DALTON
FULL PAPER

New luminescent copper(I) halide complexes containing Rb^+ complexes of 18-crown-6 as counter ions prepared from zerovalent copper

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Received 28th March 2000, Accepted 17th May 2000
Published on the Web 13th June 2000

Treatment of zerovalent copper with NH_4X (X = I, Br or SCN) in the presence of RbI and 18-crown-6 (18c6), in acetonitrile, in air, afforded a diversity of crystalline products in which halogeno- or pseudo-halogeno-cuprate(I) anions co-precipitate with the geometrically rigid crown ether cation $[Rb(18c6)]^+$. Four complexes $[\{Rb(18c6)\}_2MeCN][Cu_4I_6]$ **1**, $[Rb(18c6)][Rb(18c6)(MeCN)_3]_2[\{Rb(18c6)\}_6Cu_4I_7][Cu_7I_{10}]_2$ **2**, $\{[Rb(18c6)][Cu_3I_3Br]\}_\infty$ **3** and $\{[Rb(18c6)][Cu_2(SCN)_3]\}_\infty$ **4** have been isolated and characterised. Formation of the copper(I) species here is believed to be an autocatalytic process catalysed by the formation of copper(II) compounds *in situ*. The anions present in the initial mixture have a profound effect upon metal–halogen framework formation. There is a competition between the strongly co-ordinating anions that leads to the partial or complete replacement of iodine by bromine or thiocyanate in **3** and **4**, respectively. Complex **1** contains a discrete disordered $[Cu_4I_6]^{2-}$ species sandwiched between the $[Rb(18c6)]^+$ cations. The structural motif of **2** consists of ensembles of two $[Rb(18c6)(MeCN)_3]^+$ and one $[Rb(18c6)]^+$ cation, the bulky supramolecular cation $[\{Cs(18c6)\}_6Cu_4I_7]^{3+}$ and crown-like $[Cu_7I_{10}]^{3-}$ clusters in which seven copper atoms describe a hexagonal pyramid. In the mixed halogenocuprate(I) anion $[Cu_3I_3Br]^-_\infty$ characterised in **3** all the copper atoms of the polymeric chain lie in the same plane; the halides bridge the alternate sides of the polymer. The Br atoms form bridges between $[Cu_3I_3]_n$ chains and the $[Rb(18c6)]^+$ cations. The ability of the SCN group to act as a bridge gives rise to a one-dimensional structure for **4** which contains two copper(I) atoms each with a different stereochemistry. Complexes **1**, **2** and **3** display a change in emission spectrum with temperature in the solid state.

The simple rule that, with decreasing cation size and also changing from Cl through Br to I, the tendency to attain a higher co-ordination number and towards catenation in crystalline halogenocuprates(I) increases provides a facile framework for understanding a range of observations.[1] However, it is still true that rationalization of the detailed geometry of the particular halogenocuprate(I) ion in terms of the influence of cation shape or positive charge distribution is very complex.

Some anionic iodocuprates(I) have been reported to fluoresce in the solid state and reversibly alter their fluorescence colour with temperature (Fluorescence Thermochromism).[2] Although studies on luminescence of transition-metal complexes have produced much valuable information the nature of the excited states has not been established fully, and the validity of current models for describing these systems requires further experimental verification. The knowledge of excited states of complexes can be used to engineer potentially valuable new materials possessing desirable optical, electrooptical, photochemical, electrochemical and chemical properties.

The most widespread method for the preparation of halogenocuprates(I) is the reaction between a copper(I) halide and a halide salt of the appropriate cation dissolved in an organic solvent.[1] We have recently found that the interaction of zerovalent copper with a proton-donating agent (NH_4I) in the presence of CsX (X = Cl or I) and 18-crown-6 (18c6), in acetonitrile, in air, resulted in the mutual stabilization of Cs^+ as multidecker sandwich $[Cs_n(18c6)_m]^{n+}$ cations and Cu^+ as large iodocuprate anions in the solid state.[3] In order to determine whether other metal–18c6 complexes could have the same templating effect on the formation of halogenocuprates(I), starting from zerovalent metals, we treated copper powder with ammonium salt in the presence of RbI and 18c6, in acetonitrile. The syntheses, crystal structures and fluorescence spectra of the novel mixed-metal complexes $[\{Rb(18c6)\}_2MeCN][Cu_4I_6]$ **1**, $[Rb(18c6)][Rb(18c6)(MeCN)_3]_2[\{Rb(18c6)\}_6Cu_4I_7][Cu_7I_{10}]_2$ **2**, $\{[Rb(18c6)][Cu_3I_3Br]\}_\infty$ **3** and $\{[Rb(18c6)][Cu_2(SCN)_3]\}_\infty$ **4** containing halogeno- and pseudo-halogenocuprate(I) moieties are reported.

Experimental

All chemicals were of reagent grade and used as received; all experiments were carried out in air. Elemental analyses were performed by standard titrimetric methods (for Cu, I and SCN) and by the Department of Chemistry, Cambridge University microanalytical service (for C, H and N). Infrared spectra were recorded as KBr discs and in Nujol mulls on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques.

DOI: 10.1039/b002451l

Syntheses

$[\{Rb(18c6)\}_2MeCN][Cu_4I_6]$ 1 and $[Rb(18c6)][Rb(18c6)(MeCN)_3]_2[\{Rb(18c6)\}_6Cu_4I_7][Cu_7I_{10}]_2$ 2. Copper powder (0.064 g, 1 mmol), NH_4I (0.145 g, 1 mmol), RbI (0.21 g, 1 mmol), 18c6 (0.26 g, 1 mmol) and MeCN (20 cm^3) were heated to 60 °C, and refluxed with stirring for 4–5 h (see Results and discussion). The colourless solution gradually turned yellow. Then the mixture was allowed to stand overnight at room temperature, the solution colour deepened, after which it was heated, refluxed and stirred again until total dissolution of Cu was observed (1 h). After cooling and standing at room temperature for 24 h a light turquoise powder precipitated from the dark orange solution in a negligible quantity, which was found to be a copper(II) compound of a non-stoichiometric composition. It was filtered out and subsequently crystals of **1** and **2** separated in several days. Those were filtered off, washed with Pr^iOH and dried at room temperature to give a mixture of yellow **1** and colourless **2** in ≈75% yield (per copper) which were separated manually under a microscope. In repeated syntheses the mixture was always obtained but the ratio of **1** and **2** varied (Found for **1**: C, 18.0; H, 3.0; Cu, 14.6; I, 44.0; N, 0.9. $C_{26}H_{51}Cu_4I_6NO_{12}Rb_2$ requires C, 17.78; H, 2.93; Cu, 14.47; I, 43.36; N, 0.80. Found for **2**: C, 18.7; H, 2.9; Cu, 14.7; I, 43.5; N, 1.0. $C_{40}H_{78}Cu_6I_9N_2O_{18}Rb_3$ requires C, 18.10; H, 2.96; Cu, 14.36; I, 43.02; N, 1.06%). IR (cm^{-1}): (**1**) 3500br, 2890m, 2860sh, 2820w, 2790sh, 1640br, 1475w, 1455w, 1435w, 1355m, 1285w, 1250w, 1130sh, 1110s, 965m, 870w, 840w and 530w; (**2**) 3500br, 2890m, 2865sh, 2815w, 2790sh, 1630br, 1470w, 1450w, 1435w, 1350m, 1285w, 1250w, 1230w, 1130w, 1110s, 960m, 870w, 845w and 530w.

