The Structures of Tetrakis(pyridine oxide)copper(II)Tetrafluoroborate and Perchlorate

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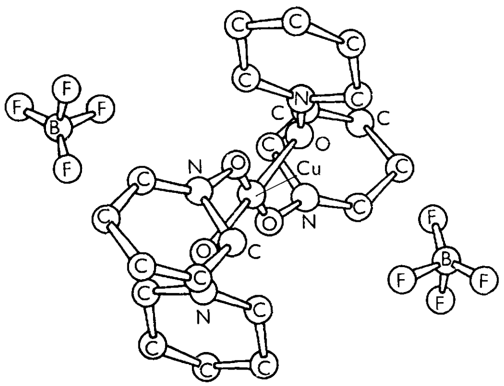
IN recent communications[1,2] we have shown the existence of interaction between a fluorine atom in $(BF_4)^-$ and copper in the crystalline complex $Cu(en)_2(BF_4)_2$, thus forming an octahedral environment for the metal. This interaction has been termed 'semi-co-ordination'. We now report the crystal structures of Cu(pyridine oxide)$_4$$(BF_4)_2$ and Cu(pyridine oxide)$_4$$(ClO_4)^2$: in neither case is there any evidence of 'semi-co-ordination'.

The structure of the two complexes is basically the same. Crystals of both complexes are monoclinic and have the space group $P2_1/c$ with two molecules per unit cell. The cell dimensions are $a = 9{\cdot}59$, $b = 14{\cdot}30$, $c = 10{\cdot}69$ Å, $\beta = 122{\cdot}0°$ for $Cu(pyO)_4(BF_4)_2$ and $a = 9{\cdot}65$, $b = 14{\cdot}30$, $c = 10{\cdot}85$ Å, $\beta = 122{\cdot}0°$ for $Cu(pyO)_4(ClO_4)_2$.

Using Patterson and Fourier techniques all atoms except hydrogen have been located, and the structures refined by a full matrix least-squares method. The reliability indices, R, are at present 10·1% for $Cu(pyO)_4(BF_4)_2$ (1019 independent X-ray reflections) and 11·0% for $Cu(pyO)_4(ClO_4)_2$ (1468 independent X-ray reflections).

The Figure shows the environment of each copper atom, the structure being centrosymmetrical about the copper. Oxygen atoms from four pyridine oxide molecules form a square-planar arrangement around the copper with Cu–O distances of 1·93 and 1·91 Å in the fluoroborate complex and 1·93 and 1·92 Å in the perchlorate complex. The four pyridine oxide molecules form a "swastika" configuration around the copper, the nitrogen atoms lying approximately in the copper–oxygen plane but the benzenoid rings lying approximately perpendicular to this plane.

In both complexes the polyanion lies in an approximately octahedral position to the copper, but no atoms are close enough to be involved in any co-ordination with the metal. The nearest approaches of the polyanions to the copper are Cu · · · F 3·34 and Cu · · · O 3·38 Å. There are a



FIGURE

large number of intermolecular contacts in the region 3·1—3·6 Å and it appears that the polyanion is held in the crystal by these lattice forces.

The BF_4^- ion is a distorted tetrahedron with apparent B–F bond lengths of 1·40, 1·36, 1·35, and 1·30 Å. This distortion may be due partly to unsymmetrical interactions around the polyanion, but the low scattering power of boron prevents very precise determination of its position. The ClO_4^- ion is much less distorted from a regular tetrahedron, with Cl–O bond lengths of 1·42, 1·42, 1·39, and 1·38 Å.

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[1] D. S. Brown, J. D. Lee, B. G. A. Melsom, B. J. Hathaway, I. M. Procter, and A. A. G. Tomlinson, *Chem. Comm.*, 1967, 369.

[2] D. S. Brown, J. D. Lee, and B. G. A. Melsom, *Acta Cryst.*, 1968, *B*, **24**, 730.