Synthetic and Structural Study of Tetra-μ-3-aminopropanolato-tricopper(II) *catena*-Pentaiodotricuprate(I) and -argentate(I)†

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The complexes $[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4][M^I_3I_5]$ (M = Cu **1** or Ag **2**) have been prepared and characterized by IR spectroscopic and conductivity measurements. The structure of **1** [monoclinic, space group *C*2/*c*, *a* = 14.350(4), *b* = 16.046(2), *c* = 13.183(3) Å, β = 101.30(2)°] has been refined to an *R* value of 0.041 (*R*′ = 0.048). The cation consists of three linearly arranged copper(II) ions chelated by four 3-aminopropanolate ligands and polymeric $(Cu^I_3I_5{}^{2-})_n$ chains. The nature of complex **2** was revealed by Fourier-transform IR measurement and elemental analyses. Its ionic conductivity (σ) is $1.13 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 50 °C. Complex **1** does not show any ionic or electronic conductivity.

This work is a continuation of our studies on copper(II)–3-aminopropanol complexes. In a recent paper[1] we described a mixed-valence copper(I,II) complex having the formula $[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4(dmf)]_2[Cu^I_6I_{10}]$ (dmf = dimethylformamide). This prompted us to study the anionic part of the complex in more detail, and to compare the behaviour of copper(I) and silver(I) ions in similar reaction systems.

There are many examples of mixed-valence copper(I,II) complexes in the literature.[2] Such compounds are of interest since it is known that electron transfer between two oxidation states is an important process in biological oxidation–reduction reactions of copper proteins.[3] One group of mixed-valence copper compounds can be formulated as $[Cu^{II}L_n][Cu^I_xX_y]$, where L = a neutral ligand with $n = 4$ for a monodentate and $n = 2$ for a didentate ligand and X = halide ion. The anion $[Cu^I_xX_y]$ can be a discrete ion, like $[CuL_2][Cu_2I_4]$ in which L = 1,1-di-2-pyridylethanol,[4] or polymeric, like $[Cu(en)_2][(CuCl_2)_2]$ in which en = 1,2-diaminoethane.[5]

Another area of interest is that the cationic copper(II)–aminoalcohol complexes with anionic halogeno–copper(I) and –silver(I) complexes can act as solid ionic conductors. Solid-ion conductors transport electric current by means of ions and have found use in fuel cells, batteries, sensors and chemotronic components.[6] Electrolytic conductivity is an inherent property associated with the crystal structure. In AgX- and CuX-based electrolytes (X = Cl, Br or I) the most important requirements for the structure are the network of passageways which are formed by face-sharing halide-ion polyhedra and disordered Ag^+ and Cu^+ cations in the halide framework.[7]

Now we report the results of synthetic, spectroscopic, structural and conductivity measurements on two new complexes containing trimeric aminoalcoholatocopper(II) cations with either iodo-cuprate(I) or -argentate(I) anions.

Experimental

Materials.—All chemicals used were of reagent grade used as received.

Physical Measurements.—Elemental analyses were done by using standard titrimetic methods (Cu and I) and with a Perkin-Elmer 2400 Series II CHNS/O analyser for C, H and N. Fourier-transform IR measurements were made on Mattson 6030 (MIR 4000–400 cm^{-1}) and 4060 (FIR 500–80 cm^{-1}) Galaxy series spectrometers in Nujol mulls. The conductivity measurements were made on pressed powder pellets with silver contacts.

Preparation of Complexes.—$[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4][Cu^I_3I_5]$ **1**. A 1.0 mol dm^{-3} MeCN solution of 3-aminopropanolate was prepared from NEt_3 and 3-aminopropanol in a 1:1 molar ratio. A 0.2 mol dm^{-3} MeCN solution of $[Cu^I_3I_5]^{2-}$ was prepared from CuI (5 mmol) and NBu_4I (3.25 mmol) in MeCN (25 cm^3). A sample of this solution (0.4 mmol Cu^I) was added with stirring to a solution containing copper(II) trifluoromethanesulfonate (0.25 mmol) and 3-aminopropanolate (0.35 mmol) in a 3:4 molar ratio in MeCN (10 cm^3). Dark green needles precipitated from the bright green solution during 15 min (99 mg, yield 69% based on Cu^{II}). The crystals were separated by decantation and washed with MeCN and diethyl ether, m.p. 200 °C (Found: C, 11.4; H, 2.3; Cu, 28.5; I, 48.5; N, 4.2. Calc. for $C_6H_{16}Cu_3I_{2.5}N_2O_2$: C, 11.0; H, 2.5; Cu, 29.1; I, 48.4; N, 4.3%).

