Copper(I) Iodide Complexes of Novel Structure: $[Cu_4I_6][Cu_8I_{13}]K_7(12\text{-crown-}4)_6$, $[Cu_4I_6]K_2(15\text{-crown-}5)_2$, and $[Cu_3I_4]K(\text{dibenzo-}24\text{-crown-}8)$

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Aqueous solutions of copper(I) iodide, potassium iodide, and crown ether form complexes of unexpectedly different and novel structure: $[Cu_4I_6][Cu_8I_{13}]K_7(12\text{-crown-}4)_6$ with two different clusters per asymmetric unit and polymeric modifications, $[Cu_4I_6]K_2(15\text{-crown-}5)_2$, and $[Cu_3I_4]K(\text{dibenzo-}24\text{-crown-}8)$ depending upon the identity of the crown ether.

Various structural formats have been observed for complexes of copper(I) iodide with electron donor ligands. The most common are cubes,[1] chairs,[2] and pleated sheets.[3] These structures have in common the Cu_2I_2 rhombohedron as a repeating structural unit. Thermochromic fluorescence has been noted for several of the distorted cubic structures;[4] *e.g.* $[CuIpyridine]_4$[5] and $[CuIpiperidine]_4$,[6] but not for others[7] such as $[CuImorpholine]_4$,[8] $[Cu_2I_2(MeCN)_2(p\text{-toluidine})_2]_2$,[9] and $[Cu_2I_2(MeCN)_2(p\text{-chloroaniline})_2]_2$.[9] Solid state materials of the other structural types display fluorescence which is not temperature dependent.[10] We find that Cu^II and aqueous solutions of potassium iodide with crown ethers of various sizes yield crystalline materials that display thermochromic fluorescence in the solid state and are of unexpectedly varied structural types previously unobserved in this series.

The addition of an acetone solution of 12-crown-4 to Cu^II in aqueous KI yields $[Cu_4I_6][Cu_8I_{13}]K_7(12\text{-crown-}4)_6$ (**1**); a = 17.702(5), b = 17.715(5), c = 10.581(4) Å, tetragonal space group $P\bar{4}$, Z = 1, D_c = 2.254 g cm^{-3}, R = 8.7%, 3290 observed reflections. Two different CuI clusters, a $[Cu_4I_6]^{2-}$

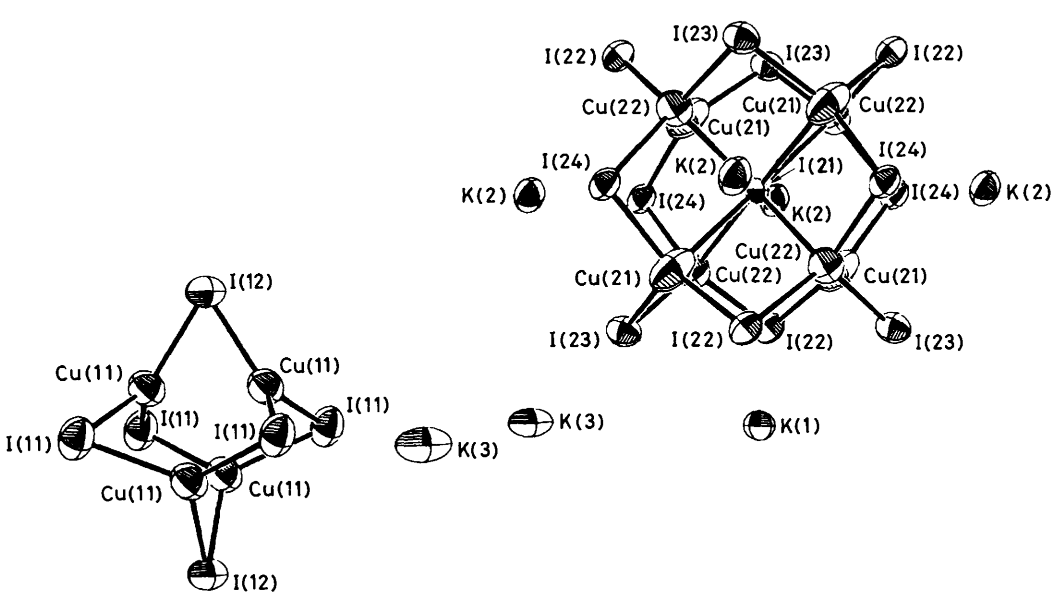

Figure 1. View of the $[Cu_4I_6]^{2-}$ and $[Cu_8I_{13}]^{5-}$ clusters of (**1**).