$\{[Rb(18c6)][Cu_3I_3Br]\}_\infty$ 3. Copper powder (0.064 g, 1 mmol), NH_4Br (0.098 g, 1 mmol), RbI (0.21 g, 1 mmol), 18c6 (0.26 g, 1 mmol) and MeCN (15 cm^3) were treated as above. After removal of the copper(II) compound of non-stoichiometric composition, colourless crystals of **3** precipitated from the clear dark orange solution over 1–2 d. They were filtered off, washed with Pr^iOH and dried at room temperature. Yield ≈70% (per copper) (Found: C, 14.6; H, 2.2; Cu, 18.9; I+Br, 46.4. $C_{12}H_{24}BrCu_3I_3O_6Rb$ requires C, 14.40; H, 2.42; Br, 7.98; Cu, 19.04; I, 38.03%). IR (cm^{-1}): 3500br, 2890m, 2855sh, 2815w, 2790sh, 1625br, 1465w, 1450w, 1430w, 1345m, 1280w, 1245w, 1230w, 1130w, 1105s, 960m, 835w, 530w and 420w.

$\{[Rb(18c6)][Cu_2(SCN)_3]\}_\infty$ 4. Copper powder (0.064 g, 1 mmol), NH_4SCN (0.76 g, 1 mmol), RbI (0.21 g, 1 mmol), 18c6 (0.26 g, 1 mmol) and MeCN (15 cm^3) were treated as for complex **1** (dissolution of Cu in 1.5 h). After removal of the copper(II) compound of non-stoichiometric composition colourless crystals of **4** precipitated from the clear dark orange solution over 3 d. They were filtered off, washed with Pr^iOH and dried at room temperature. Yield ≈80% (per copper) (Found: C, 27.6; H, 3.6; Cu, 19.3; N, 6.4; SCN, 27.2. $C_{15}H_{24}Cu_2N_3O_6RbS_3$ requires C, 27.67; H, 3.72; Cu, 19.52; N, 6.46; SCN, 26.76%). IR (cm^{-1}): 3000sh, 2890m, 2820w, 2125s (CN), 2095s (CN), 1470w, 1450w, 1350m, 1285w, 1250w, 1130w, 1110s, 960m, 835w and 770w (CS).

All the compounds are stable in air for periods of months, insoluble in water and soluble in acetonitrile.

Fluorescence spectra

The measurements were made at 300 and 77 K with powders slowly pressed and then sealed into quartz ampoules that had previously been found to be non-emitting under the conditions of the experiment. Low-temperature measurements were made using a cryogenic cooler with liquid nitrogen. The emission spectra were produced upon excitation at 337.1 nm with the ILGI-501 nitrogen laser and measured with a DFS-12 diffraction spectrometer (600 lines per mm) using a cooled photomultiplier tube (PMT) PEU-79 as detector. The detector signal was passed to a lock-in amplifier of the output of which was stored by an IBM PC. The spectra were corrected for spectral sensitivity of the PMT and transmission of the spectrometer using standard techniques.

Crystallography

Details of the data collection and processing, structure analysis and refinement are summarized in Table 1. Diffraction experiments were performed on an Enraf Nonius CAD-4 diffractometer operating in the ω–2θ scan mode equipped with graphite monochromated Cu-Kα radiation ($\lambda = 1.54178$ Å) (**1**) and Mo-Kα radiation ($\lambda = 0.71073$ Å) (**3**, **4**) and on an Enraf Nonius Kappa CCD area detector, fitted with an Oxford cryostream low-temperature attachment (**2**) and graphite monochromated Mo-Kα radiation. Data sets were corrected for the effects of absorption. The structures were solved by direct methods and subjected to full-matrix least-squares refinement on F^2 [programs SHELXL 97 (**1**, **2**) and SHELXL 93 (**3**, **4**)].[4] All non-hydrogen atoms were refined anisotropically, except for the light atoms (N, C, O) in complex **1**. Hydrogen atoms were included using rigid methyl groups or a riding model.

Disorder of copper atoms of the $[Cu_4I_6]^{2-}$ core in complex **1** was modelled in terms of two sets of positions, common occupancy of Cu(1a), Cu(2a), Cu(3a) and Cu(4a) refined to 80% and Cu(1b), Cu(2b), Cu(3b) and Cu(4b) to 20%, respectively. All copper atoms in **1** were refined anisotropically with restrained displacement parameters. The Flack x parameter for the non-centrosymmetric structure **1** refined to 0.00(2).[5]

The $[Cu_4I_7]^{3-}$ core next to Rb(1) in complex **2** is badly disordered over two symmetry related sites with occupation factors 0.5. Unreasonably short Cu–Cu distances (2.19(2) Å) were consequences of disorder. Owing to the large anisotropic displacement parameters of Rb(3) in the x direction an attempt was made to refine this atom over two positions. Those positions did not refine well; after a few cycles electron density on the former Rb(3) position reappeared. Therefore it was decided not to split Rb(3). The residual electron density next to this atom is probably due to the unresolved disorder of Rb(3) in the x direction, along the threefold axis. Clearly the dimensions of this disordered structure should be interpreted with caution.

For complexes **1** and **2** an extensive system of restraints to displacement parameters was employed to improve refinement stability of light atoms in the presence of copper and rubidium. Short C–C and C–O distances (1.33(4) and 1.24(6) Å, respectively) in **1** were consequences of disorder. The bond lengths of disordered carbon and oxygen atoms of the unique crown molecule in **4** O(5)–C(12), O(1)–C(15) and C(14)–C(15) were constrained to 1.48(1), 1.52(1) and 1.55(1) Å, respectively.[6]

CCDC reference number 186/1989.

See http://www.rsc.org/suppdata/dt/b0/b002451l/ for crystallographic files in .cif format.

Results and discussion

We have already shown that the interaction of zerovalent copper with NH_4I in the presence of CsX (X = I or Cl) and 18c6, in acetonitrile, in air, leads to the formation of iodocuprate(I) anions with different architectures.[3] X-Ray studies of the products have revealed that the bulkier structural moieties dominate the structures. We therefore anticipated the formation of similar halogenocuprate(I) moieties when substituting CsX for rubidium salts and were interested to study whether Rb^+–18c6 cations could have the same templating effect on the formation of halogenocuprates(I) starting from zerovalent copper.

Treatment of zerovalent copper with ammonium iodide/bromide/thiocyanate in the presence of the crown ether and rubidium iodide in solution affords a diversity of crystalline products in which halogeno- or pseudo-halogenocuprates(I) all co-precipitate with the same geometrically rigid cation $[\mathrm{Rb(18c6)}]^+$, eqns. (1)–(3). The formulations of the complexes

$$\mathrm{Cu + NH_4X + RbI + 18c6 + O_2 + MeCN} \begin{cases} \quad [\{\mathrm{Rb(18c6)}\}_2\mathrm{MeCN}][\mathrm{Cu_4I_6}]\ \mathbf{1} & \\ \xrightarrow{\mathrm{X = I}} [\mathrm{Rb(18c6)}][\mathrm{Rb(18c6)(MeCN)_3}]_2\text{-} & \\ \quad [\{\mathrm{Rb(18c6)}\}_6\mathrm{Cu_4I_7}][\mathrm{Cu_7I_{10}}]_2\ \mathbf{2} & (1) \\ \xrightarrow{\mathrm{X = Br}} \{[\mathrm{Rb(18c6)}][\mathrm{Cu_3I_3Br}]\}_\infty\ \mathbf{3} & (2) \\ \xrightarrow{\mathrm{X = SCN}} \{[\mathrm{Rb(18c6)}][\mathrm{Cu_2(SCN)_3}]\}_\infty\ \mathbf{4} & (3) \end{cases}$$

are based on carbon, nitrogen, hydrogen, halogen, and copper analyses, solid-state IR spectra and single-crystal X-ray diffraction crystallography studies. The counter anions present in the initial mixture have a profound effect upon metal–halogen framework formation. The competition between the strongly co-ordinating anions is evident and leads to a partial (**3**) or full (**4**) replacement of iodide by bromide or thiocyanate in the copper co-ordination sphere of the final product. Remarkably, in **3** bromide appears not to be "strong" enough to replace all the iodide atoms, but replacement of even one of the four $\mathrm{I^-}$ by $\mathrm{Br^-}$ gives rise to the polymeric structure, **3**, in contrast to the finite clusters in **1** and **2**.