$[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4][Ag^I_3I_5]$ **2**. A 0.5 mmol sample of Ag^+ (1 cm^3 0.5 mol dm^{-3} $AgNO_3$ in MeCN) and 0.83 mmol of I^- (1.67 cm^3 0.5 mol dm^{-3} NBu_4I in MeCN) were added to a solution containing copper(II) trifluoromethanesulfonate (0.5 mmol) and 3-aminopropanolate (0.67 mmol) in a 3:4 molar ratio in MeCN (10 cm^3). The yellowish AgI precipitated immediately, but dissolved during 1 d while dark blue, needle crystals formed (181 mg, yield 70% based on Cu^{II}). The crystals were separated by decantation and washed with MeCN and diethyl ether, m.p. 186 °C (Found: C, 10.3; H, 2.1; Cu, 13.1; N, 4.0. Calc. for $C_6H_{16}AgCu_2I_{2.5}N_2O_2$: C, 10.0; H, 2.2; Cu, 13.2; N, 3.9%).

Both compounds are insoluble in water, MeOH, EtOH, MeCN, tetrahydrofuran and CH_2Cl_2, but are slightly soluble in dmf giving a green solution. They decompose in acetic acid resulting in precipitation of CuI or AgI and leaving a blue solution.

Crystal Structure Determination of Complex **1**.—*Crystal data.* $C_6H_{16}Cu_3I_{2.5}N_2O_2$, $M = 656.10$, monoclinic, space group *C*2/*c* (no. 15), *a* = 14.350(4), *b* = 16.046(2), *c* = 13.183(3) Å, β = 101.30(2)°, *U* = 2977(1) $Å^3$ [by least-squares refinement on setting angles ($38.8 < 2\theta < 44.7°$) for 25 carefully centred reflections], *Z* = 8, $D_c = 2.928$ g cm^{-3}, *F*(000) = 2412. Dark green needle, dimensions 0.160 × 0.160 × 0.180 mm, μ(Mo-Kα) = 93.86 cm^{-1}.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Data collection and processing. All data were collected at room temperature on a Rigaku AFC5S diffractometer with graphite-monochromatized Mo-Kα (λ = 0.710 69 Å) radiation. The intensity data were collected in an ω–2θ scan mode at an ω-scan speed 4.0° min^{-1} with ω-scan width = 1.63 + 0.30 tanθ. A total of 2849 reflections were measured to $\theta_{\max}$ = 50°, R_{int} = 0.033; 1806 reflections having $I > 3.00\sigma(I)$ were used. All data were corrected for Lorentz-polarization effects and an empirical absorption correction based on ψ scans of three reflections (maximum, minimum transmission factors = 0.81, 1.00). The intensities of three representative reflections decayed by −1.60%; a linear correction factor was applied to account for this.

Structure analysis and refinement. The structure was solved by direct methods[8,9] followed by successive Fourier syntheses, and refined by least-squares techniques to an R value of 0.041 [R' = 0.048, $w = 1/\sigma^2(F_o)$] with all non-hydrogen atoms anisotropic. Hydrogen atoms were included with fixed thermal parameters in calculated positions. Neutral atom scattering and dispersion factors were taken from ref. 10. All calculations were performed using the TEXSAN[11] crystallographic software. The figures were drawn with the PLUTO[12] and ORTEP[13] programs. The atomic coordinates are listed in Table 1.

The copper atom, Cu(4) in the $[\text{Cu}^{\text{I}}_3\text{I}_5]^{2-}$ chain was disordered in an abnormal way for heavy atom. It is in a general position with occupancy factor $\frac{1}{2}$. Symmetry generates another atom Cu(4$^{\text{II}}$) (II $-x$, y, $\frac{1}{2} - z$) very close to Cu(4) (1.360 Å). Chemically this means that Cu(4) cannot be at both positions at the same time. If there is a copper atom at the position of Cu(4) there is none at Cu(4$^{\text{II}}$), and *vice versa*. Consequently there are two $[\text{Cu}^{\text{I}}_3\text{I}_5]^{2-}$ chains (A and B) which have different Cu(4) positions. Another possibility is that Cu(4) is statistically disordered over these two positions. The solution obtained when the structure was solved in space group *Cc* did not have the above problem, but the bond lengths and angles of carbon atoms in the cation became very distorted.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Atomic positional parameters for $[\text{Cu}^{\text{II}}_3(\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_4][\text{Cu}^{\text{I}}_3\text{I}_5]$

