Preparation and Structure of an Anionic Cu^{2+} Alkoxy Complex containing a Sixteen-membered, H-Bonded, Fluorinated Macrocyclic Ring

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In the complex $[Ph_4P^+]_2[Cu\{OC(CF_3)_2OH\}_4]^{2-}$, four-co-ordinate, square-planar Cu^{2+} lies at the centre of a 16-membered macrocycle held together by hydrogen-bonding between four fluorinated alkoxide ligands.

We have recently shown that the fluorinated alcohol hexafluoropropane-2,2-diol, $(CF_3)_2C(OH)_2$, forms complexes with a variety of metals.[1] Three modes of co-ordination are found: as the chelating di-alkoxide $[(CF_3)_2C(-O)_2]^{2-}$, forming a four-membered ring; as the condensed di-alkoxide $[O-C(CF_3)_2-O-C(CF_3)_2-O]^{2-}$, forming a six-membered chelate ring; or as the bridging di-alkoxide $[O-C(CF_3)_2-O)]^{2-}$. Stable complexes of metal ions such as Cu^{2+}, Ni^{2+}, Co^{3+}, Mn^{2+}, or Pt^{2+} are formed by the use of additional co-ligands (amines, phosphines, or Cl^-) to produce neutral species.

We now find that reaction of $(CF_3)_2C(OH)_2$ with Cu^{2+} in the absence of co-ligands produces complexes where the dinegative anion has a ratio of four diol residues per metal ion. The counterions can be K^+, $Pr^n{}_4N^+$, or Ph_4P^+. Previous work on complexes of the dianion of perfluoropinacol, $[O{-}C(CF_3)_2C(CF_3)_2{-}O]^{2-}$, PFP^{2-}, has shown that anionic complexes $[Ni(PFP)_2]^{2-}$ or $[Cu(PFP)_2]^{2-}$ are formed; these contain two five-membered chelate rings.[2] A similar formulation of the $(CF_3)_2C(OH)_2$ anionic complexes, with six-membered chelate rings, would be possible, but a complete structural determination showed that condensation of two diol residues had not occurred. Instead, four-co-ordinate Cu^{2+} is bonded to four monodentate, singly ionized $HOC(CF_3)_2{-}O^-$ units as shown in Figure 1.

The complexes were prepared by the reaction of $CuCl_2$ with $K[OC(CF_3)_2OH]$ in ethanol in the presence of excess diol, followed by cation exchange.† Diffraction-quality crystals of the tetraphenylphosphonium salt were grown from a methanolic solution containing a large excess of diol, without which decomposition occurred. The IR spectrum (Nujol mull) showed two bands attributable to alcohol O–H at 2560 and 2720(br.) cm^{-1}, and indicative of hydrogen bonding. The visible spectrum (ethanol solution) showed peaks at 662 (ε = 40 $m^2\,mol^{-1}$) and 563 (24) nm. The structure was determined by *X*-ray crystallography,‡ and is the first reported example of a copper complex with four alkoxide ligands.

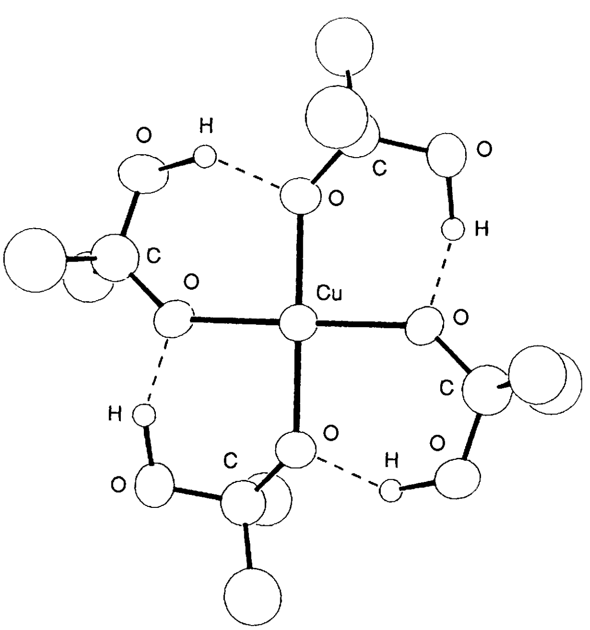

Figure 1. ORTEP drawing showing the arrangement of the ligands in the anion $[Cu\{OC(CF_3)_2OH\}_4]^{2-}$ (fluorine atoms omitted).