The progress of the reaction has some interesting features. It is apparent that the temperature of the initial heating of the reaction mixture and the length of stirring of the reaction did not lead to substantial changes in the reaction products or yields, and these procedures were necessary only to dissolve the salts and the crown ether. Standing overnight, at room temperature, apparently affords a copper(II) compound. This complex appeared as very small blue-violet crystals on the surface of the copper powder at the bottom of the flask, in a quantity that was too small to be characterized. We propose that this compound is formed *via* reaction (4) that has been reported previously.[7a] A

$$\mathrm{Cu^0 + 2NH_4X + \tfrac{1}{2}O_2 \longrightarrow Cu(NH_3)_2X_2 + H_2O\ (X = Cl, Br, I\ or\ SCN)} \qquad (4)$$

rapid dissolution of the remaining copper powder takes place when the reaction mixture is heated and stirred again.

A mechanism for the spontaneous ionization of copper in solution in the presence of various oxidizing agents has received much attention.[7b] The metal dissolution with eventual formation of copper(II) ions in the presence of dioxygen from the air, eqn. (5), was suggested to be facilitated by the autocatalytic reaction (6). Then copper(I) ions formed are further oxidized in

$$\mathrm{2Cu^0 + O_2 + 4H^+ \longrightarrow 2Cu^{2+} + 2H_2O} \qquad (5)$$

$$\mathrm{Cu^{2+} + Cu^0 \longrightarrow 2Cu^+} \qquad (6)$$

solution by dioxygen. The inhibition period is possibly related with time necessary for the copper(II) ion concentration to reach a critical value in order to initiate the autocatalytic process.

To ascertain whether the reactions (1)–(3) are autocatalytic and to formulate a satisfactory mechanism a detailed kinetic study would be necessary, however it is reasonable to suppose that these reactions are in fact autocatalytic and that the autocatalytic species is a copper(II) intermediate formed *in situ*. Interestingly, we did not detect the formation of compounds containing copper(II) ions and crown ether ligand, although these might be expected knowing that examples of copper(II) salts co-precipitated with this ligand (containing both complexed and free crown ether rings) from aqueous solutions have been characterized.[8] It is known that the copper(I) ion normally disproportionates in water, eqn. (7). However, in the presence of

$$\mathrm{Cu^0 + Cu^{2+}} \overset{K_1}{\rightleftharpoons} \mathrm{2Cu^+} \qquad (7)$$

MeCN, K_1 changes from 10^{-6} in water to about 10^{10} mol dm^{-3} in MeCN–water.[9] Copper(II) salts are powerful oxidizing agents in nitrile containing solutions.

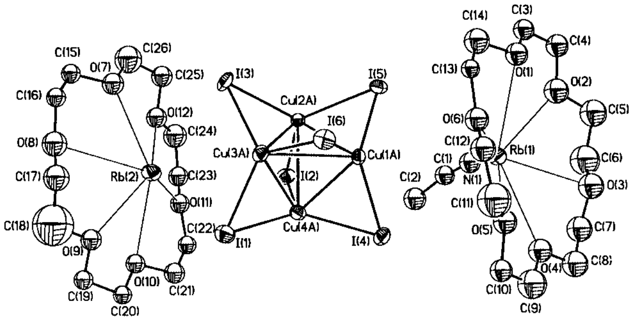

Fig. 1 Structure of $[\{\mathrm{Rb(18c6)}\}_2\mathrm{MeCN}][\mathrm{Cu_4I_6}]$ **1** showing the hexa-μ-iodo-*tetrahedro*-tetracuprate(I) anion sandwiched between the $[\mathrm{Rb(18c6)}]^+$ cations (the non-hydrogen atoms are shown as 20% thermal ellipsoids, H atoms omitted for clarity; only one of the two possible sets of the copper atoms is shown).

The IR spectra of all four complexes show the typical absorptions corresponding to 18-crown-6. The spectra of **1** and **2** show no apparent CN stretching vibrations even though elemental analysis indicates the presence of MeCN in the compounds. This is not considered to be unusual, however, since ν(CN) associated with "end-on" co-ordinated nitriles may be very weak in intensity or undetectable in IR spectra, even in copper(I) complexes.[10] In Nujol mull and KBr disk the very strong split ν(CN) vibration (2125 and 2095 cm^{-1}) and the weak ν(CS) absorption (770 cm^{-1}) of a thiocyanate group can be identified easily for **4**.[11] The δ(NCS) mode is obscured. The frequencies of the observed bands and the splitting of the ν(CN) mode imply co-ordination of the $\mathrm{NCS^-}$ groups through sulfur and in a bridging mode,[11] in accord with the crystal structure of **4**.

Crystal structure of complex 1

The compound $[\{\mathrm{Rb(18c6)}\}_2\mathrm{MeCN}][\mathrm{Cu_4I_6}]$ features a discrete disordered $[\mathrm{Cu_4I_6}]^{2-}$ anion sandwiched between the two $[\mathrm{Rb(18c6)}]^+$ ions (Fig. 1). The $\mathrm{Rb^+}$ ions are in typical "sunrise" co-ordination[6] to the 18c6 [0.99(1) and 1.11(1) Å above the best planes of the six crown oxygens, Rb–O distances in the range 2.88(2)–3.20(2) Å], which have distorted D_{3d} symmetry. The distances and angles in $[\mathrm{Rb(18c6)}]^+$ are comparable to those found in similar compounds.[6]

The tetranuclear iodocuprate(I) species $[\mathrm{Cu_4I_6}]^{2-}$ can best be described as an octahedron of iodide ions containing a tetrahedron of copper(I) ions. The hexa-μ-iodo-*tetrahedro*-tetracuprate(I) ion was the first of the series of tetranuclear halogenocuprates(I) to be prepared and characterized[12] and it has subsequently been found in many crystal structures.[1] The Cu · · · Cu distances vary from 2.58(4) to 2.81(3) and the Cu–I bond lengths from 2.36(3) to 2.77(3) Å (Table 2). Metal atoms have a nearly planar trigonal co-ordination (the maximum shift of a copper atom from the plane of three iodides is 0.31(3) Å). In this example, the four copper atoms within the $[\mathrm{Cu_4I_6}]^{2-}$ are disordered over two sites in a 80 to 20% ratio, with an unexplained preferential ordering within the crystal.

