethyl] pyridine.

[f] Anion folded 146.61(4)° about $I_b — I_b$.

[g] Anion folded 146.34° about $I_b — I_b$.

cuprate(I) series and between the chloro-, bromo-, and iodocuprate(I) series, suggesting lack of direct attractive interaction between the copper(I) nuclei.

Dinuclear three-coordinated $[Ag_2X_4]^{2-}$ species (X = Cl, Br) were characterized first in 1988 as the tetraphenylphosphonium salts (*69*); similar species were also isolated subsequently with the tetraphenylarsonium cation (*70*) as well as a heteronuclear $[AgCuBr_4]^{2-}$ ion in $[P(C_6H_5)_4]_2[AgCuBr_4]$ (*71*). Although the $[Ag_2Br_4]^{2-}$ species contain approximately trigonally coordinated metal centers, the $[Ag_2Cl_4]^{2-}$ ions are severely distorted in both di-μ-chloro-dichlorodiargentates(I) such that the ions are perhaps most adequately described as a loose association of two bent $[AgCl_2]^-$ moieties (*69, 70*). A similar description is undoubtedly valid for the $[Cu_2Cl_4]^{2-}$ anion isolated with the tetraethylphosphonium cation (*72*; see Table III). Recently, a dinuclear $[Ag_2I_4]^{2-}$ anion, in which silver(I) exhibits more regular three coordination, has been prepared using $[K(crypt\text{-}2,2,2)]^+$ as cation (*21*). Interatomic distances and angles reported for $[M_2X_4]^{2-}$ species (M = Cu or Ag) are summarized in Table III (*21, 36, 59, 65–78*). In addition to those species for which connectivity relationships are given explicitly in the literature, the crystal structures of $[N(C_2H_5)_4]_2[Cu_2I_4]$ (*79*) and $[Cu(LH)_2]_2[Cu_2I_4]$ (LH = 1,1-di-2-pyridylethanol) (*80*) have also been determined.

3. *Trinuclear Anions*

Discrete trinuclear halogenocuprate(I) or halogenoargentate(I) species containing solely three-coordinated metal centers have not been reported hitherto. An $[Ag_3I_6]^{3-}$ ion in which one of the silver(I) atoms is three coordinated, whereas the remaining two exhibit tetrahedral coordination geometry has, however, recently been isolated (*81*) (cf Section II,C,3).

4. *Tetranuclear Anions*

The existence of tetranuclear halogenoargentate(I) anions composed soley of three-coordinated silver(I) has yet to be documented; discrete tetranuclear halogenoargentate(I) ions that contain four-coordinated or both three- and four-coordinated metal centers are described in Section II,C,4. The tetranuclear halogenocuprate(I) species $[Cu_4X_6]^{2-}$ (Fig. 6) is composed of four copper(I) halide triangles linked through common vertices. The aggregate can also be seen as an octahedron of halide ions containing a tetrahedron of copper(I). The hexa-μ-iodo-

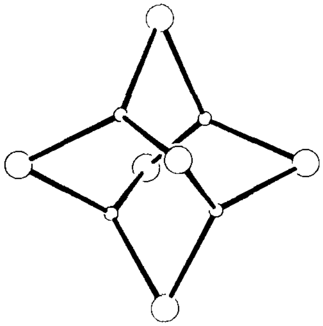

FIG. 6. The tetranuclear $[Cu_4X_6]^{2-}$ cluster; X = Br or I.

tetrahedro-tetracuprate(I) ion was the first of this series to be prepared and characterized, its structure being deduced from infrared and Raman spectra (*82*) and subsequently confirmed by crystal structure analysis (*83*). A further $[Cu_4I_6]^{2-}$ anion has been found in K_7(12-crown-4)$_6[Cu_4I_6][Cu_8I_{13}]$ (*84*). Two bromocuprate(I) analogs are known (*42*, *85*) but, as yet, no hexa-μ-chloro-*tetrahedro*-tetracuprate(I) ion has been prepared. The hexa-μ-bromo-*tetrahedro*-tetracuprate(I) cluster can also be seen as being composed of two edge-sharing $[Cu_2Br_5]^{3-}$ ions (cf. Section II,B,2). Distances and angles reported in the literature for $[Cu_4X_6]^{2-}$ clusters are summarized in Table IV. The copper(I) tetrahedra in the anions in $[P(CH_3)(C_6H_5)_3]_2[Cu_4I_6]$ (*83*), $[N(C_3H_7)_4]_2[Cu_4Br_6]$ (*85*), and $[P(C_4H_9)(C_6H_5)_3]_2[Cu_4Br_6]$ (*42*) all exhibit disorder with respect to inversion through the center of the iodide or bromide octahedron.

5. *Polynuclear Anions*

Hitherto, chains in which the dominant coordination number of copper(I) or silver(I) is three have been documented solely for a chlorocuprate(I), i.e., $[Cu_7Cl_{10}]^{3-}$, determined in $[N(C_2H_5)_4]_3[Cu_7Cl_{10}]$ (*54*). The anion is composed of six vertex-sharing copper(I)-chloride triangles, joined by a nonlinear Cl—Cu—Cl linkage (cf. Fig. 7). A rubidium compound with the same stoichiometric Cu : Cl ratio, viz. $Rb_3Cu_7Cl_{10}$, has been shown to exhibit a high Cu^+ conductivity (*86–88*).

In tris[bis(1,2-diaminoethane)platinum(II)dichlorobis(1,2-diaminoethane)platinum(IV)] tetrakis[tetrachlorocuprate(I)] (*52*), the anion is a chain in which two- and three-coordinated copper(I) alternate (see Section II,A,2). Pairs of three- and four-coordinated copper(I) atoms alternate in $[P(CH_3)_4][Cu_2Cl_3]$ (*60*). The $[Cu_2Cl_3]^-$ anion in the tetra-

TABLE IV

DISTANCES AND ANGLES REPORTED FOR $[Cu_4X_6]^{2-}$ AGGREGATES[a]

Compound	Cu — X (Å)	Cu — Cu (Å)	Cu — X — Cu (°)	X — Cu — X (°)	*d*	Ref.
Hexa-μ-bromo-tetrahedro-tetracuprates(I)						
$[N(C_3H_7)_4]_2[Cu_4Br_6]$	2.373(5)–2.422(5)	2.718(7)–2.750(7)	69.0(2)–70.2(2)	117.7(2)–122.4(2)	0.015(5)–0.029(5)	*85*
$[P(C_4H_9)(C_6H_5)_3]_2[Cu_4Br_6]$	2.358(4)–2.443(4)	2.719(6)–2.755(6)	69.2(2)–69.5(2)	117.9(1)–122.0(2)	0.023(3)–0.030(3)	*42*
Hexa-μ-iodo-tetrahedro-tetracuprates(I)						
$[P(CH_3)(C_6H_5)_3]_2[Cu_4I_6]$	2.539(5)–2.638(5)	2.742(7)–2.757(7)	63.9(2)–65.2(2)	117.9(2)–121.6(2)	0.100–0.240	*83*

[a] For each type of distance or angle the range observed is cited; *d* is the displacement (Å) of copper(I) from the plane through the three ligand atoms.

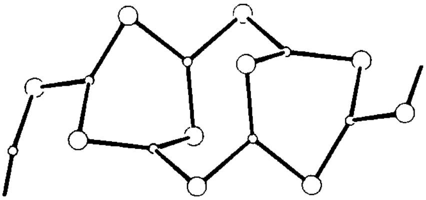

FIG. 7. The $[Cu_7Cl_{10}]^{3-}$ chain polymer.

methylphosphonium salt is essentially a very distorted version of the chain of edge- and face-sharing copper(I) halide tetrahedra (Section II,C,8c), first observed in tetraethylammonium triiododicuprate(I) and in dimethyl-(3-dimethylamino-2-aza-2-propenylidene)ammonium triiododicuprate(I) (*89*). In the $[Cu_2Cl_3]^-$ ion in $[P(CH_3)_4][Cu_2Cl_3]$ (*60*), the closest copper(I) chloride contact associated with the three-coordinated copper(I) atom is >3.8 Å, so that it is not possible to regard this atom as being other than three coordinated. A similar chain composed of alternately three-coordinated and four-coordinated copper(I) has been found in $[S_2C_3(SCH_3)_3][Cu_2I_3]$ (*90*). This is a somewhat less distorted form of the chain composed of edge- and face-sharing copper(I) halide tetrahedra, the shortest Cu—I distance involving the three-coordinated copper(I) atom being 3.452(3) Å.