Atom	*x*	*y*	*z*
I(1)	0	−0.118 72(6)	$\frac{1}{4}$
I(2)	−0.065 30(6)	0.109 61(5)	0.072 56(6)
I(3)	0.224 39(6)	0.049 79(5)	0.176 85(6)
Cu(1)	$\frac{1}{2}$	−0.028 9(1)	$\frac{1}{4}$
Cu(2)	0.361 3(1)	−0.022 15(8)	0.385 1(1)
Cu(3)	0.059 6(2)	−0.021 3(1)	0.096 0(2)
Cu(4)	0.047 1(3)	0.045 9(2)	0.248 7(3)
O(1)	0.423 3(5)	−0.102 4(4)	0.311 2(6)
O(2)	0.465 5(6)	0.041 8(4)	0.352 7(6)
N(1)	0.257 5(8)	−0.098 5(6)	0.406 5(8)
N(2)	0.330(1)	0.065 4(7)	0.481(1)
C(1)	0.391 6(9)	−0.183 5(7)	0.278(1)
C(2)	0.289(1)	−0.198 6(7)	0.278(1)
C(3)	0.262(1)	−0.186 3(8)	0.380(1)
C(4)	0.484(1)	0.125 5(8)	0.370(2)
C(5)	0.443(1)	0.166 6(9)	0.443(1)
C(6)	0.352(1)	0.151 1(8)	0.467(1)

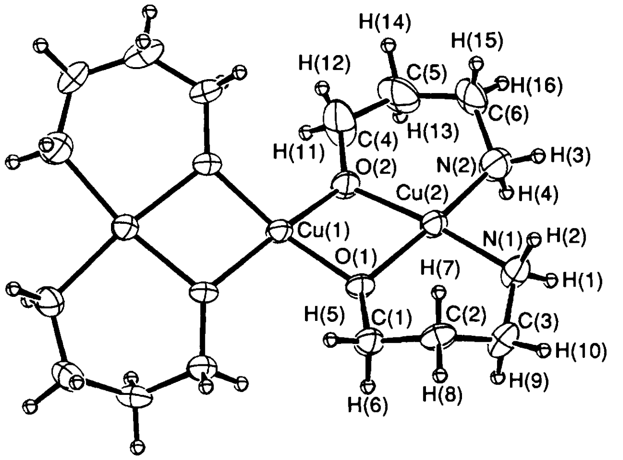

Fig. 1 The trinuclear cation in $[\text{Cu}^{\text{II}}_3(\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_4][\text{Cu}^{\text{I}}_3\text{I}_5]$ **1**. The cations consist of three copper(II) ions with four chelated 3-aminopropanolate ligands. Thermal ellipsoids are plotted at the 30% probability level

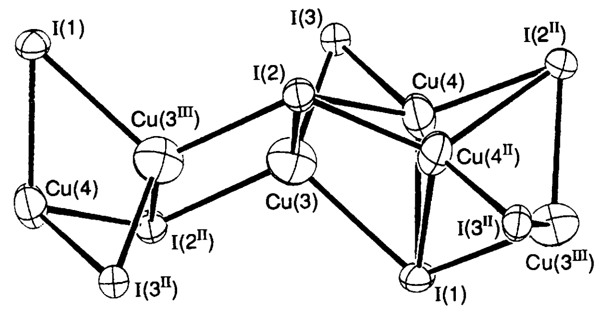

Fig. 2 A part of the polymeric $(\text{Cu}^{\text{I}}_3\text{I}_5{}^{2-})_n$ chain in complex **1**. The chains are situated between the trimeric units and are expanded along the $\bar{c}$ axis. Atom Cu(4) is disordered as explained in the text