The rubidium atoms bonded to oxygen atoms of crown ether rings show very weak interactions with the iodide atoms of the anion (the shortest Rb · · · I distance is 3.904(6) Å). Rb(1) is bonded to the nitrogen atom of the acetonitrile molecule at 3.04(3) Å, a distance that has been considered previously to represent semi-coordination. The MeCN molecule is structurally normal [C≡N 1.09(4), C–C 1.52(5) Å, N–C–C 171(7)°].

Crystal structure of complex 2

The rubidium iodocuprate(I) complex **2** with 18c6 of composition $[\mathrm{Rb(18c6)}][\mathrm{Rb(18c6)(MeCN)_3}]_2[\{\mathrm{Rb(18c6)}\}_6\mathrm{Cu_4I_7}]$-

Table 1 Crystal data for $[\{Rb(18c6)\}_2MeCN][Cu_4I_6]$ **1**, $[Rb(18c6)][Rb(18c6)(MeCN)_3]_2[\{Rb(18c6)\}_6Cu_4I_7][Cu_7I_{10}]_2$ **2**, $\{[Rb(18c6)][Cu_3I_3Br]\}_\infty$ **3** and $\{[Rb(18c6)][Cu_2(SCN)_3]\}_\infty$ **4**

	1	2	3	4
Formula	$C_{26}H_{51}Cu_4I_6NO_{12}Rb_2$	$C_{120}H_{234}Cu_{18}I_{27}N_6O_{54}Rb_9$	$C_{12}H_{24}BrCu_3I_3O_6Rb$	$C_{15}H_{24}Cu_2N_3O_6RbS_3$
M	1756.18	7964.38	1001.01	651.10
Crystal system	Orthorhombic	Cubic	Orthorhombic	Triclinic
Space group	$Pna2_1$	$Pa\bar{3}$	$Pbca$	$P\bar{1}$
a/Å	31.099(6)	28.0474(6)	7.954(2)	10.624(2)
b/Å	10.908(2)	28.0474(6)	24.316(5)	10.862(2)
c/Å	14.867(3)	28.0474(6)	25.291(4)	11.206(2)
α/°				84.36(3)
β/°				75.44(3)
γ/°				77.33(3)
U/Å^3	5043 (2)	22063.7(8)	4892(2)	1219.9(4)
Z	4	4	8	2
μ/cm^{-1}	334.60(Cu-Kα)	75.10(Mo-Kα)	100.06(Mo-Kα)	40.16(Mo-Kα)
T/K	293(2)	220(2)	293(2)	293
Total number of reflections	3528	148113	4436	4537
Number of unique reflections (R_{int})	3525 (0.0107)	8435 (0.1216)	3125	4282 (0.0237)
$R1$ (obs.)	0.0654	0.0676	0.0528	0.0496
$wR2$ (obs.)	0.1404	0.1753	0.1049	0.1146

Table 2 Selected bond distances (Å) and angles (°) for $[Cu_4I_6]^-$ anion of complex **1**[a]

I(1)–Cu(3A)	2.51(1)	I(1)–Cu(1B)	2.48(3)
I(1)–Cu(4A)	2.52(1)	I(1)–Cu(2B)	2.63(3)
I(2)–Cu(2A)	2.56(1)	I(2)–Cu(1B)	2.42(2)
I(2)–Cu(4A)	2.57(1)	I(2)–Cu(3B)	2.60(1)
I(3)–Cu(2A)	2.56(1)	I(3)–Cu(4B)	2.53(3)
I(3)–Cu(3A)	2.63(1)	I(3)–Cu(1B)	2.77(3)
I(4)–Cu(1A)	2.49(1)	I(4)–Cu(3B)	2.36(3)
I(4)–Cu(4A)	2.56(1)	I(4)–Cu(2B)	2.46(3)
I(5)–Cu(2A)	2.55(1)	I(5)–Cu(4B)	2.61(3)
I(5)–Cu(1A)	2.64(1)	I(5)–Cu(3B)	2.69(3)
I(6)–Cu(1A)	2.514(4)	I(6)–Cu(2B)	2.60(3)
I(6)–Cu(3A)	2.516(4)	I(6)–Cu(4B)	2.62(3)
I(4)–Cu(1A)–I(6)	123.3(5)	I(2)–Cu(1B)–I(1)	128(1)
I(4)–Cu(1A)–I(5)	117.6(2)	I(2)–Cu(1B)–I(3)	116(1)
I(6)–Cu(1A)–I(5)	118.6(5)	I(1)–Cu(1B)–I(3)	112.9(6)
I(5)–Cu(2A)–I(3)	120.8(4)	I(4)–Cu(2B)–I(6)	121(1)
I(5)–Cu(2A)–I(2)	119.2(4)	I(4)–Cu(2B)–I(1)	123(1)
I(3)–Cu(2A)–I(2)	118.4(4)	I(6)–Cu(2B)–I(1)	116(1)
I(1)–Cu(3A)–I(6)	123.3(5)	I(4)–Cu(3B)–I(2)	127(1)
I(1)–Cu(3A)–I(3)	116.5(2)	I(4)–Cu(3B)–I(5)	121.5(5)
I(6)–Cu(3A)–I(3)	119.9(5)	I(2)–Cu(3B)–I(5)	113.0(9)
I(1)–Cu(4A)–I(4)	122.8(4)	I(3)–Cu(4B)–I(5)	120(1)
I(1)–Cu(4A)–I(2)	118.4(4)	I(3)–Cu(4B)–I(6)	120(1)
I(4)–Cu(4A)–I(2)	118.4(4)	I(5)–Cu(4B)–I(6)	116(1)

[a] Copper atoms are disordered on two positions 'A' and 'B' with population 0.8 and 0.2, respectively.

$[Cu_7I_{10}]_2$ crystallizes in cubic space group $Pa\bar{3}$ ($a = 28.0474(6)$ Å) and is isomorphous with the caesium complex $[\{Cs(18c6)\}_6Cu_4I_7][Cs_3(18c6)_3][Cu_7I_{10}][Cu_{13}I_{14}]I_2$ ($a = 28.2558(1)$ Å) reported by us recently.[3] This fact is somewhat intriguing as the two compounds have very different compositions. In the latter case we have identified the formation of the novel triple-decker club sandwich $[Cs_3(18c6)_3]^{3+}$ and the structure of the rubidium compound is of special interest in this context. There have been no previous crystallographic reports of Rb–18c6 club sandwich compounds.

The structural motif of complex **2** consists of two different cations $[Rb(18c6)(MeCN)_3]^+$ and $[Rb(18c6)]^+$, and two different iodocuprate(I) anions $[Cu_4I_7]^{3-}$ and $[Cu_7I_{10}]^{3-}$ (Figs. 2, 3). In the cluster anion $[Cu_4I_7]^{3-}$ four copper atoms are arranged in a tetrahedron with all its faces capped by iodide atoms, plus three iodide atoms bonded to three metal centres (Fig. 2). Six rubidium atoms bonded to oxygen atoms of six crown ether rings [1.116(4) Å above the best planes of the six crown oxygens, Rb–O 2.918(8)–3.113(8) Å] are involved with the iodide atoms of the anion (Rb···I 3.592(4)–3.954(4) Å) yielding the bulky supramolecular cation $[\{Rb(18c6)\}_6Cu_4I_7]^{3+}$. Its structure takes clear resemblance to the similar fragment found in $[\{Cs(18c6)\}_6Cu_4I_7][Cs_3(18c6)_3][Cu_7I_{10}][Cu_{13}I_{14}]I_2$.[3]