Several types of $[M_3X_4]^-$ ions in which the metal(I) atoms are four coordinated have been documented (Section II,C,8,d); the anion in $[K(dibenzo\text{-}24\text{-}crown\text{-}8)][Cu_3I_4]$ (*84*) is, however, a pleated sheat of edge-sharing Cu_2I_2 rhombohedra, in which one of the crystallographically independent copper(I) atoms is three coordinated and the remaining two are four coordinated.

C. SPECIES CONTAINING FOUR-COORDINATED METAL CENTERS

A metal coordination number of four is undoubtedly that most commonly exhibited in halogenocuprates(I) and halogenoargentates(I), vertex, edge, and face sharing of metal(I)–ligand tetrahedra leading to a wealth of structural motifs, especially where polymeric anions are concerned.

1. Mononuclear Anions

To our knowledge no mononuclear MX_4^{3-} anions have been proved to exist in the solid state. There would, however, appear to be evidence for the existence of such species in solution (see Ref. *1* and references therein).

2. *Dinuclear Anions*

A dinuclear $[Cu_2I_5]^{3-}$ anion that can be described as a trigonal bipyramid of iodide ions with copper(I) occupying tetrahedral interstices has been determined in $Cs_3[Cu_2I_5]$ (*91, 92*). Cu—I bonds range from 2.575(3) to 3.351(3) Å and 2.561(3) to 2.788(2) Å for the two copper(I) centers, respectively, with a short Cu—Cu contact of 2.538(4) Å (*92*). The anion can, alternatively, be seen as a trigonal-planar CuI_3 unit joined to a CuI_4 tetrahedron through a mutual edge (*92*) and is quite different from the $[Ag_2Cl_5]^{3-}$ (*63*) and $[Cu_2Br_5]^{3-}$ (*64*) anions described in Section II,B,2. The two crystallographically independent cesium ions in $Cs_3[Cu_2I_5]$ are eight and nine coordinated by iodide and there are three Cs^+—Cu contacts, 3.840(6), 3.937(2), and 4.099(5) Å, of the same order of magnitude as the Cs^+—I interactions (*92*).

Dinuclear iodocuprate(I) and iodoargentate(I) $[M_2I_6]^{4-}$ anions, composed of two MI_4 tetrahedra with a common edge (cf. Fig. 8), have been prepared and characterized in bis(dipyridiniomethane) di-μ-iodo-bis[diiodocuprate(I)] (*68*), tetrathallium di-μ-iodo-bis[diiodocuprate (I)] (*93*), and bis(ethylenediamine)diiodoplatinum(IV) di-μ-iodo-bis [diiodoargentate(I)] (*94*). In $[Py_2CH_2]_2[Cu_2I_6]$ (*68*), the anion is centrosymmetric with a long Cu—Cu separation and asymmetry in the Cu—I—Cu bridges [Cu—I = 2.681(1) and 2.850(1) Å]. Two cations are associated with each anion such that there are several I—C or I—N contacts marginally longer than 3.5 Å (*68*). The anion in $Tl_4Cu_2I_6$, on the other hand, exhibits a very short Cu—Cu separation [2.612(3) Å] (*93*); crystallographic symmetry requires that bridging Cu—I distances are exactly equal, nor do these differ from terminal Cu—I distances. Each thallium ion is coordinated by eight iodide ligands, arranged as a capped trigonal prism, a further thallium ion, and a copper(I) center also lying within the coordination sphere affording a short Tl—Cu contact of 3.438(2) Å (*93*).

The $[Ag_2I_6]^{4-}$ ion in $[Pt(C_2H_8N_2)_2I_2]_2[Ag_2I_6]$ (*94*) is well isolated from the cation; equality in bridging Ag—I distances is imposed by symmetry and these bonds are longer than the four terminal Ag—I bonds (also

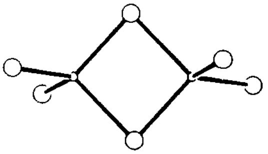

FIG. 8. The dinuclear $[M_2I_6]^{4-}$ ion.

exactly equal owing to crystallographic symmetry), viz. 2.918(1) Å as compared to 2.828(1) Å.

3. *Trinuclear Anions*

The only reported discrete trinuclear halogenocuprate(I) species composed of four-coordinated metal(I) centers is $[Cu_3I_6]^{3-}$, which contains three face-sharing copper(I) iodide tetrahedra (*91, 95*). Terminal Cu—I bonds are 2.505(5) and 2.519(6) Å, whereas bridging Cu—I bonds range from 2.529(6) to 3.205(8) Å; the face sharing of tetrahedra results in very short Cu—Cu contacts [2.518(6) and 2.519(6) Å] involving the middle copper(I) center (*95*).

A somewhat different silver(I) ion has been isolated in $NaAgI_2 \cdot 4DMSO$ (DMSO = dimethyl sulfoxide) (*81*) and is the sole trinuclear halogenoargentate(I) species reported to date. The crystals contain discrete $[Ag_3I_6]^{3-}$ ions that can be described in terms of two face-sharing silver(I) iodide tetrahedra joined by a common edge to an AgI_3 triangle; the Ag—I bonds associated with the three-coordinated silver(I) center are 2.67, 2.76, and 2.80 Å, and for the four-coordinated silver(I) atom Ag—I distances range from 2.66 to 3.08 Å (*81*). The Ag—Ag separation between the face-sharing tetrahedra is 2.96 and 3.49 Å between three- and four-coordinated silver(I) (*81*).

4. *Tetranuclear Anions*

Several tetranuclear ions have been reported. Recently, a $[Cu_4I_7]^{3-}$ cluster has been prepared and characterized in $[N(C_4H_9)_4]_3[Cu_4I_7]$ (*96*). This anion is composed of three edge-sharing $Cu—I_4$ tetrahedra with a fourth copper(I) in a trigonal-planar site (*96*). $[M_4X_8]^{4-}$ ions containing two four-coordinated and two three-coordinated metal(I) centers (cf. Fig. 9a) exist for copper(I) (*95*), silver(I) (*21, 70*), and as heteronuclear Cu/Ag species (*71*). The first such cluster to be reported was $[Cu_4I_8]^{4-}$ in $[Co(Cp)_2]_4[Cu_4I_8]$ (Cp = η^5-C_5H_5) (*95*). Silver(I) analogs, $[Ag_4I_8]^{4-}$, have been prepared with the tetraphenylarsonium and tetraphenylphosphonium cations (*70*) and a $[Ag_4Br_8]^{4-}$ cluster has been isolated recently with $[K(crypt\text{-}2,2,2)]^+$ as cation (*21*). From solutions of tetraphenylphosphonium iodide, copper(I) iodide, and silver(I) iodide in acetonitrile, it has proved possible to prepare the heteronuclear clusters $[Ag_2Cu_2I_8]^{4-}$ and $[Ag_3CuI_8]^{4-}$ in which copper(I) occupies or partially occupies the three-coordinated metal site (*71*). Selected distances within this type of $[M_4X_8]^{4-}$ cluster are given in Table V.

A completely different isolated tetranuclear $[Ag_4I_8]^{4-}$ ion (cf. Fig. 9b)

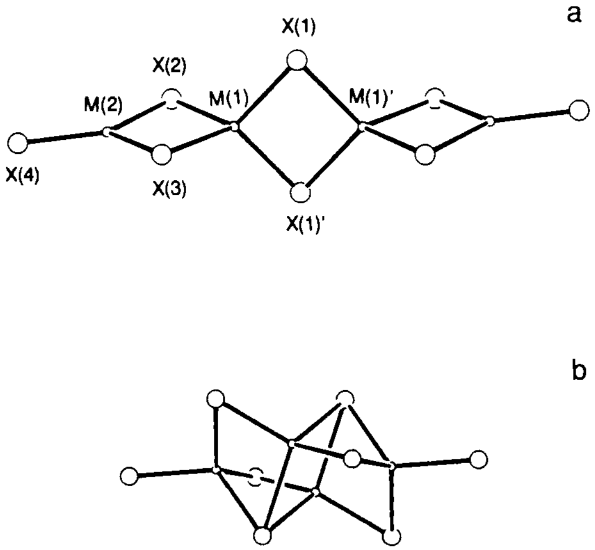

FIG. 9. Tetranuclear $[M_4X_8]^{4-}$ clusters containing (a) three- and four-coordinated metal(I) centers and (b) solely four-coordinated metal centers.

has been determined in $[C_{15}H_{30}N_2]_2[Ag_4I_8]$ (*97*). Here, a centrosymmetric cluster is formed from four edge-sharing silver(I) iodide tetrahedra; the four silver atoms are coplanar, forming a rhomb with Ag—Ag edges of 3.125(4) and 3.283(4) Å and diagonals 2.967(4) and 5.680(4) Å (*97*).