Results and Discussion

Syntheses.—Compound **1** is formed easily in acetonitrile when the molar ratio of Cu$^{\text{II}}$ to 3-aminopropanolate is 3 : 4 and that of Cu$^{\text{I}}$: I$^-$ is between 1 : 1 and 1 : 2. The molar ratio Cu$^{\text{II}}$: Cu$^{\text{I}}$ should be *ca.* 1 : 1. Another complex, $[\text{Cu}^{\text{II}}_3(\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_4(\text{dmf})]_2[\text{Cu}^{\text{I}}_6\text{I}_{10}]$, is obtained if the solvent contains dmf and methanol.[1]

Many efforts have been made to prepare compound **2** as pure crystals. The main impurity is a white powder, probably AgI, and X-ray-quality crystals have not been obtained. We have tried to synthesise **2** by using silver(I) nitrate and tetrabutylammonium iodide solutions, or by using a $[\text{Ag}^{\text{I}}_3\text{I}_5]^{2-}$ solution, from which the nitrate ions have been removed. It was found that **2** can be obtained reasonably pure when the molar ratio Ag : I$^-$ is 1 : 1.67 and Cu$^{\text{II}}$: 3-aminopropanolate is 3 : 4. The aminopropanol has to be deprotonated otherwise it is not totally bonded to the copper(II) ion. Another important factor in the synthesis is stirring. The whole anionic $[\text{Ag}^{\text{I}}_3\text{I}_5]^{2-}$ or I$^-$ solution, when using silver nitrate as silver(I) source, should be added at once and immediately efficiently mixed. The AgI powder will not dissolve properly if the anionic solution is added with slow stirring. Extra solvents, like dmf and CH_2Cl_2, slow the formation of product, but they do not prevent precipitation, as does EtOH.

Crystal Structure.—Compound **1** consists of trinuclear $[\text{Cu}^{\text{II}}_3(\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_4]^{2+}$ cations (Fig. 1) and polymeric $(\text{Cu}^{\text{I}}_3\text{I}_5{}^{2-})_n$ anions (Fig. 2). Important structural parameters are given in Table 2. In the trimer two of the three copper(II) ions are bonded to two oxygen atoms and two nitrogen atoms of chelated 3-aminopropanolate ligands. The third copper atom is bonded to four oxygen atoms of four ligands. The copper atoms have a linear arrangement. The CuO_2N_2 co-ordination planes of the cation are twisted by 40°. The trinuclear units are stacked along the $\bar{c}$ axis, and hydrogen bonded to I$^-$ ions through NH • • • I hydrogen bonds (Table 3).

The anionic part consists of polymeric $(\text{Cu}^{\text{I}}_3\text{I}_5{}^{2-})_n$ chains running between cations along the $\bar{c}$ axis. One of the copper(I) ions in the chain is disordered as mentioned in the Experimental section. The Cu(3) and Cu(4) atoms are tetrahedrally co-

Table 2 Bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4][Cu^I_3I_5]$

Around Cu^I			
Cu(3)–I(1)	2.823(3)	Cu(4)–I(2)	2.727(4)
Cu(3)–I(2)	2.740(2)	Cu(4)–I(2)	2.752(4)
Cu(3)–I(2^{III})	2.650(3)	Cu(4)–I(2^{II})	2.535(4)
Cu(3)–I(3)	2.654(3)	Cu(4)–I(3)	2.883(4)
Cu(3) ··· Cu(4)	2.321(4)	Cu(3) ··· Cu(4^{II})	2.988(5)
Cu(3) ··· Cu(3^{III})	2.847(5)		
I(1)–Cu(3)–I(2)	102.84(8)	I(1)–Cu(4)–I(2)	105.1(1)
I(1)–Cu(3)–I(2^{III})	111.76(8)	I(1)–Cu(4)–I(2^{II})	111.4(1)
I(1)–Cu(3)–I(3)	108.71(9)	I(1)–Cu(4)–I(3)	105.0(1)
I(2)–Cu(3)–I(2^{III})	116.25(9)	I(2)–Cu(4)–I(2^{II})	124.8(2)
I(2)–Cu(3)–I(3)	103.13(8)	I(2)–Cu(4)–I(3)	97.1(1)
I(2^{III})–Cu(3)–I(3)	113.26(9)	I(2^{II})–Cu(4)–I(3)	111.1(1)
Cu(3)–I(1)–Cu(4)	49.39(9)	Cu(3)–I(2)–Cu(3^{III})	63.75(9)
Cu(3)–I(2)–Cu(4)	50.00(9)	Cu(3)–I(3)–Cu(4)	49.34(9)
Around Cu^{II}			
Cu(1)–O(1)	1.899(7)	Cu(2)–O(2)	1.928(7)
Cu(1)–O(2)	1.905(7)	Cu(2)–N(1)	1.990(9)
Cu(2)–O(1)	1.933(7)	Cu(2)–N(2)	2.00(1)
O(1)–Cu(1)–O(1^I)	103.1(4)	O(1)–Cu(2)–N(1)	95.3(4)
O(1)–Cu(1)–O(2)	79.3(3)	O(1)–Cu(2)–N(2)	166.0(5)
O(1)–Cu(1)–O(2^I)	157.7(4)	O(2)–Cu(2)–N(1)	173.0(4)
O(1)–Cu(2)–O(2)	77.9(3)	O(2)–Cu(2)–N(2)	92.8(4)
Cu(1)–O(1)–Cu(2)	99.3(3)	N(1)–Cu(2)–N(2)	94.2(4)
Cu(1)–O(2)–Cu(2)	99.3(3)		