Unlike the structure of the caesium compound, there are neither $[Rb_n(18c6)_m]^{n+}$ club sandwich encapsulates nor $[Cu_{13}I_{14}]^-$ anions in the structure. The region in the crystal corresponding to the $[\{Cs_3(18c6)_3\}I_2\{Cu_7I_{10}\}\{Cu_{13}I_{14}\}]$ supramolecular unit is occupied by ensembles of two $[Rb(18c6)(MeCN)_3]^+$ cations [Rb atom is 0.823(4) Å above the best planes of the six crown oxygens, Rb–O 3.046(8)–3.160(8) Å], one $[Rb(18c6)]^+$ cation and two $[Cu_7I_{10}]^{3-}$ clusters. The Rb(2) is weakly bonded to the three nitrogen atoms of the acetonitrile molecules at 3.09(1) Å. These fragments of the two structures have different compositions and structures, but the same charge, shape and size (Fig. 3). The cluster anion $[Cu_7I_{10}]^{3-}$ has a crown-like structure, in which seven copper atoms describe a hexagonal pyramid (Cu···Cu 2.543(2)–3.026(3) Å). Six iodide atoms form μ bridges between the six copper atoms of the hexagonal basal plane (Cu–I 2.527(2)–2.642(2) Å) (Table 3). Three of the six triangulated faces formed by the six basal and the apical copper atom are μ_3-capped by iodines (Cu–I 2.621(1)–2.711(1) Å). The remaining iodine forms a μ_4 cap (Cu–I 2.850(4)–2.936(2) Å), linking to the apical copper and three copper atoms in the basal plane. The copper atoms adopt distorted tetrahedral or trigonal planar coordination.

The Rb(3) atom of the central $[Rb(18c6)]^+$ fragment is found in the centre of the crown macrocycle displaying large anisotropic displacement parameters in the direction of the threefold axes (Rb–O 2.83(2) Å). As was pointed out in the Experimental section, two split positions of this metal atom, equally disordered above and below the crown ether plane, did not refine well. We cannot rule out the possibility that this rubidium atom can occupy several positions passing through the centre of the crown molecule, and it is likely that X-ray methods alone cannot resolve this ambiguity due to the very high symmetry of the compound. It should be noted that even on the disordered positions the rubidium atom still lies nearly within the crown ether plane exemplifying how the crystal environment may stabilize the centrosymmetric structure of the $[M(18c6)]^+$ moiety even for alkali metal atoms of larger size. The perfect fit of the rubidium atom inside the crown ether cavity has been documented.[13]

The macrocyclic molecules [C–O 1.34(2)–1.45(2), C–C 1.47(2)–1.54(3) Å] as well as the MeCN molecules [C≡N 1.11(2), C–C 1.41(2) Å, N–C–C 178(2)°] are structurally normal.

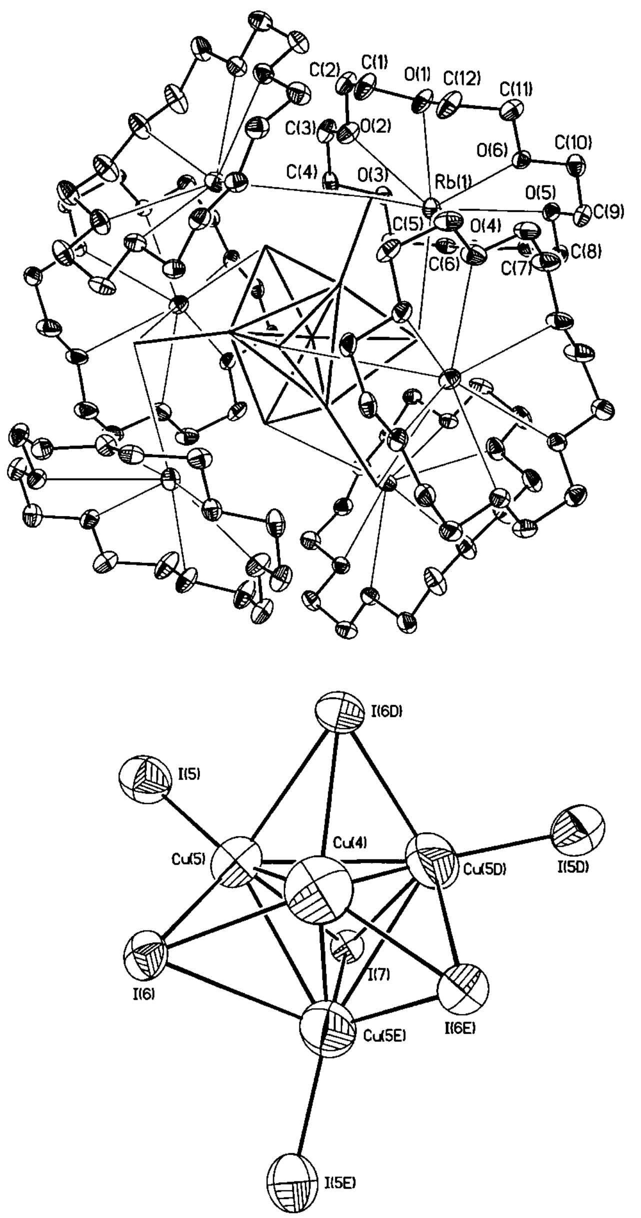

Fig. 2 View of the $[\{Rb(18c6)\}_6Cu_4I_7]^{3+}$ unit in complex **2** (the non-hydrogen atoms are shown as 20% thermal ellipsoids, H atoms omitted for clarity), showing the arrangement of six Rb(18c6) around the central iodocuprate(I) core. Also shown at the bottom is one of the two possible orientations of the $[Cu_4I_7]^{3-}$ core.

Table 3 Selected bond distances (Å) and angles (°) for iodocuprate(I) clusters of complex **2**[a]

$[Cu_7I_{10}]^{3-}$			
Cu(1)–I(1)	2.850(4)	I(2)–Cu(1)–I(2^1)	112.87(7)
Cu(1)–I(2)	2.621(1)	I(2)–Cu(1)–I(1)	105.81(9)
Cu(2)–I(1)	2.936(2)	I(3)–Cu(2)–I(4^2)	120.92(7)
Cu(2)–I(3)	2.540(2)	I(3)–Cu(2)–I(2^2)	117.71(7)
Cu(2)–I(4^2)	2.642(2)	I(4^2)–Cu(2)–I(2^2)	104.08(6)
Cu(2)–I(2^2)	2.711(2)	I(3)–Cu(2)–I(1)	111.23(7)
Cu(3)–I(2)	2.665(2)	I(4^2)–Cu(2)–I(1)	98.39(6)
Cu(3)–I(3)	2.527(2)	I(2^2)–Cu(2)–I(1)	101.21(6)
Cu(3)–I(4)	2.606(2)	I(3)–Cu(3)–I(4)	126.13(7)
		I(3)–Cu(3)–I(2)	118.94(7)
		I(4)–Cu(3)–I(2)	106.41(6)
$[Cu_4I_7]^{3-}$			
Cu(4)–I(6)	2.611(5)	I(6)–Cu(4)–I(6^3)	118.2(2)
Cu(5)–I(5)	2.328(13)	I(5)–Cu(5)–I(7)	119.2(6)
Cu(5)–I(6)	2.714(14)	I(5)–Cu(5)–I(6)	113.0(4)
Cu(5)–I(6^4)	2.997(13)	I(7)–Cu(5)–I(6)	113.9(4)
Cu(5)–I(7)	2.502(10)	I(5)–Cu(5)–I(6^4)	99.5(3)
		I(7)–Cu(5)–I(6^4)	105.0(4)
		I(6)–Cu(5)–I(6^4)	103.3(4)

[a] Symmetry transformations used to generate equivalent atoms (indicated by superscript): 1 $-y+1, z+\frac{1}{2}, -x+\frac{1}{2}$; 2 $-z+\frac{1}{2}, -x+1, y-\frac{1}{2}$; 3 y, z, x; 4 z, x, y.