5. *Pentanuclear Anions*

Discrete pentanuclear clusters, $[Cu_5I_7]^{2-}$ (*98*) and $[Cu_5Br_7]^{2-}$ (*99*), have been prepared and characterized in the tetrapropylammonium and methyltributylammonium salts, respectively. A schematic drawing of the $[Cu_5X_7]^{2-}$ anion is shown in Fig. 10. In $[Cu_5I_7]^{2-}$, the seven iodide ions form a pentagonal bipyramid with only slight deviation from C_{5h} symmetry and the anion can be considered to be composed of five face-sharing copper(I) iodide tetrahedra (*98*). The copper(I) atoms exhibit disorder with respect to the pentagonal plane (*98*). In $[N(CH_3)(C_4H_9)_3]_2[Cu_5Br_7]$, however, the ligand pentagonal bipyramid is distorted such that the five equatorial bromide ligands are no longer coplanar (*99*). Metal coordination polyhedra in the latter ion are therefore perhaps more adequately described as two copper(I) atoms with (2 + 2) coordination and three with (3 + 1) coordination rather than as five tetrahedrally coordinated centers (*99*). Cu—Cu contacts are very

TABLE V

Selected Distances (Å) in $[M_4X_8]^{4-}$ Clusters Containing Three- and Four-Coordinated Metal Centers[a]

	M(1) — X(1)	M(1) — X(2)	M(2) — X(2)		M(1) — M(1)'			
Compound	M(1) — X(1)'	M(1) — X(3)	M(2) — X(3)	M(2) — X(4)	M(1) — M(2)	*d*	Comment	Ref.
$[Co(Cp)_2]_4[Cu_4I_8]$	2.653(2)	2.703(3)	2.580(2)	2.486(2)	2.690(3)	—	Cp = $\eta^5 - C_5H_5$; no distinction made between Cu — Cu	*95*
	2.690(3)	2.761(2)	2.551(2)		2.710(3)			
$[K(crypt\text{-}2,2,2)]_4[Ag_4Br_8]$	2.696(2)	2.750(2)	2.651(2)	2.518(2)	3.595(2)	0.030	—	*21*
	2.722(2)	2.799(2)	2.631(2)		3.562(1)			
$[As(C_6H_5)_4]_4[Ag_4I_8]$	2.847(1)	2.973(1)	2.757(1)	2.721(1)	3.306(2)	0.026(1)	—	*70*
	2.846(1)	2.897(1)	2.766(1)		3.198(1)			
$[P(C_6H_5)_4]_4[Ag_4I_8]$	2.846(1)	2.991(2)	2.765(2)	2.727(2)	3.256(2)	0.054(1)	—	*70*
	2.842(1)	2.901(2)	2.763(2)		3.171(2)			
$[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$	2.824(1)	2.948(1)	2.601(2)	2.577(1)	3.195(2)	0.050(1)	M(1) = Ag	*71*
	2.816(1)	2.864(2)	2.599(1)		3.119(2)		M(2) = Cu	
$[P(C_6H_5)_4]_4[Ag_3CuI_8]$	2.839(1)	2.968(1)	2.670(1)	2.638(1)	3.224(1)	0.057(1)	M(2) = "AgCu"; Ag, Cu share this site	*71*
	2.834(1)	2.880(1)	2.678(1)		3.147(1)			

[a] The atomic numbering is as in Fig. 9a; *d* is the displacement of the three-coordinated metal from the ligand plane.

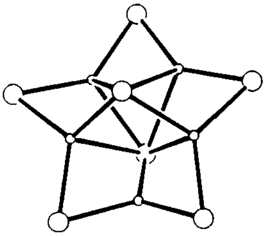

FIG. 10. The pentanuclear $[Cu_5X_7]^{2-}$ cluster; X = Br or I.

similar in both ions, i.e., 2.57–2.62 Å in $[Cu_5I_7]^{2-}$ (*98*) and 2.566(7)–2.637(6) Å in $[Cu_5Br_7]^{2-}$ (*99*).

The chlorocuprate(I) anion in $[Co(NH_3)_6]_4[Cu_5Cl_{16}]Cl$, viz. $[Cu_5Cl_{16}]^{11-}$, has been shown to be composed of five vertex-linked tetrahedra, i.e., a central $CuCl_4$ unit linked via all four vertices to four copper(I) chloride tetrahedra (*100, 101*).

Isolated pentanuclear halogenoargentate(I) species have yet to be documented.

6. *Hexanuclear Anions*

Hexanuclear anions are of two types and again have been reported hitherto solely for halogenocuprate(I) ions. In $[Cu_6I_{11}]^{5-}$ (cf. Fig. 11), determined in $[N(C_2H_5)_4]_6[Cu_6I_{11}]I$ (*79*) and $[Co(Cp)_2]_9[Cu_6I_{11}][(Cu_6I_8)_2]$ (*57*), six copper(I) iodide tetrahedra are connected via five common faces and six common edges to give a trigonal-prismatic metal core with fairly long (≈3 Å) Cu—Cu distances. Cu—I distances vary from 2.567(3) to 2.749(2) Å in $[N(C_2H_5)_4]_6[Cu_6I_{11}]I$ (*79*) and from 2.519(6) to 2.746(6) Å in the $[Cu_6I_{11}]^{5-}$ ion in $[Co(Cp)_2]_9[Cu_6I_{11}][Cu_6I_8)_2]$ (*57*).

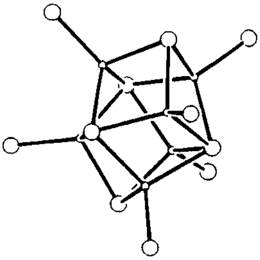

FIG. 11. The hexanuclear $[Cu_6I_{11}]^{5-}$ cluster.

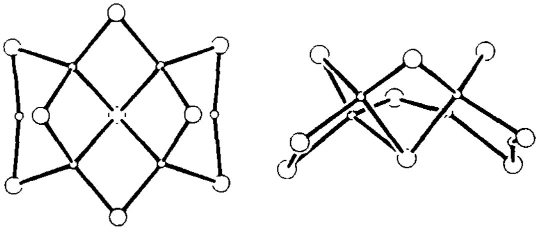

FIG. 12. The $[Cu_6Br_9]^{3-}$ anion viewed along (left) and perpendicular to (right) the twofold axis.

The other hexanuclear cluster is the $[Cu_6Br_9]^{3-}$ ion (Fig. 12), prepared and characterized in $[N(CH_3)(C_2H_5)_3]_3[Cu_6Br_9]$ (55). The anion has C_{2v} symmetry and can be visualized as being composed of four edge-sharing copper(I) bromide tetrahedra, two pairs of tetrahedra also being linked by a two-coordinated copper(I) atom situated between vertices. The Cu—Br distance involving this center is 2.285(2) Å, the Br—Cu—Br angle is 162.6(1)°, and the closest contact to a further bromide ligand is 2.866(4) Å, it thus also being possible to regard this copper(I) center as having (2 + 1) coordination (55). The Cu—Br distances associated with the four-coordinated copper(I) atom lie in the range 2.386(3)–2.697(3) Å (55).

7. *Discrete Clusters with Higher Nucleicity*

Four larger discrete halogenocuprate(I) clusters have been reported: a $[Cu_8I_{13}]^{5-}$ anion, which can be described as a cube of copper atoms bridged on all edges by iodide ligands and centered by a further iodide ligand, has been determined in $K_7(12\text{-crown-}4)_6[Cu_4I_6][Cu_8I_{13}]$ (*84*). With the *N,N*-(dimethyl) isopropylidenimmonium cation, a $[Cu_8I_{13}]^{5-}$ cluster with a completely different structure has been isolated (*102*). This anion contains six tetrahedrally coordinated and two trigonal-planar coordinated copper(I) centers (*102*). With dipyridiniomethane, a $[Cu_{19}I_{27}]^{8-}$ anion, which can be described as a centrosymmetric icosahedron composed of face-sharing copper(I) iodide tetrahedra, has been obtained (*103*). The linking of tetrahedra through two and three faces results in very short Cu—Cu contacts, leading to disorder of the copper(I) positions (*103*). Determination of the crystal structure of $(pyH)_2[Cu_3I_5]$ (pyH = pyridinium) revealed the presence of a discrete $[Cu_{36}I_{56}]^{20-}$ cluster, composed of 36 edge-sharing copper(I) iodide tetrahedra, requiring reformulation of the compound as $(pyH)_{24}[Cu_{36}I_{56}]I_4$ (*104*).