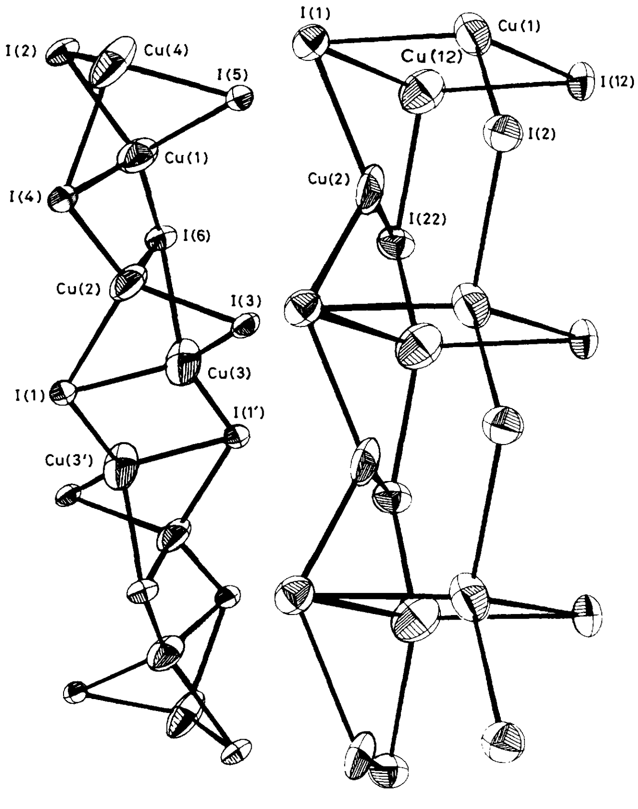

Figure 2. Projection view of the polymeric bridged pleated sheet of (**2**) (left) and of the polymeric copper–iodide bonding in (**3**) (right).

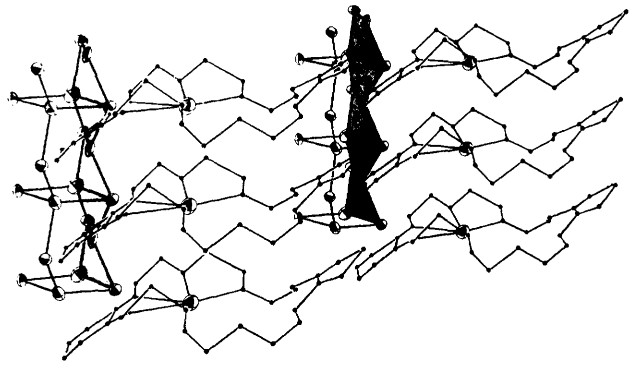

Figure 3. Packing of polymeric Cu_3I_4 chains and dibenzo-24-crown-8 bound potassium atoms in (**3**).

cluster in which four copper atoms are arranged in a tetrahedron bridged on all edges by iodides [Cu–Cu, av. 2.76(1) Å] and $[Cu_8I_{13}]^{5-}$ in which a cubic arrangement of eight copper atoms [Cu–Cu, 3.35(1) Å] centred by an iodide and bridged on all 12 edges by further iodides, exist in the unit cell. The larger clusters pack parallel to the *c* axis, separated by potassium atoms at ionic distances [K–I av. 3.76(1) Å]. Six other potassium atoms, each co-ordinated to a crown ether, are positioned at the other faces of the $[Cu_8I_{13}]^{5-}$ cluster and in the voids of the cell between the two types of clusters. The larger cluster is reminiscent of the Cu^I framework seen for $Cu^{II}_6Cu^I_8S_{12}N_{12}Cl$ [Cu^I–Cu^I av. 3.30(2) Å][11] but the smaller one is of unknown precedence (Figure 1).