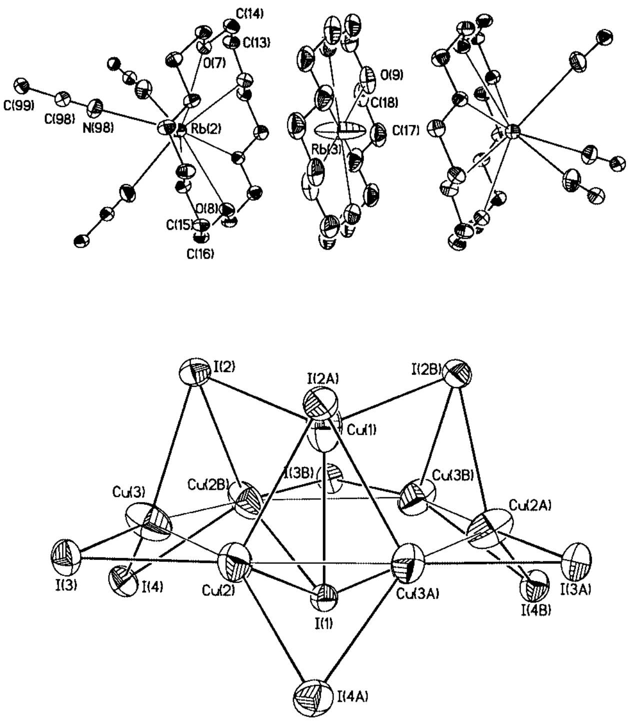

Fig. 3 View of $[Rb(18c6)(MeCN)_3]^+$ and $[Rb(18c6)]^+$ cations and the $[Cu_7I_{10}]^{3-}$ anion present in the crystal structure of complex **2** (the non-hydrogen atoms are shown as 30% thermal ellipsoids, H atoms omitted for clarity).

Crystal structure of complex 3

The compound **3** (Fig. 4) is built up from $[Rb(18c6)]^+$ cations and polymeric mixed halogenocuprate(I) anions $[Cu_3I_3Br]^-{}_\infty$. The anion chains are composed of edge-sharing copper(I) halide tetrahedra, the inner iodides bridge four copper atoms, the peripheral iodides bridge two and the peripheral bromides bridge two copper and one rubidium atom. All copper atoms of the polymeric anion lie in the same plane, the halides bridge the alternate sides of the polymer. The Cu···Cu distances vary from 2.803(3) to 2.948(3) and the Cu–I/Br bond lengths from 2.481(3) (Br) to 2.729(3) Å (I) (Table 4). Chain anions $[M_3I_4]^-{}_\infty$ of this structural type have been isolated in $[P(CH_3)(C_6H_5)_3][Cu_3I_4]$,[14a] $[As(C_6H_5)_4][Ag_3I_4]$,[14b] and $[P(C_6H_5)_4][Ag_3I_4]$,[14b] for example. Replacement of one of the iodide atoms with bromide in **3** favours the polymeric structure of the anion compared with the discrete iodocuprates(I) found in **1** and **2**. The Rb^+ cations are involved with bromides (Rb–Br 3.375(2) Å) and located on one side of the plane of copper atoms.

The rubidium atoms exhibit the typical "sunrise" co-ordination to 18c6 [0.937(5) Å above the best planes of the six oxygen atoms, Rb–O distances are in the range 2.82(1)–3.01(1) Å],[6] which has slightly distorted D_{3d} symmetry. The macrocyclic molecules are structurally normal, both the C–O (av. 1.41 Å) and C–C (av. 1.49 Å) distances are typical for macrocyclic polyethers.[6]

Crystal structure of complex 4

Within the $[Cu_2(SCN)_3]^-{}_\infty$ polymeric chain of complex **4** the two unique copper(I) centres are co-ordinated by three and four thiocyanate ligands, respectively (Fig. 5, Table 5). The different co-ordination modes adopted by the thiocyanate groups (μ-S, N; μ_3-2S, N and μ_4-3S, N) lead to the formation of four- and sixteen-membered $[(Cu–S)_2$, $(Cu–SCN–Cu–NCS)_2$ and (Cu–

Table 4 Selected bond distances (Å) and angles (°) for the $[Cu_3I_3Br]^-_\infty$ anion of complex **3**[a]

I(1)–Cu(1)	2.626(2)	Cu(1)–Cu(3)	2.803(3)
I(1)–Cu(2)	2.667(3)	Cu(1)–Cu(3^1)	2.902(3)
I(1)–Cu(3)	2.688(3)	Cu(1)–Cu(2)	2.915(3)
I(2)–Cu(1)	2.608(2)	Cu(1)–Cu(2^2)	2.948(3)
I(2)–Cu(3^1)	2.698(3)	Cu(2)–I(3^1)	2.666(2)
I(2)–Cu(2^2)	2.716(3)	Cu(2)–I(2^1)	2.716(3)
I(3)–Cu(2^2)	2.666(2)	Cu(2)–Cu(1^1)	2.948(3)
i(3)–Cu(3)	2.698(2)	Cu(3)–Br^3	2.481(3)
I(3)–Cu(1^2)	2.708(3)	Cu(3)–I(2^2)	2.698(3)
I(3)–Cu(1)	2.729(3)	Cu(3)–Cu(1^2)	2.902(3)
Cu(1)–I(3^1)	2.708(3)		
I(2)–Cu(1)–I(1)	116.40(9)	Br–Cu(2)–I(2^1)	98.17(9)
I(2)–Cu(1)–I(3^1)	114.26(8)	I(3^1)–Cu(2)–I(2^1)	111.19(8)
I(1)–Cu(1)–I(3^1)	106.60(8)	I(1)–Cu(2)–I(2^1)	115.04(9)
I(2)–Cu(1)–I(3)	112.61(8)	Br^3–Cu(3)–I(1)	115.31(9)
I(1)–Cu(1)–I(3)	110.55(8)	Br^3–Cu(3)–I(3)	105.60(9)
9(3^1)–Cu(1)–I(3)	94.11(7)	I(1)–Cu(3)–I(3)	109.63(8)
Br–Cu(2)–I(3^1)	104.80(9)	Br^3–Cu(3)–I(2^2)	98.59(9)
Br–Cu(2)–I(1)	120.49(10)	I(1)–Cu(3)–I(2^2)	115.31(9)
I(3^1)–Cu(2)–I(1)	106.63(8)	I(3)–Cu(3)–I(2^2)	111.67(8)

[a] Symmetry transformations used to generate equivalent atoms (indicated by superscript): 1 $-x+\frac{1}{2}, y, -z+\frac{1}{2}$, 2 $x-\frac{1}{2}, y, -z+\frac{1}{2}$, 3 $x-1, y, z$.