8. Polymeric Anions

Extreme diversity is exhibited in the coupling of metal halide tetrahedra to form polymeric halogenocuprate(I) and halogenoargentate(I) ions, there being an abundance of different types of infinite chains, layers, and three-dimensional arrays. Because the object of this article is to focus on variations in metal coordination number, and, in particular, on trends associated with the nature of the cation, structural description will be limited to those types of polymeric anion most frequently encountered hitherto in crystalline halogenocuprates(I) and halogenoargentates(I).

a. Species with Stoichiometry MX_2^-. The most common type of polymeric anion with this stoichiometry is an infinite chain of edge-sharing metal(I) halide tetrahedra (Fig. 13a). This has been found for

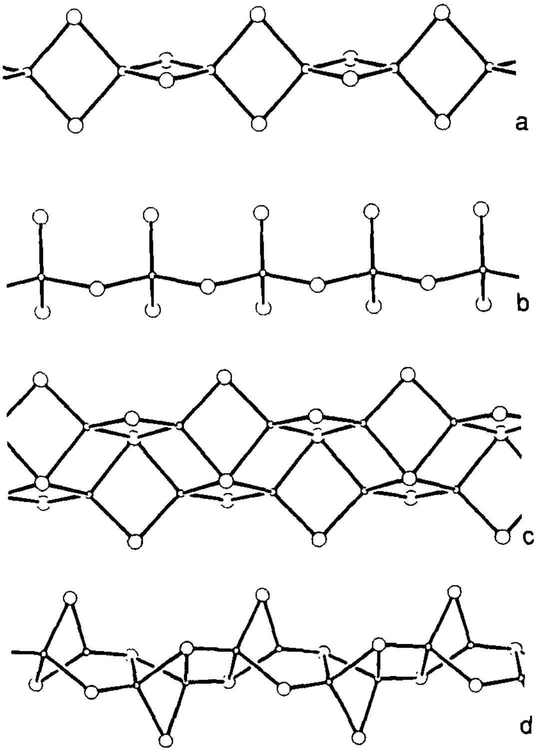

FIG. 13. Infinite-chain polymers: (a) MX_2^-, composed of edge-sharing tetrahedra; (b) MX_3^{2-}, composed of vertex-linked tetrahedra; (c) $M_2X_3^-$, composed of edge-sharing tetrahedra; (d) $M_2X_3^-$, composed of edge- and face-sharing tetrahedra.

chlorocuprates(I) and chloroargentates(I) in (pq)$[CuCl_2]_2$ (pq^{2+} = *N,N'*-dimethyl-4,4'-dipyridylium) (*105*), $[Cu(NH_3)_4][CuCl_2]_2 \cdot H_2O$ (*106*), $[Cu(en)_2][CuCl_2]_2$ (en = ethylenediamine) (*107*), and $[N(CH_3)_4][AgCl_2]$ (*108*); for bromocuprates(I) and bromoargentates(I), in $[Cu(NH_3)_4][CuBr_2]_2$ (*106*), $[Ni(en)_2][AgBr_2]_2$ (*109*), and $[S(CH_3)_3][AgBr_2]$ (*110*); and for iodocuprates(I) and iodoargentates(I), in $[Cu(NH_3)_4][CuI_2]_2$ (*111*), $[Cu(en)_2][CuI_2]_2$ (*112*), $[C_6H_8N][CuI_2]$ (*113*), $[C_6H_{14}N_3][CuI_2]$ (*113*), $[Na(H_2O)_4][CuI_2]$ (*114*), $[Rb_2H_2O][CuI_2]_2$ (*114*), $[(NH_4)_2H_2O][CuI_2]_2$ (*114*), $[Ni(en)_2][AgI_2]_2$ (*109*), $[C_8H_{22}N_2][AgI_2]_2]$ (*115*), $Sr[AgI_2]_2 \cdot 8H_2O$ (*116*), and $[N(CH_3)_4][AgI_2]$ (*117*). Selected interatomic distances reported for these chain anions are given in Table VI. The mixed-valence

TABLE VI

DISTANCES AND ANGLES REPORTED FOR SINGLE CHAINS OF STOICHIOMETRY $[MX_2]^-$[a]

Compound	M—X (Å)	M—M (Å)	X—M—X (°)	Ref.
Chlorocuprates(I)				
(pq)$[CuCl_2]_2$[b]	2.34–2.38	2.95	101–113	*105*
$[Cu(NH_3)_4][CuCl_2]_2 \cdot H_2O$	2.359(6)	2.734(4)	109.2(1)– 109.6(1)	*106*
$[Cu(en)_2][CuCl_2]_2$	2.297(3)–2.531(2)	3.119(2)	—	*107*
Chloroargentates(I)				
$[N(CH_3)_4][AgCl_2]$	2.599(1)–2.618(1)	3.137(1)–3.433(1)	98.08(4)–113.31(2)	*108*
Bromocuprates(I)				
$[Cu(NH_3)_4][CuBr_2]_2$	2.503(4)	2.857(4)	109.0(2)–110.4(2)	*106*
Bromoargentates(I)				
$[Ni(en)_2][AgBr_2]_2$	2.689(2)–2.742(2)	2.99–3.59	97.71(8)–113.30(6)	*109*
$[S(CH_3)_3][AgBr_2]$	2.661(4)–2.789(3)	—	102.4(1)–123.0(1)	*110*
odocuprates(I)				
$[Cu(NH_3)_4][CuI_2]_2$	2.575(15)–2.959(15)	3.506(2)	98.5(5)–118.9(5)	*111*
$[Cu(en)_2][CuI_2]_2$	2.646–2.706	2.987–3.581	97.2–111.6	*112*
$[C_6H_8N][CuI_2]$	2.61(1)–2.74(1)	3.01(3)–3.54(3)	98.7(6)–116.2(3)	*113*
$[C_6H_{14}N_3][CuI_2]$	2.680(1)–2.685(1)	3.362(1)	102.12(2)–117.34(3)	*113*
odoargentates(I)				
$[Ni(en)_2][AgI_2]_2$	2.845(2)–2.895(1)	3.09–3.79	98.29(5)–114.46(5)	*109*
$[C_8H_{22}N_2][AgI_2]_2$	2.856(3)–2.857(3)	3.81	96.3(1)–112.8(1)	*115*
$Sr[AgI_2]_2 \cdot 8H_2O$	2.879(2)	2.78(1)	—	*116*
$[N(CH_3)_4][AgI_2]$	2.756(3)–2.806(2)	—	97.5(1)–112.5(1)	*117*

[a] In those cases for which more than one value has been reported a range is given.

[b] pq^{2+}, *N,N'*-dimethyl-4,4'-dipyridylium.

Cu(I)–Cu(II) chain in $[N(C_2H_5)_4][Cu_2Cl_4]$ (*118*) is also of similar type, with Cu(I) and Cu(II) localized at alternate tetrahedral sites.

Recently, evidence has been provided for the existence of polymeric $[AgI_2]^-$ ions in fairly concentrated solutions of sodium diiodoargentate(I) in acetonitrile (*119*). In bis(2,2-bipyridyl)copper(II) bis[dichlorocuprate(I)] (*24*), the polymeric anion is composed of pairs of edge-sharing tetrahedra linked via linear Cl—Cu—Cl units (see Section II,A,2).

b. Species with Stoichiometry MX_3^{2-}. Such anions are typically infinite chains of vertex-linked tetrahedra (Fig. 13b) and are most often found in conjunction with alkali metal ions. Many of these compounds were the first halogenocuprates(I) and halogenoargentates(I) characterized by means of crystal structure determination. The crystal structures of $K_2[CuCl_3]$, $Cs_2[AgCl_3]$, and $Cs_2[AgI_3]$ were reported in 1949 (*120*). Other compounds that have similar structures are $K_2[AgI_3]$ (*121–123*), $Rb_2[AgI_3]$ (*121, 124*), $(NH_4)_2[CuCl_3]$ (*125*), and $(NH_4)_2[CuBr_3]$ (*125*), and the relationships between these and other structures derived from complex halogenides of type R_2MX_3 have been reviewed (*126*). More recently, the structure of $(NH_4)_2[AgI_3]\cdot H_2O$ has been shown (*127*) to be isomorphous with that of $K_2[AgI_3]$.

c. Species with Stoichiometry $M_2X_3^-$. Here the most common anionic configuration for both halogenocuprates(I) and halogenoargentates(I) is a band, or double chain, of edge-sharing metal(I) halide tetrahedra (Fig. 13c). Like the MX_3^{2-} chain polymer, this anion is most often found in compounds with relatively small cations. For chlorocuprates(I), anions of this type have been documented in $Cs[Cu_2Cl_3]$ (*128, 129*) and $[N(CH_3)_4][Cu_2Cl_3]$ (*130*); for bromocuprates(I), in $[C_6H_5N_2][Cu_2Br_3]$ (*131*), $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$ (*132*), and $Cs[Cu_2Br_3]$ (*129*), and for iodocuprates(I), in $Cs[Cu_2I_3]$ (*133*), $Rb[Cu_2I_3]$ (*92*), $[C_6H_8N][Cu_2I_3]$ (*134*), $[S(CH_3)_3][Cu_2I_3]$ (*135*), $[(CH_3)_2NH_2][Cu_2I_3]$ (*102*), $[(CH_3)_3NH][Cu_2I_3]$ (*102*), and $[(CH_3)_2CHNH_3][Cu_2I_3]$ (*102*). In addition, the mixed halide species $[Cu_2Cl_2I]^-$ and $[Cu_2ClI_2]^-$ have also been prepared and characterized as the cesium salts (*136*).