Symmetry codes: I $1 - x, y, \frac{1}{2} - z$; II, $-x, y, \frac{1}{2} - z$; III $-x, -y, -z$.

Table 3 Hydrogen-bond distances (Å) and angles (°) with e.s.d.s in parentheses

	N-H	H···I	N···I	N-H···I
N(1)-H(1) ··· I(3^I)	0.95	2.84	3.77(1)	166
N(1)-H(2) ··· I(1)	0.95	3.06	3.88(1)	146
N(2)-H(3) ··· I(2^{II})	0.95	2.88	3.79(1)	160
N(2)-H(4) ··· I(3^I)	0.95	3.25	3.73(1)	113

Symmetry codes: I $x, -y, \frac{1}{2} + z$; II, $-x, y, \frac{1}{2} - z$.

Table 4 Comparison of MIR spectral bands (cm^{-1}) for the copper(II) complexes

$[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4][Cu_3I_5]$	$[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4][Ag^I_3I_5]$	Assignment
3246s, 3211s, 3126m	3260s, 3248(sh), 3215s, 3128m	$\nu(NH)_{sym,asym}$
1578s, 1562s	1578s, 1566s	$\delta(NH_2)$
1310w, 1283w, 1260w	1308w, 1283w, 1260w	*a*
1169m, 1145s	1169m, 1144s	*a*
1072s, 1943s	1070s, 1053s, 1041s	*a*
935s	934s	*b*
821w, 726w, 698w	822w, 726w, 698w	*a*
637m, 605m	634m, 603m	*a*

Intensities: s = strong, m = medium, w = weak, sh = shoulder.

[a] Incompletely resolved bands, most due to ν(CC), ν(CN), ν(CO), $\delta(CH_2)$ and $\delta(NH_2)$. [b] Due to chelated aminopropanolate ligand.[16]

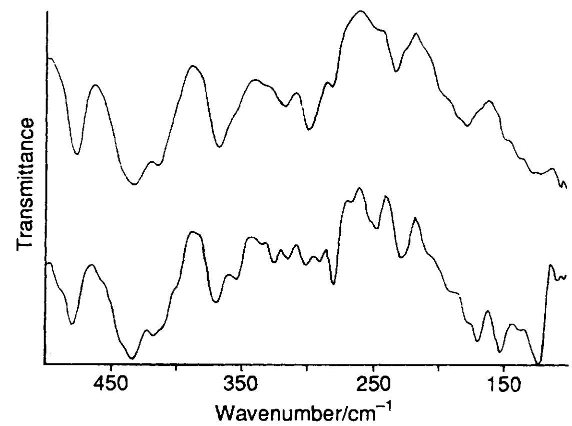

Fig. 3 Fourier-transform FIR spectra of $[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4][Cu^I_3I_5]$ **1** (lower) and $[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4][Ag^I_3I_5]$ **2** (upper)

ordinated by iodide ions. Distances between the Cu^+ and I^- ions are 2.535–2.823 Å. The $Cu^II_4^-$ tetrahedra share faces and edges in the following order: –face–edge–edge–face–edge–edge–face, *etc.*

It is interesting that the $[Cu^I_6I_{10}]^{4-}$ anion in $[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4(dmf)]_2[Cu^I_6I_{10}]$ is made of two $[Cu^I_3I_5]^{2-}$ ions in the solid state. Possibly the presence of dmf in this compound influences the anion structure.