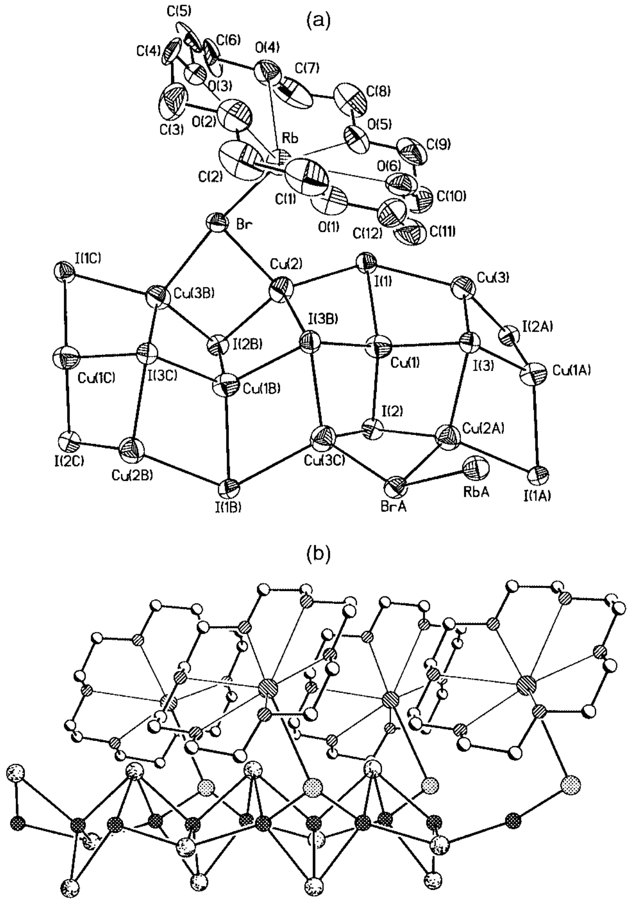

Fig. 4 (a) Plan view of part of the polymeric chain present in the crystal structure of $\{[Rb(18c6)][Cu_3I_3Br]\}_\infty$ **3** (the non-hydrogen atoms are shown as 40% thermal ellipsoids, H atoms omitted for clarity). (b) Projection view of **3** showing in plane arrangement of copper atoms and unilateral co-ordination of $[Rb(18c6)]^+$ cations.

SCN)$_4$] rings interlocked with each other. Propagation of multidimensional rings fused to each other in various ways often gives rise to two- and three-dimensional charged or uncharged networks as seen in $\{[(C_6H_5)_3NH][Cu_2(SCN)_3]\}_\infty$,[15a] $\{[(CH_3)_3NH][Cu_2(SCN)_3]\}_\infty$,[15b] $[CuSCN\cdot MeCN]_\infty$[15b] and $[Cu_2(SCN)_2(L)]_\infty$ (L = pyrazine, 4,4′-bipyridine or *trans*-1,2-bis(4-pyridyl)ethene).[15c] Although sixteen-membered rings exist in the anionic $[Cu_2(SCN)_3]^-_\infty$[15a,b] lattices the topologies of these systems are quite different from that found in **4** demonstrating the rich structural chemistry of CuSCN in the formation of polymeric arrays.

Table 5 Selected bond distances (Å) and angles (°) for the $[Cu_2(SCN)_3]^-_\infty$ polymeric anion of complex **4**[a]

Cu(1)–N(1)	1.941(6)	Cu(2)–Cu(2^2)	2.907(2)
Cu(1)–S(3)	2.284(2)	S(1)–C(1)	1.646(7)
Cu(1)–S(2^1)	2.440(2)	S(2)–C(2)	1.659(7)
Cu(1)–S(2)	2.474(2)	S(3)–C(3)	1.640(8)
Cu(2)–N(3)	1.891(6)	N(1)–C(1)	1.149(8)
Cu(2)–N(2^2)	1.898(6)	N(2)–C(2)	1.141(8)
Cu(2)–S(1^1)	2.329(2)	N(3)–C(3)	1.158(8)
N(1)–Cu(1)–S(3)	124.1(2)	C(1)–N(1)–Cu(1)	162.1(6)
N(1)–Cu(1)–S(2^1)	105.7(2)	C(2)–N(2)–Cu(2^2)	169.5(5)
S(3)–Cu(1)–S(2^1)	105.73(8)	C(3)–N(3)–Cu(2)	173.0(5)
N(1)–Cu(1)–S(2)	97.5(2)		
S(3)–Cu(1)–S(2)	111.57(7)	N(1)–C(1)–S(1)	177.5(6)
S(2^1)–Cu(1)–S(2)	112.18(6)	N(2)–C(2)–S(2)	177.9(6)
N(3)–Cu(2)–N(2^2)	139.1(2)	N(3)–C(3)–S(3)	176.9(6)
N(3)–Cu(2)–S(1^1)	110.6(2)		
N(2^2)–Cu(2)–S(1^1)	109.8(2)		

[a] Symmetry transformations used to generate equivalent atoms (indicated by superscript): 1 $-x, -y+2, -z+1$; 2 $-x+1, -y+2, -z+1$.

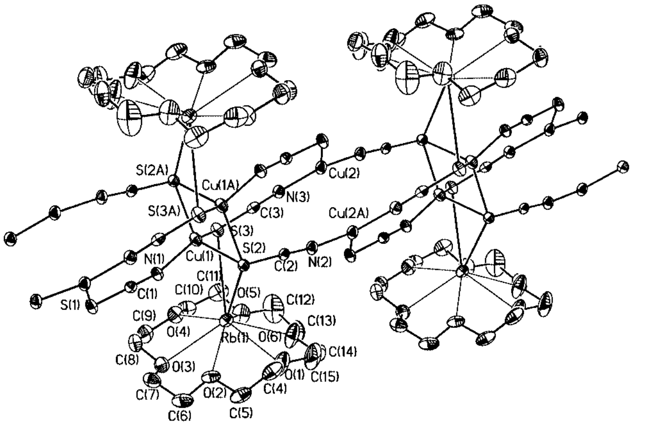

Fig. 5 Projection of part of the polymeric chain present in the crystal structure of $\{[Rb(18c6)][Cu_2(SCN)_3]\}_\infty$ **4** (the non-hydrogen atoms are shown as 20% thermal ellipsoids, H atoms omitted for clarity).

The Cu(1) ion is bonded to one nitrogen and three sulfur atoms from four bridging thiocyanate groups, displaying a distorted tetrahedral geometry. The two copper(I) ions, Cu(1) and Cu(1a) ($-x$, $2-y$, $1-z$), and the bridging sulfur atoms lie strictly in a plane, forming a Cu_2S_2 core with approximately equal Cu–S distances (2.440(2) and 2.474(2) Å). The core also contains a relatively short Cu···Cu separation of 2.742(2) Å, a narrow bridging Cu(1)–S(2)–Cu(1a) angle of 67.82(6)° and a wide S(2)–Cu(1)–S(2a) angle of 112.18(6)°. The planar or approximately planar Cu_2S_2 structural motif shows considerable structural flexibility in structures built up from copper(I) centres and thiocyanato groups. Various geometries have been observed,[15,16] ranging from rather short approximately equivalent Cu–S bonds of *ca.* 2.38(1) Å and a wide S–Cu–S* angle of 108.0°, which results in a Cu···Cu separation of 2.796(8) Å,[16a] to strikingly non-equivalent bond lengths at the copper(I) centre as seen in $[Cu(SCN)(NC_5H_4Me\text{-}2)]_\infty$[16b] (2.363(1), 2.806(1) Å, S–Cu–S* 106.30(4)°) and in $\{[Cu^{II}(dmf)_4][Cu^{I}_4(SCN)_4(CN)_2]\}_\infty$[16c] (Cu–S distances of *ca.* 2.36(4) and 2.78(3) Å, angles at the copper(I) atoms *ca.* 94°) where the Cu···Cu separation increases to 3.120(1)[16b] and more than 3.5 Å,[16c] respectively.