Analogous halogenoargentate(I) $[M_2X_3]^-$ ions have been determined in $[N(C_2H_5)_4][Ag_2Cl_3]$ (*137*), $[N(CH_3)_4][Ag_2Br_3]$ (*138*), $[N(C_2H_5)_4][Ag_2Br_3]$ (*137*), $Cs[Ag_2I_3]$ (*128*), and $[N(CH_3)_4][Ag_2I_3]$ (*127, 139*). A common feature of these anions, with some exceptions, e.g., $[N(C_2H_5)_4][Ag_2Cl_3]$ (*137*), is that M—M separations perpendicular to the length of the chain are slightly shorter than the corresponding distances along the chain. Selected interatomic distances reported for

$[M_2X_3]^-$ double chains of edge-sharing metal(I) halide tetrahedra are given in Table VII.

Another type of $[M_2X_3]^-$ chain, which was unknown until 1981 but which has since been documented to occur in several halogenocuprates(I), is depicted in Fig. 13d. To our knowledge this single chain of edge- and face-sharing metal(I) halide tetrahedra has not been reported for a halogenoargentate(I). The anion was first characterized as the triiododicuprate(I) in the tetraethylammonium and dimethyl-(3-dimethylamino-2-aza-2-propenylidene)ammonium salts (*89*). Similar $[Cu_2I_3]^-$ anions were subsequently determined in the 2,4,6-triphenylthiopyrylium (*140*), 3,4,5-tris(methylthio)-1,2-dithiolium (*90*), tetramethylammonium (*141*), K(15-crown-5)$^+$ (*84*), and *N*-isopropylidenisopropylimmonium (*102*) compounds. A very distorted variant has been found in $[P(CH_3)_4][Cu_2Cl_3]$ (*60*), in which pairs of three- and four-coordinated copper(I) atoms alternate. The $[Cu_2I_3]^-$ anion has been documented in an unusual layer structure, composed of edge- and vertex-linked tetrahedra, in $[(CH_3)_3CNH_3][Cu_2I_3]$ (*102*).

d. Species with Stoichiometry $M_3X_4^-$. There appear to be at least seven types of polymeric $[M_3X_4]^-$ anion, and relationships between four of these have been discussed in a recent publication (*142*). A chain anion composed of edge- and face-sharing copper(I) iodide tetrahedra has been isolated in $[N(C_3H_7)_4][Cu_3I_4]$ (*134*); of face-sharing tetrahedra, in $[P(C_6H_5)_4][Cu_3I_4]$ (*142*); and of edge-sharing metal(I) halide tetrahedra, in $[P(CH_3)(C_6H_5)_3][Cu_3I_4]$ (*134*), $[As(C_6H_5)_4][Ag_3I_4]$ (*70*), and $[P(C_6H_5)_4][Ag_3I_4]$ (*70*). The anion in $[P(C_6H_5)_4][Ag_3I_4]$ (*70*) is depicted in Fig. 14a. Several heteronuclear, mixed-halide species (*142*) assume a fourth $[M_3X_4]^-$ structural type (Fig. 14b), a triple chain of edge-linked tetrahedra, in which the peripheral halogens bridge two metal atoms and the inner halogens bridge four, i.e., analogous to the $[M_2X_3]^-$ double chain (Fig. 13c). The compounds are $[(DMF)_2H][M_3I_{4-n}X_n]$, where M = Cu/Ag, X = I/Br/Cl, and $n = 0$, 1, and 2 (*142*). A fifth type of chain, composed of pairs of edge-sharing metal(I) halide tetrahedra linked to similar units through the four free vertices, has been found in $[N(C_4H_9)_4][Ag_3I_4]$ (*143*), whereas in $[(CH_3)_3NCH_2CH_2N(CH_3)_3][Ag_3I_4)_2]$ (*144*), edge-linked tetrahedra form a layer. A chain containing one three-coordinated and two four-coordinated copper(I) centers has been determined in [K(dibenzo-24-crown-8)]$[Cu_3I_4]$ (*84*) (cf. Section II,B,5).

e. Species with Stoichiometry $M_4X_5^-$. The majority of these species, such as $Rb[Ag_4I_5]$ (*145*) and its analogs, are important solid electro-

TABLE VII

Distances and Angles Reported for Double Chains of Stoichiometry $[\mathrm{M_2X_3}]^-$[a]

Compound	M — X (Å)	M — M (Å)	X — M — X (°)	Ref.
Chlorocuprates(I)				
$\mathrm{Cs[Cu_2Cl_3]}$	2.283–2.490	2.800–3.113	102.7–119.2	*129*
$\mathrm{[N(CH_3)_4][Cu_2Cl_3]}$	2.254(2)–2.574(2)	2.869(2)–3.197(2)	96.28(7)–125.15(9)	*130*
Chloroargentates(I)				
$\mathrm{[N(C_2H_5)_4][Ag_2Cl_3]}$	2.514(2)–2.778(2)	3.348(2)–3.486(2)	94.45(7)–123.09(8)	*137*
Bromocuprates(I)				
$\mathrm{[C_6H_5N_2][Cu_2Br_3]}$	2.45–2.57	2.86–3.09	—	*131*
$\mathrm{[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]}$	2.427(2)–2.609(2)	2.904(2)–3.224(3)	103.55(6)–119.40(7)	*132*
$\mathrm{Cs[Cu_2Br_3]}$	2.426–2.587	2.909–3.094	106.5–117.0	*129*
Bromoargentates(I)				
$\mathrm{[N(CH_3)_4][Ag_2Br_3]}$	2.612(2)–2.833(2)	3.078(3)–3.526(3)	99.05(6)–122.35(9)	*138*
$\mathrm{[N(C_2H_5)_4][Ag_2Br_3]}$	2.630(2)–2.844(2)	3.250(2)–3.547(2)	97.62(5)–120.96(6)	*137*
Iodocuprates(I)				
$\mathrm{Cs[Cu_2I_3]}$	2.599(2)–2.694(2)	3.036(3)–4.361(3)	—	*133*
$\mathrm{Rb[Cu_2I_3]}$	2.592(5)–2.716(4)	2.864(2)–3.427(6)	101.8(2)–115.8(2)	*92*
$\mathrm{[C_6H_8N][Cu_2I_3]}$	2.615(3)–2.714(3)	2.947(4)–3.144(2)	106.6(1)–114.1(1)	*134*
$\mathrm{[S(CH_3)_3][Cu_2I_3]}$	2.601(4)–2.753(4)	2.941(6)–3.432(7)	101.0(1)–118.1(1)	*135*
$\mathrm{[(CH_3)_2NH_2][Cu_2I_3]}$	2.554(7)–2.811(7)	2.942(6)–3.260(7)	101.4(2)–120.4(2)	*102*
$\mathrm{[(CH_3)_2CHNH_3][Cu_2I_3]}$	2.599(2)–2.768(2)	2.882(1)–3.310(2)	103.10(7)–116.72(7)	*102*
$\mathrm{[(CH_3]_3NH][Cu_2I_3]}$	2.594(7)–2.745(7)	2.894(8)–3.470(11)	100.5(3)–117.0(2)	*102*
Iodoargentates(I)				
$\mathrm{Cs[Ag_2I_3]}$	2.79–2.90	—	—	*128*
$\mathrm{[N(CH_3)_4][Ag_2I_3]}$	2.780(2)–2.966(2)	—	99.84(5)–119.86(7)	*127*

[a] For each type of distance or angle the range observed is cited.

