C-186 09. STRUCTURES OF ORGANIC AND COORDINATION COMPOUNDS


To progress in the study of magneto-structural correlations in polynuclear Cu(II) complexes we have approached the structural analysis of Cu(BPCA)Br (I) and Cu(BPCA)(H₂O)(CH₃OD)⁻(H₂O)⁺ (II). Both structures have been solved using the MULTAN 87/84 system and refined by weighted anisotropic full-matrix least-squares with the SHELX 76 system. The final wR values were 0.005 for I and 0.049 for II.

Complex I, Cu₃BrCu₂O₄, is monoclinic, space group P2₁/a, a = 3.888(3), b = 8.641(3), c = 17.944(11), β = 92.63(2), V = 602(2)Å³, Z = 1, D = 2, D = 2.04 g cm⁻³, F(000) = 362, μ(MoKα) = 51.0 cm⁻¹. Complex II, Cu₃H₂BrCu₂O₄, is triclinic, space group P1, a = 7.416(9), b = 8.632(4), c = 13.034(3), α = 74.35(3), β = 111.58(3), γ = 118.54(5), V = 92.04(5), F(000) = 39.4, μ(MoKα) = 14.1 cm⁻¹.

Figure 1 shows a view of the unit cell of complex I. The structure consists of infinite chains along [010]. These are built up by parallel Cu₃(BPCA)Br units with the bromine atoms bridging two copper(II) ions. The copper atom environment is described as a distorted square pyramid. Basal positions are occupied by the three nitrogen atoms from BPCA ligand and the bromine atom, while the apical site is occupied by another bromine atom (Br⁻) belonging to an adjacent molecule. Basal atoms are coplanar (ε = 0.08 Å) and the copper atom lies 0.14 Å above this plane. Figure 2 shows a perspective view of complex II. As occurs in I, the copper(II) environment is close to square pyramidal. The nitrogen atoms from BPCA and one oxygen atom from the monodentate acetate anion occupy the basal positions. One of the two water molecules is coordinated to Cu(II) ion in the apical site. The second water molecule is hydrogen-bonded to the non-coordinated oxygen atoms of two acetate groups. These last belong to two different molecules which are related through a symmetry center, resulting in this way "pseudo-dimeric" (Cu(BPCA)(H₂O)(CH₃OD)⁻(H₂O)⁺:BPCA:CuO) entities.

Figure 1.

Figure 2.