The Cu(2) centre is bonded to two nitrogen and one sulfur atom from three bridging thiocyanate groups and adopts a tri-

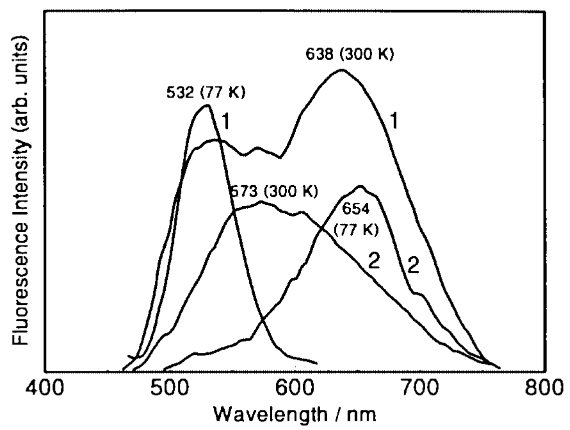

Fig. 6 Emission spectra of complexes **1** and **2** at 300 and 77 K.

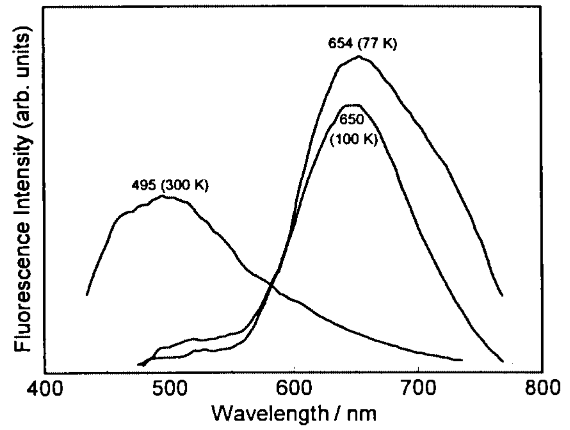

Fig. 7 Emission spectra of complex **3** at 300, 100 and 77 K.

angular planar co-ordination. Two Cu(2) atoms linked by the symmetry operation of the inversion centre $(1 - x,\ 2 - y,\ 1 - z)$ are separated at 2.907(2) Å.

The Rb^+ cations are in typical "sunrise" co-ordination to 18c6 [1.053(4) Å above the best planes of the six oxygen atoms, Rb–O distances in the range 2.869(7)–2.977(6) Å], which has slightly distorted D_{3d} symmetry. The sulfur atoms S(2) and S(3) forming strong bonds to Cu atoms are also weakly bonded to the Rb atom at 3.737(2) and 3.545(2) Å, respectively. This arrangement of bulky $[Rb(18c6)]^+$ cations on both sides of the $[Cu_2(SCN)_3]^-{}_\infty$ chains apparently prevents polymerization of the anion into the three-dimensional networks seen in structures with smaller cationic fragments.[15]

Luminescence

Figs. 6 and 7 show the emission spectra of complexes **1**, **2** and **3** at 77 and 300 K. Compound **4** does not display any solid-state emission. The emission spectrum of **1** at 300 K is broad, consisting of several spectral bands with peak positions at 540, 573 and 638 nm with the most intense band situated on the low energy side of the spectrum. At 77 K the low energy peak disappears and intensity of the high energy band increases with a slight shift to shorter wavelengths (532 nm). In the spectrum of **2** a red shift of the fluorescence band takes place on lowering the temperature (Fig. 6). The luminescent properties of **1** and **2** were used as a convenient and rapid means for the identification of the product of the reaction (1). As was mentioned above, a mixture of two complexes may result: **1** and **2** are readily distinguishable by their emission; the former appears bright green while the latter yellow-red at 77 K. The blue-green emission of **3** at 300 K is broad and featureless displaying a maximum at 495 nm. On lowering the temperature the emission peak shifts to longer wavelengths (Fig. 7) with increase of intensity and a minor sharpening.

Luminescent copper(I) systems for which single-crystal X-ray data are available have been well studied.[2] The observed luminescence could be attributed to any one of the transitions: ligand-centred, metal-centred, or charge transfer in character. The systems described display no possibility of metal–ligand charge-transfer transitions because of the absence of ligands co-ordinated to copper atoms as such. Although the presence of a crown ether in the unit cell reportedly changes the wavelength of the fluorescent emission of an iodocuprate(I) complex,[17] clearly Rb^+–18c6 moieties in the present case cannot be responsible for the emission observed as no fluorescence is detected for **4** and for other iodocuprates(I) with M^+–crown cations (M = K, Rb or Cs).[18] The possibility that the emission reflects a metal-centred process involving more than one metal centre is reasonable, and is consistent with assignments given in the literature (all the three compounds show Cu···Cu distances of less than 3.0 Å).[2a] Also, we cannot rule out the possibility that the Cu–I bond is a source of emission in **1**, **2** and **3**. CuI in the solid state has been reported to display the 420 nm emission when excited with a nitrogen laser.[19] The material also displays a series of narrow band emissions at lower and higher wavelengths attributed to exciton phenomena.[18] All Cu–I distances in solid CuI are 2.617 Å, comparable to those found in the present compounds (Tables 2–4).

All the three compounds reversibly alter their fluorescence colour with temperature and their thermochromic behaviour is different. In the spectrum of **1** a blue shift of the fluorescence band takes place while maxima of the broad emission envelopes of **2** and **3** are red-shifted at low temperature. Among series of copper(I) halide complexes thermochromic fluorescence has been noted for several of the distorted cubic structures $[Cu^IIL]_4$ (L = cyclic nitrogen base).[2b] Although it has been suggested that the thermochromicity of the systems may be correlated with the lack of symmetry element in the cluster[2b] the empirical evidence is ambiguous.[2a] The differences between the present and reported structures make comparison of their fluorescence difficult. We can presume only that, because of rather short metal distances, an increase of electronic interactions between adjacent copper ions in the excited state with lowering of the temperature is the reason for the shifts of the emission band.

Conclusion

The solid-state structures of the products of the interaction of zerovalent copper with ammonium halides in the presence of Rb^+–18c6 cations display stoichiometries and geometries of halogeno-/pseudo-halogeno-cuprate(I) anionic counterparts which vary while the same geometrically rigid cation $[Rb(18c6)]^+$ is present. As the reaction conditions are similar the influence of the counter anions on the topology of the system is self-evident. X-Ray studies of the products have also revealed that the larger the amount of iodide ion in the original reaction mixture the more complex is the final product. The fluorescence thermochromism of the obtained complexes is thought to originate from an increase of electronic interactions between adjacent copper ions in the excited state with lowering of the temperature. The possibility that the reactions studied might be autocatalytic is also discussed.

Acknowledgements

The work was in part supported by the Fundamental Research State Fund of Ukraine. The RSC Journals Grant for International Authors (O. Yu. V.) and Deutsche Akademische Austauchdienst grant (Gemeinsames Hochschulsonderprogramm III von Bund und Ländern) (B. A.) are gratefully acknowledged. The EPSRC is thanked for funding for the purchase of the Enraf Nonius Kappa CCD Diffractometer.

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