Tetrakisimidazolecopper(II) Iodide; a Non-chelated Cupric Iodide Complex

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Although copper(II) ions are normally reduced by iodide ions, we find that in the presence of imidazole (L), but not with 2-substituted imidazoles, the copper(II) ion is stable in solutions containing iodide ions. Crystalline CuL_4I_2 may be obtained by slow evaporation of an ethanolic solution containing a slight excess of imidazole.

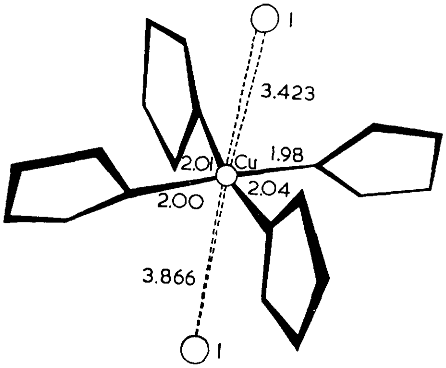
This compound has an electronic spectrum typical of copper(II) ions in a strongly tetragonal environment, and a magnetic moment of 1·81 B.M. It therefore appeared to be a complex of copper(II) iodide which does not contain chelating ligands. This has been fully confirmed by three-dimensional *X*-ray structure analysis. The only other non-chelated complexes of this type are $CuI_2,6NH_3$, $CuI_2,5NH_3$, and $CuI_2,2NH_3$,[1] but these have not been investigated structurally.

Tetrakisimidazolecopper(II) iodide crystallises as violet prisms of orthorhombic symmetry. Unit-cell dimensions are $a = 14{\cdot}55$, $b = 9{\cdot}48$, $c = 13{\cdot}41$ Å, $U = 1848$ Å^3, $D_m = 2{\cdot}11$, $Z = 4$, $D_c = 2{\cdot}12$. The space group has proved to be $Pna2_1$.

The structure was solved by Patterson and Fourier methods on the basis of 1189 independent reflections, recorded with Cu-K_α radiation and visually estimated. Least-squares refinement has now reached $R = 0{\cdot}082$.

The molecular structure is shown in the Figure. The co-ordination about the copper atom is essentially square-planar with two rather distant iodine atoms completing the very distorted octahedron. The Cu–N distances are in the range 1·98—2·04 Å, which is normal. The orientation of the imidazole rings is such as to allow maximum π-bonding and also least interference between the rings. The only known Cu^{II}–I covalent distance is 2·70 Å found in iodobis-(2,2′-bipyridyl)copper(II) iodide.[2] The two Cu–I distances found for the imidazole complex (3·42 and 3·87 Å) suggest that the Cu–I interaction is at best a weak one.

FIGURE. *The co-ordination about the copper atom. The standard deviations are*: Cu–I, 0·008 and Cu–N, 0·03 Å



The stability of the complex in solution is solvent dependent. Copper(I) iodide is precipitated from solutions in relatively non-polar solvents such as nitrobenzene, more rapidly with increasing temperature. In ethanol there is an equilibrium between Cu^{I} and Cu^{II}, in which the copper(II) complex is favoured by low temperature and addition of excess of ligand. In water the copper(II) species is so strongly favoured that reaction of copper(I) iodide and iodine, in the presence of imidazole, results in the formation of CuL_4I_2, together with iodinated imidazoles.

The e.s.r. spectrum of powdered CuL_4I_2 at room temperature indicates a tetragonal ligand field, with $g_{\perp} = 2{\cdot}03$. At 80° K, the e.s.r. spectrum of an ethanol solution, stabilised with excess to ligand, shows copper hyperfine splitting, and also hyperfine splitting due to the nitrogen atoms. There is therefore appreciable delocalisation of the unpaired electron on to the imidazole rings.

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[1] F. Ephraim, *Ber.*, 1919, **52**, 940.
[2] G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 1963, 5691.