The bis(*N*-benzoylhydrazine)copper(II) pentachlorotricuprate(I)[14] contains a polymeric $[Cu^I_3Cl_5]^{2-}$ ion with some structural similarities with the present $[Cu^I_3I_5]^{2-}$ ion. The polymeric $[Cu^I_3Br_5]^{2-}$ anion of $[Pt(pn)_2][Pt(pn)_2Br_2][Cu^I_3Br_5]_2$ (pn = 1,2-diaminopropane)[15] can be described as a single-strand $[Cu^IBr_2]^-$ polymer intertwined with a linear Br–Cu–Br chain. One copper(I) ion has a co-ordination number of four and another of five.

FTIR Spectroscopic Studies.—The Fourier-transform IR spectra of complexes **1** and **2** in the range 4000–200 cm^{-1} are quite similar (Table 4). The IR spectra confirm that the cation, $[Cu^{II}_3(OCH_2CH_2CH_2NH_2)_4]^{2+}$, is similar in both compounds, and that an aminopropanolate group is present.[16] The FIR spectra of the compounds differ considerably below 215 cm^{-1}, as expected, due to the M–I vibrations (Fig. 3). Their frequencies are dependent on the metal ion and its co-ordination number.[17] The broad absorption band between 180 and 130 cm^{-1} is consistent with anionic chains of Cu^II_4 tetrahedra joined by sharing edges.[18] The bands at 152s, 139s and 122s cm^{-1} may be due to Cu–I stretching vibrations.[19–21] The relevant vibrations in the $[Cu^I_6I_{10}]^{4-}$ ion, synthesised as described in ref. 1, are at 150m, 137s and 128s cm^{-1}. In the case of the silver derivative, the Ag–I vibrations can be assigned to the bands at 150m, 127s, 120s and 106s cm^{-1}.[20,22] The compound $[NBu_4][Ag_3I_4]$ has bands at 150m, 123s, 117s and 101s cm^{-1}.[23]

Conductivity.—The highest conductivities for copper(I) and silver(I) halide-based ionic conductors have been observed when the halide framework is formed by polymeric face-sharing halide-ion polyhedra, and when the anionic part of the complex comprises silver(I) iodide or copper(I) chloride. This apparent preference for a specific halide in the anion may be due to an effective ionic radius, which for Ag^+ (co-ordination number 4) and I^- are 1.14 and 2.06 Å, respectively ($r^+/r^- = 0.55$); the ionic radii for Cu^+ and Cl^- are 0.74 and 1.67 Å, respectively ($r^+/r^- = 0.44$).[24]

The silver(I) cation fits well in iodide tetrahedra. There will be a strong repulsive interaction between the silver(I) ions if they occur in two neighbouring tetrahedra and providing that the distance between the tetrahedra is very short, as is the case with face-sharing tetrahedra. It may then be impossible for two adjacent sites to be simultaneously occupied. If Ag^+ ions can move between these sites this causes ionic conductivity. The distances are too long to result in good diffusion, which is needed for good ionic conductivity, when the framework is made up of edge-sharing tetrahedra. Also the silver(I) cation is too big to fit easily in bromide or chloride tetrahedra. Thus the tetrahedra expand and the possibility of face sharing is diminished.

Conversely, iodide tetrahedra are too large for copper(I) cations, and the repulsive interaction does not exceed the activation energy of diffusion. The size of chloride tetrahedra is such that Cu$^+$ cations are able to diffuse as silver(I) cations do in silver(I) iodide.

Conductivity measurements show that the copper complex is an insulator, and the silver complex a poor ionic conductor. For example, the conductivity (σ) of the silver(I) compound is 1.13×10^{-5} at 50 °C and 6.12×10^{-5} Ω^{-1} cm^{-1} at 84 °C. The Arrhenius plot (log σT *versus* T) for a heating cycle from 30 to 130 °C is linear up to 90 °C. Reliable values could not be obtained for the conductivity above 100 °C because the samples softened or melted. Although the conductivity of the silver(I) compound is much lower than the value of 0.270 Ω^{-1} cm^{-1} for Rb[Ag$_4$I$_5$] at 25 °C,[25] the results are promising, and we now intend to concentrate on complexes which contain more dense Ag^{I}I and Cu^{I}Cl polymeric anionic parts.

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