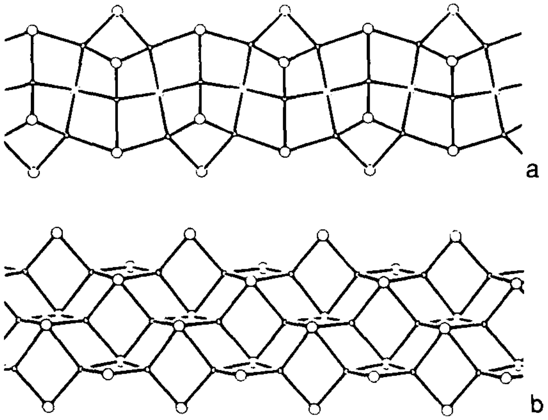

FIG. 14. The triple $[M_3X_4]^-$ chains of edge-linked tetrahedra as in (a) $[P(C_6H_5)_4][Ag_3I_4]$ and (b) $[(DMF)_2H][M_3I_{4-n}X_n]$.

lytes. In the unit cell of $Rb[Ag_4I_5]$ (*145*), Ag^+ diffusion paths are provided by 56 face-linked iodide tetrahedra that form a three-dimensional network. A large number of such phases, including $CsCu_4Cl_3I_2$ (*146*), $RbCu_4Cl_3(I_{2-x}Cl_x)$ (*87*), and $(Cs_{1-y}Rb_y)Cu_4Cl_3(I_{2-x}Cl_x)$ (*147*), have been prepared and characterized, showing a variety of three-dimensional patterns. The solid electrolytes $[N(CH_3)_4]_2[Ag_{13}I_{15}]$ (*148*), $[N(CH_3)_2(C_2H_5)_2]_2[Ag_{13}I_{15}]$ (*149*), and $[C_5H_5NH]_2[Cu_5Br_7]$ (*150*) can also be considered to be of this type. Recently, a one-dimensional solid electrolyte $DMM[Ag_4I_5]$ (DMM = *N,N′*-dimethylmorpholinium), in which Ag^+ ions are constrained to move only in one direction via an infinite chain of face-sharing icosahedra of iodide ions, has been reported (*151*). In $[Te(C_2H_5)_3][Ag_4I_5]$, the anion is an infinite layer of linked trigonal bipyramids formed from pairs of face-sharing tetrahedra (*152*). It is, however, often somewhat difficult to distinguish the presence of halogenocuprate(I) or halogenoargentate(I) anions, as such, in these solid electrolytes, which are primarily matrices for mobile Cu^+ or Ag^+ ions, and detailed treatment of the rich structural chemistry exhibited by this type of compound is therefore considered to be beyond the scope of the present article.

f. Miscellaneous Polymeric Anions. Unusual polymeric anions reported include a $[Ag_5Br_8]^{3-}$ band that is related to the $[M_3X_4]^-$ triple chain (cf. Fig. 14b) by loss of every second spinal metal atom (*153*), an $[Ag_5I_6]^-$ chain that can be seen as a decagonal tube (*154*), and an infinite $[Cu_3Cl_5]^{2-}$ cylinder (*155*). In $[Pt(dapn)_2][Pt(dapn)_2Br_2]$

$[(Cu_3Br_5)_2]$ (dapn = 1,2-diaminopropane) (*156*), a single-strand $[CuBr_2]^-$ polymer is intertwined with a linear Br—Cu—Br chain, so that one copper(I) atom is tetrahedrally coordinated and the other has distorted trigonal-bipyramidal coordination geometry (cf. Section II,D). A polymeric $[Cu_6I_8]^{2-}$ layer is present in $[Co(Cp)_2)]_9[Cu_6I_{11}][(Cu_6I_8)_2]$ (*57*) and a $[Ag_7I_{11}]^{4-}$ layer is present in $[(CH_3)_3CNH_3]_4[Ag_7I_{11}]$ (*102*).

D. SPECIES CONTAINING FIVE-COORDINATED METAL CENTERS

Halogenocuprates(I) or halogenoargentates(I) in which the metal is five coordinated are rare. One of the copper(I) centers in tris[bis(1,2-diaminoethane)platinum(II)dichlorobis(1,2-diaminoethane)platinum(IV)] tetrakis[tetrachlorocuprate(I)] (*52*) [cf. Section II,A,2], i.e., that trigonally coordinated by three chloride ligands at 2.291(9) Å and with apical contacts where Cu—Cl = 3.10(1) Å, could be regarded as having trigonal-bipyramidal coordination. Similar considerations apply to one of the crystallographically independent copper(I) atoms in $[Pt(dapn)_2][Pt(dapn)_2Br_2][Cu_3Br_5)_2]$ (dapn = 1,2-diaminopropane) (*156*) (Section II,C,7,f). Silver(I) has distorted trigonal-bipyramidal coordination geometry in $Cs[AgCl_2]$ with equatorial Ag—Cl distances of 2.49 and 2.67 (×2) Å and apical Ag—Cl bonds of 2.87 Å, the Cl—Ag—Cl apical angle being 164° (*157*). Layer formation is effected by linking through four vertices of the polyhedra (*157*). Comparison of X-ray powder patterns indicates that $Cs[AgBr_2]$ has an analogous structure (*158*).

III. Influence of Cation Properties on Metal(I) Coordination Number

It has been recognized that cationic properties, such as size, shape, and distribution of the positive charge, are of importance for the anionic configurations assumed in iodocuprates(I) (*89*) and iodoargentates(I) (*159*). Several independent systematic studies have been carried out in order to investigate possible correlations between cationic properties, in particular, cation size, and the structure of the halogenocuprate(I) or halogenoargentate(I) anion coprecipitated. Thus many of the anions whose structures have been described in the preceding section have been prepared and characterized in connection with such investigations. In this section an attempt will be made to summarize those correlations that have been previously reported.

A. THE EFFECT OF CATION SIZE

Investigations concerning the role of cation size have mainly been carried out using bulky unipositive cations (R^+) with a well-screened positive charge. The most usual method of preparation is reaction between the appropriate metal(I) halide and RX in an organic solvent. In the majority of cases a single product is obtained independent of the solvent used and of the total molar ratios M : X in the system. In some systems, however, solvent effects have been shown to be important, leading to different products. This seems to be particularly true for iodocuprates(I) (see, e.g., Ref. *57* and references therein) and for iodoargentates(I) (*70*). A cation that has proved exceptionally versatile in the preparation of halogenocuprates(I) and halogenoargentates(I) is methyltriphenylphosphonium, which crystallizes with discrete anions such as $[Cu_4I_6]^{2-}$ (*82, 83*), $[CuI_3]^{2-}$ (*56*), $[CuBr_3]^{2-}$ (*46, 56*), $[AgI_3]^{2-}$ (*46, 56*), $[CuBr_2]^-$ (*46*), and $[Cu_2Br_4]^{2-}$ (*76*), as well as with a $[Cu_3I_4]^-$ triple chain (*134*). In addition, for a few tetraalkylammonium and related chlorocuprates(I) and bromocuprates(I), for which total molar ratios Cu : X of 1 : 2 have been employed during preparation and for which the primary product has a stoichiometry different from this value, a second phase has been obtained at the end of the crystallization, invariably containing an anion with a lower copper(I) coordination number than that in the major product (*42, 45, 60*).