The crystals are built up from well-separated tetraphenylphosphonium cations and $[Cu\{OC(CF_3)_2OH\}_4]^{2-}$ anions, which lie on inversion centres. The Cu atom is bonded to four monodentate ligands in square-planar co-ordination geometry, with an average Cu–O bond length of 1.933(6) Å and O–Cu–O angles of 89.9(2) and 90.1(2)°. Each free alcohol group is hydrogen bonded to the ligating alkoxide atom of the adjacent ligand O(1) · · · O(4) 2.590, O(2) · · · O(3)′ 2.554 Å. The hydroxy protons were located in a final difference Fourier synthesis, but not refined [*e.g.* O(2)–HO2 1.15, O(3)′–HO2 1.58 Å, and O(2)–HO2 · · · O(3)′ 138°]. The anion does not have exact four-fold symmetry; in one pair of ligands C(4) and O(4) are 0.11 and 0.47 Å respectively from the co-ordination plane of the Cu atom, whilst in the other pair, C(1) and O(2) are displaced by 0.13 and 0.25 Å respectively. This difference is presumably due to geometrical constraints, as evidenced by the non-linear hydrogen bond.

The environment of Cu^{2+} resembles that found in tenorite, CuO,[3] in $Na_2[Cu(C_2O_4)_2]$,[4] and in $Cu(acac)_2$ (acac = acetylacetonate).[5] The arrangement of the ligands is very similar to that found by Roesky *et al.* for the anion derived from $(CF_3)_2C(OH)_2$, where four singly-ionized molecules form a hydrogen-bonded sixteen-membered ring around two bridging protons.[6] (In contrast to the indirect route used by those authors, we find that such salts are readily made by direct neutralization of the diol.)

We were unable to prepare anionic complexes of $(CF_3)_2C(OH)_2$ with other metals. This structural result illustrates the tendency of Cu^{2+} to bond strongly through oxygen, and the common occurrence of hydrogen bonding in fluorinated alcohols and their derivatives.[7]

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† Satisfactory elemental analyses were obtained for new compounds reported.

‡ *Crystal data* for bis(tetraphenylphosphonium)tetra(hexafluoropropane-2,2-diolato)copper(II): $C_{60}H_{44}CuF_{24}O_8P_2$, M = 1474.5, monoclinic, space group $P2_1/c$, a = 10.947(2), b = 15.901(3), c = 17.733(3) Å, β = 92.50(2)°, U = 3084(2) Å^3, Z = 2, D_m = 1.62, D_c = 1.59 Mg m^{-3}, $F(000)$ = 1486e, graphite monochromated Mo radiation, $\lambda(\text{Mo-}K_\alpha)$ = 0.71073 Å, μ = 5.27 mm^{-1}, T = 295 K. Data were recorded on an Enraf-Nonius CAD4F diffractometer out to a $\theta_{max.}$ of 20°. A Gaussian absorption correction was applied. The structure was solved with the SHELXS-86 software (G. M. Sheldrick, Göttingen, FRG, 1986), and refined with SHELX-76 (G. M. Sheldrick, Cambridge, UK, 1976), treating the four phenyl rings as rigid groups. The twenty phenyl H atoms were included in 'riding' fashion with idealised geometries and Debye parameters 10% greater than those of the bonded carbon atoms. After refinement converged, the two hydroxy protons on the diol ligands were located in a difference Fourier synthesis. They were included in the model with fixed parameters. Two additional cycles employing 1948 reflections with $I > 2.5\,\sigma(I)$ were used to refine 203 variables on F giving agreement factors of R_1 = 0.061 and R_2 = 0.068. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.