The use of 15-crown-5 yields $[Cu_4I_6]K_2(15\text{-crown-}5)_2$ (**2**); $a = 11.131(7)$, $b = 13.313(6)$, $c = 16.396(8)$ Å, $\alpha = 92.89(4)$, $\beta = 70.20(4)$, $\gamma = 65.34(5)°$, triclinic space group $P\bar{1}$, $Z = 2$, $D_c = 2.516$ g cm^{-3}, $R = 9.5\%$, 4016 observed reflections. The polymeric pleated sheet of edge sharing Cu_2I_2 rhombohedra resembles that of $[CuIMeCN]_x$[12] and $[CuIpyridine]_x$[13] with the addition of an iodide atom bridging the copper atoms of every other rhombohedron and thus bringing the copper atoms of these rhombohedra into closer proximity [Cu–Cu, bridged, av. 2.466(8) Å; Cu–Cu, nonbridged, av. 2.716(8) Å]. Potassium atoms bound to the oxygen atoms of 15-crown-5 molecules show ionic involvement with the iodide atoms, each potassium having three K–I distances of less than 3.852(10) Å. This structural motif has not previously been observed for Cu^I iodide structures (Figure 2, left).

A third novel structural geometry is shown by the crystalline product of CuI, aqueous KI, and dibenzo-24-crown-8: $[Cu_3I_4]K(\text{dibenzo-24-crown-8})$, (**3**); $a = 4.500(2)$, $b = 20.217(6)$, $c = 18.797(9)$ Å, $\beta = 95.00(4)°$, monoclinic space group $P2_1$, $Z = 2$, $D_c = 2.312$ g cm^{-3}, $R = 6.9\%$, 2234

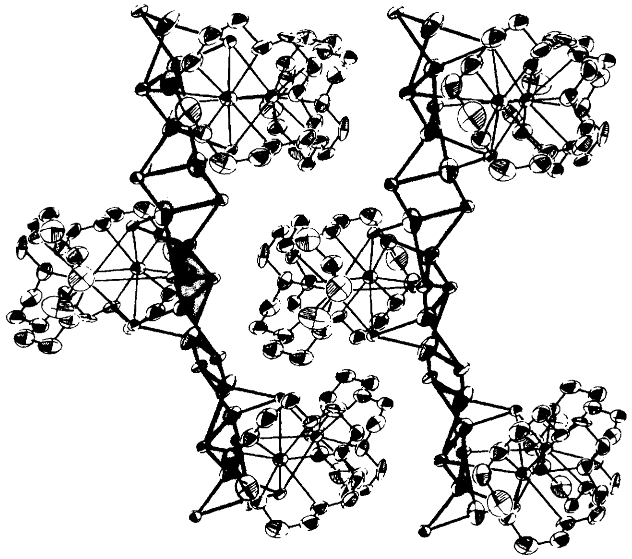

Figure 4. Packing of (**2**) in the unit cell.

observed reflections. The single crystal X-ray data reveal a polymeric pleated sheet structure of edge sharing Cu_2I_2 rhombohedra with an additional rhombohedron sharing every other shared edge. These additional rhombohedra are parallel to each other (perpendicular to the polymeric direction) and are linked by an additional iodide atom bridging the copper atoms of the projecting rhombohedra (Figure 2, right). Potassium atoms show no involvement with the iodide atoms and are each bonded to four oxygen atoms of a crown ether ring containing eight oxygen atoms [K–O less than 3.07(3) Å].

Structural information was obtained by full matrix least-squares refinement of single crystal X-ray data collected at room temperature using Mo-K_α radiation on an automated single crystal X-ray diffractometer.†

Thus the solid state structures of complexes of copper(I), iodide, and potassium display stoicheiometries and geometries which vary with the crown ether present. The differing structures are perhaps attributable to the varying interaction with iodide possible for a potassium ion complexed to a crown ether of specific ligand (oxygen) content and cavity size. Thus the potassium is more completely encapsulated by the 24-crown-8 molecule in (**3**) (Figure 3) and is not involved with iodide, whereas the 12-crown-4 molecule in (**1**) and 15-crown-5 in (**2**) (Figure 4) display cavities insufficiently large to surround potassium and the more exposed potassium is able to display simultaneous interaction with iodide.

Received, 22nd January 1985; Com. 102

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.