Comparison of halogenocuprate(I) anions obtained with symmetrically substituted unipositive quaternary ammonium, phosphonium, and arsonium cations indicates a distinct correlation between cation size and the coordination number of copper(I) in the resulting anion (*32*), further substantiated for chlorocuprates(I) (*60*) and bromocuprates(I) (*59*). The trend is such that copper(I) assumes digonal, trigonal, and finally tetrahedral coordination geometry with decreasing size of the cation. Calculation of the concentration of halide ligand in the crystalline phase, which can be considered to be an indicator of cation size, shows that this parameter also increases regularly with copper(I) coordination number (*32, 59, 60*). This is illustrated in Fig. 15. In addition to the values of the ligand concentration given in the references cited, a chloride concentration of 10.6 mol dm^{-3} for $[P(C_2H_5)_4]_2[Cu_2Cl_4]$ (*72*) and iodide concentrations of 5.7 mol dm^{-3} for $[P(C_6H_5)_4]_2[Cu_2I_4]$ (planar and folded anions) (*68*) and of 6.2 mol dm^{-3} for $[N(C_4H_9)_4]_3[Cu_4I_7]$ (*96, 103*) have been calculated. In $[N(C_2H_5)_4]_6[Cu_6I_{11}]I$ (*79*), the total concentration of iodide is estimated to be 10.0 mol dm^{-3}. For those anions in which copper(I) exhibits more than

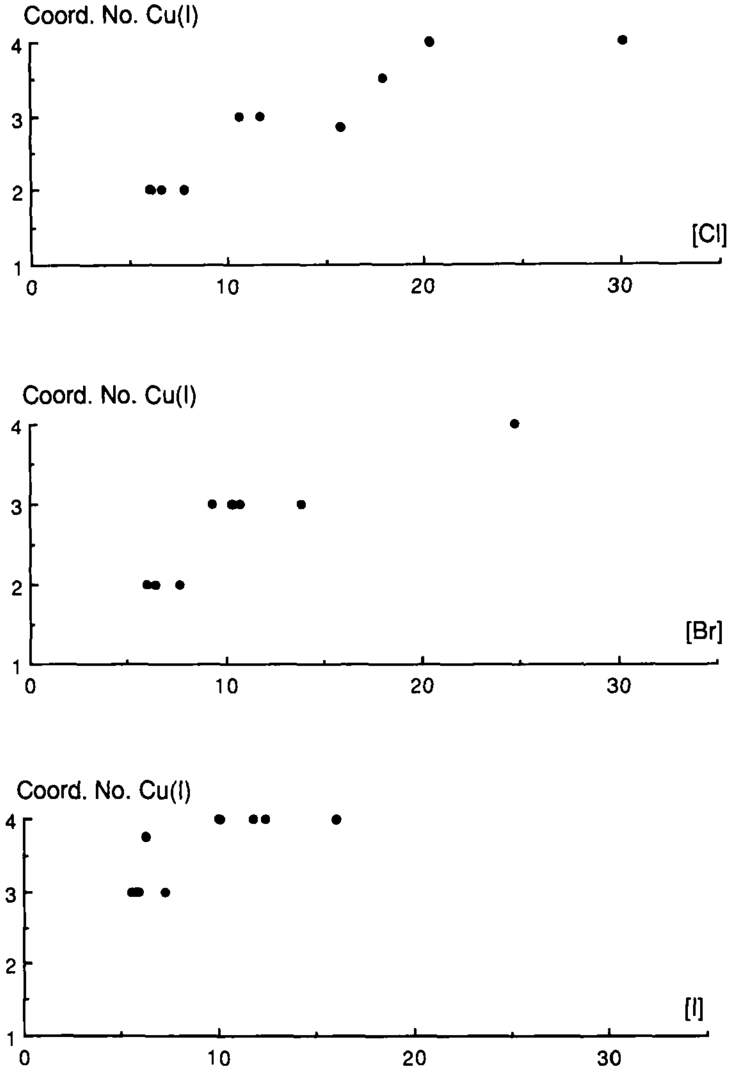

FIG. 15. The copper(I) coordination number as a function of the concentration of the halogenide ligand (mol dm^{-3}) in halogenocuprates(I) crystallizing with symmetrically substituted quaternary ammonium, phosphonium, and arsonium cations.

one coordination number, a mean coordination number has been employed. As is apparent from the diversity in stoichiometry of the various halogenocuprate(I) species obtained, there is no correlation between the coordination of copper(I) and the concentration of this metal ion in the crystalline phase (cf. Ref. *32*).

Examination of the three graphs in Fig. 15 shows that the coordination number of copper(I) increases with increasing concentration of ligand in the solid (decreasing cation size) in all three halogenocuprate(I) series, larger cations being required to promote lower coordination numbers the heavier the halogenide ligand. It has not yet proved possible to prepare an iodocuprate(I) in which copper(I) is two coordinated using cations of this type. As mentioned in Section II,A,1, monomeric $[CuI_2]^-$ has, however, been isolated with the K(18-crown-6)$^+$ and K(dicyclohexano-18-crown-6)$^+$ cations (*17*). These crown ether-based cations differ in shape from the effectively spherical quaternary ammonium, phosphonium, and arsonium cations under discussion, and, consequently, also with respect to the exposure of the positive charge. Both, however, give rise to relatively low solid-state ligand concentrations, viz. 6.2 and 4.8 mol dm^{-3}, respectively.

That there exists a correlation between the copper(I) coordination number in the relevant anion and the concentration of halide ligand in the solid has been interpreted as suggesting that dilution of the ligand ions by the cations is a determinative factor for the attainment of a particular copper(I) coordination number and thus for the resulting configuration of the anion (*32*). Large cations hinder the accumulation of a high ligand concentration and thus suppress catenation, leading to the formation of small, discrete anions in which the metal exhibits a low coordination number. Small cations, on the other hand, are less effective in the suppression of catenation and tend to promote the formation of polynuclear species in which copper(I) attains a high coordination number.

Indirect evidence for the importance of cation–halogenide ligand packing for the determination of a particular coordination number has been provided by showing that the halogenocuprate(I) species in solution at the onset of crystallization may differ from that present in the crystals (*45*). Thus, infrared spectroscopic investigation of ethanolic solutions from which the $[Cu_4Br_6]^{2-}$ cluster, composed of three-coordinated copper(I) (cf. Section II,B,3), crystallizes ($[Br^-]_{max.} \approx 0.16$ *M*) demonstrate that the centrosymmetric $[CuBr_2]^-$ monomer, $\nu_3 = 323$ cm^{-1}, is the dominant and probably the sole bromocuprate(I) species present in solution (*45*). More concentrated solutions ($[Br^-] \approx 0.30$ *M*) of solids containing bromocuprate(I) anions in which copper(I) is three coordinated, obtained by dissolving $[N(C_3H_7)_4]_2[Cu_4Br_6]$ (*85*), $[P(CH_3)_4]_2[CuBr_3]$ (*59*), and $[N(CH_3)_4]_3[Cu_2Br_5]$ (*64*) in nitromethane, also contained $[CuBr_2]^-$ as the sole observable species (*45*). Identical results had been obtained previously for the dissolution of the tetraethylammonium dibromocuprate(I) in nitromethane (*2*), the solid compound subsequently being shown to contain a dinuclear anion in which copper(I) is trigonally coordinated (*66*). Although the existence of three-coordinated halogenocuprate(I) species such as $[CuCl_3]^{2-}$ (*160–162*) and $[Cu_2I_4]^{2-}$ (*163*) in solution has been demonstrated by means of techniques other than vibrational spectroscopy, media permitting far higher concentrations of halogenocuprates(I) have been employed. Indeed the total halogenide concentrations in some cases (*163*) approach the lower limits of those estimated for the relevant halogenocuprate(I) species, here $[Cu_2I_4]^{2-}$, in the solid state. Similarly, monomeric $[AgI_3]^{2-}$ ions (*81*) and various oligomeric (*81*) or polymeric (*119*) iodoargentate(I) species have been shown to exist in concentrated solutions, and also in fused $(K,Na)NO_3$ (*164*).

It has been suggested that cation–halogenide ligand packing may be envisaged as the primary process occurring during crystal nucleation, copper(I) attaining the appropriate coordination number by diffusion into available interstices, subsequent rearrangement then resulting in the specific anion (*45*). Such a "mechanism" would imply a rapid ligand exchange rate for copper(I) in solution, the dihalogenocuprate(I) anion providing a source of the "naked" metal ion. Although it has not yet proved possible to substantiate the latter hypothesis, the extreme reversibility of copper(I) complexes is well documented in electrochemical applications. Moreover, the high polarizability associated with Cu^+ (*165*) is not inconsistent with easy adaptability of copper(I) to the wide variety of coordination situations that might be envisaged to ensue from cation–halogenide ligand packing.

Silver(I) is another ion commonly associated with electrochemical reversibility and is also readily polarizable (*165*). One might therefore expect an analogous correlation between the coordination number of silver(I) in crystalline halogenoargentates(I) and the size of the cation. The variation in silver(I) coordination number as a function of the concentration of ligand in crystalline halogenoargentates(I) containing symmetrically substituted quaternary ammonium, phosphonium, and arsonium cations is illustrated in Fig. 16, the ligand concentrations having been taken from Ref. *70*. The graphs demonstrate the dominance of coordination number four for silver(I), coordination number three being found only with the larger cations. Silver(I) would, however, appear to show a tendency toward the trends observed for

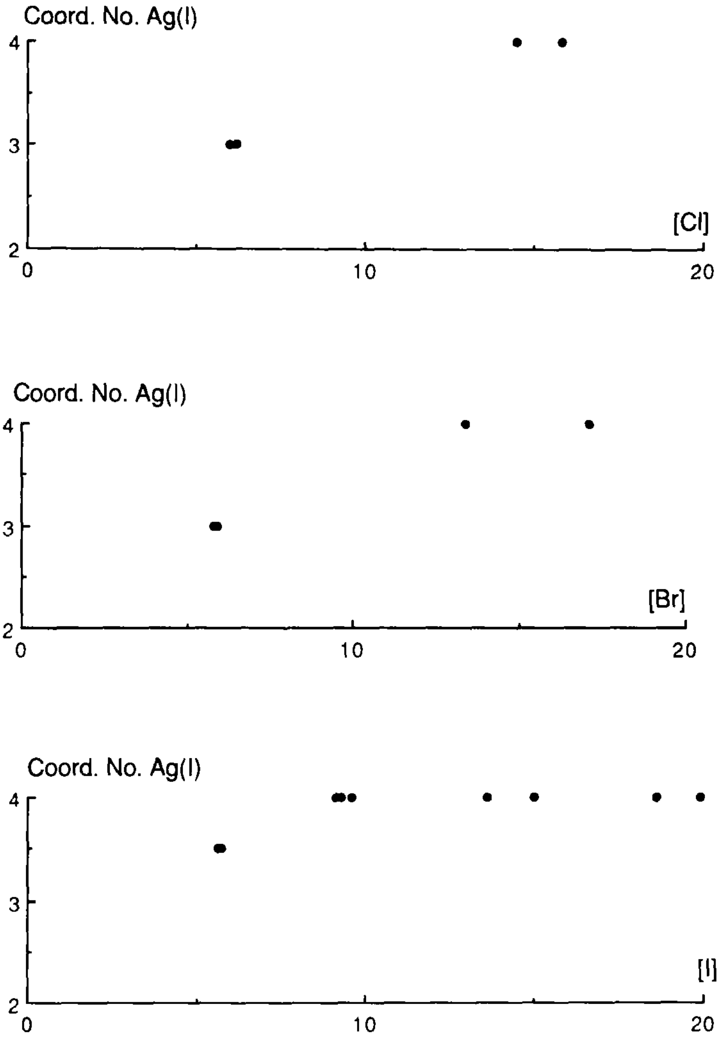

FIG. 16. The silver(I) coordination number as a function of the concentration of the halogenide ligand (mol dm^{-3}) in halogenoargentates(I) crystallizing with symmetrically substituted quaternary ammonium, phosphonium, and arsonium cations.

copper(I) in halogenocuprates(I) with this type of cation, even if there is less variation in the silver(I) coordination number. By employing a larger cation of spherical type, viz. K(crypt-2,2,2)$^+$, it has proved possible to isolate a linear, monomeric dichloroargentate(I) anion in the solid state (*21*); the chloride concentration in this compound is

5.1 mol dm^{-3}. This, in itself, suggests that cation–halogenide packing is also of importance for the determination of the metal coordination number in crystalline halogenoargentates(I).

The successful preparation in $[P(C_6H_5)_4]_4[Ag_2Cu_2I_8]$ and $[P(C_6H_5)_4]_4[Ag_3CuI_8]$ (*71*) of heteronuclear $[Ag_2Cu_2I_8]^{4-}$ and $[Ag_3CuI_8]^{4-}$ clusters, in which copper(I) is three coordinated, whereas silver(I) is four coordinated or both three and four coordinated, respectively, from the metal(I) iodides and tetraphenylphosphonium iodide in acetonitrile solution, may also be seen as lending support to the hypothesis that the primary process at the solution–crystal interface is cation–halide packing, the "naked" metal ion diffusing into the appropriate interstices.

B. THE EFFECTS OF CHARGE AND SHAPE

In general, it is true to say that relatively small cations with exposed positive charge, such as the alkali metal ions, tend to crystallize with polymeric halogenocuprates(I) or halogenoargentates(I) in which the metal exhibits tetrahedral coordination geometry, the most common anion being the dinegative MX_3^{2-} chain (Section II,C,8,b). Complexed cations with higher positive charge, e.g., $[Cu(en)_2]^{2+}$ or $[Ni(en)_2]^{2+}$, are also associated with polymeric anions in which the metal is four coordinated, but in this case the MX_2^- chain of edge-sharing tetrahedra appears to be prevalent (Section II,C,8,a). For a series of iodocuprates (I) containing polymeric $[Cu_3I_4]^-$, $[Cu_2I_3]^-$, and $[CuI_2]^-$ anions composed of shared copper(I) iodide tetrahedra (Section II,C,8), Hartl and Mahdjour-Hassan-Abadi have demonstrated that with decreased polarizing ability of the cation, anions with progressively lower negative charge distribution, i.e., decreased I^-: CuI ratio, are obtained (*134*). Thus it would seem that for a given metal(I) coordination number in a polymeric species, the general trend is that the higher the effective charge of the cation, the higher the net charge of the anion, whereas within a group of anions bearing the same negative charge, the charge distribution and thus the I^- : MI ratio tend to increase with increased polarizing power of the cation.

Whereas the metal(I) coordination number would appear to be largely determined by cation size, distribution of positive charge is undoubtedly determinative for the detailed structure of the anion. This has been further demonstrated by Hartl and co-workers in studies involving pairs of isomeric cations, e.g., $[N(CH_3)_4]^+$ and $[(CH_3)_3CNH_3]^+$ and $[(CH_3)_3NH]^+$ and $[(CH_3)_2CNH_3]^+$ (*102*). All four cations crystallize with iodocuprate(I) anions of stoichiometry $[Cu_2I_3]^-$ composed of copper(I) tetrahedra. Whereas $[N(CH_3)_4]^+$ gives rise to a single chain of edge- and face-sharing tetrahedra (*141*), a layered anion is formed with the isomeric cation $[(CH_3)_3CNH_3]^+$ (*102*); both $[(CH_3)_3NH]^+$ and $[(CH_3)_2CNH_3]^+$ crystallize with double chains of edge-sharing tetrahedra (cf. Section II,C,8,c), differing slightly from one another with respect to distortion (*102*).

Investigation of a series of bromocuprates(I) crystallizing with unsymmetrically substituted quaternary ammonium and phosphonium cations, with well-screened positive charge (see Ref. *55* and references therein), has shown that, whereas the copper(I) coordination number increases with increasing concentration of bromide ligand in the crystalline phase, correlation between the copper(I) coordination number and decreasing overall volume of the cation, as estimated from volume increments for the relevant substituents (*166*), is somewhat less pronounced (*55*), perhaps reflecting the role of shape in cation–halogenide packing.

C. CONCLUSIONS

A feature of halogenocuprates(I) and, to a somewhat lesser degree, of halogenoargentates(I) that is consistent with their apparent adaptability to cation dictates is the observed variation in metal–ligand distances for a given anionic species. This is particularly marked for anions in which the metal exhibits coordination numbers of three or four (cf. Tables II–VII). The observed spread in bond distances suggests that halogenocuprates(I), in particular, are rather polar assemblies of metal(I) cations and individual halide ions held together by electrostatic forces. Although there is less variation in the connectivity relationships shown by a given discrete, digonal MX_2^- ion in different environments, nuclear quadrupole resonance (NQR) spectra for monomeric $[CuCl_2]^-$ and $[CuBr_2]^-$ indicate an ionic character of 82 and 80% in the Cu—Cl and Cu—Br bonds, respectively (*2*), which can be compared with an ionic character of 68% for the Au—Cl bond in $[AuCl_2]^-$ (*167*).

That there is a relationship between the coordination number of the metal in crystalline halogenocuprates(I) and halogenoargentates(I) and the properties of the cation with which it is coprecipitated would now seem to be well established. The tuning of anionic configurations to cation properties reflects the versatility in coordination requirements not only of the metal but also of the ligands. Cation size would appear to be of prime importance for the determination of a particular metal(I) coordination number, the tendency to attainment of a higher coordination number and to catenation increasing with decreasing cation size and also from Cl through Br to I. Larger cations are required to promote the formation of monomeric or dimeric halogenoargentates(I) with a low silver(I) coordination number than is the case for halogenocuprates(I).

Rationalization of the detailed geometry of the particular halogenocuprate(I) or halogenoargentate(I) ion in terms of the influence of cation shape or positive charge distribution is, however, much more complex. Whereas it has proved possible to employ cations predictively for anion design in series of compounds containing comparable cations, e.g., symmetrically substituted tetraalkylammonium and phosphonium analogs (cf. *60, 71, 72*), it seems doubtful that cations of disparate shape can be used as other than predictors of metal(I) coordination number.

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