

Crystal Structure of the Triclinic Form of $(2\text{tbpo}\cdot\text{H}^+)_2\text{tetrachlorocuprate(II)}$ $\{[(\text{PhCH}_2)_3\text{PO}]_2\text{H}\}_2\text{CuCl}_4$: the Presence of Extremely Short O–H–O Interactions

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The structure of $\{[(\text{PhCH}_2)_3\text{PO}]_2\text{H}\}_2\text{CuCl}_4$ has been shown to contain four $[(\text{PhCH}_2)_3\text{PO}]_2\text{H}^+$ cations with extremely short O–H–O distances of 2.295, 2.364, 2.394, and 2.404 Å, respectively.

In a previous paper,¹ one of us reported on the preparation and structure of protonated phosphine oxide salts of copper(II) halides of stoichiometry $[(\text{tbpo})_2\cdot\text{H}]_2\text{CuX}_4$ (where tbpo = tribenzylphosphine oxide and $\text{X} = \text{Cl}$ or Br). The structure of tetragonal crystals of the chloride salt was particularly interesting in two respects: i, the CuCl_4^{2-} anion attained a unique elongated tetrahedral geometry of D_{2d} symmetry and ii, the cation contained a very short O–H–O distance [2.324(6) Å] as a result of the H^+ ion bridging two tbpo molecules. This O–H–O distance is surpassed in shortness only by a distance of 2.29 Å for an H_3O_2^- species found in a complex inorganic salt.²

The uniqueness of the CuCl_4^{2-} geometry in this tetragonal phase prompted us to reinvestigate the structure of the chloride salt. Four-coordinate Cu(II) species invariably show a compressed tetrahedral geometry between tetrahedral and square planar.^{3,4} The elongated D_{2d} geometry would leave the CuCl_4^{2-} with an orbitally degenerate ground state, in apparent violation of the Jahn–Teller theorem. The structural results indicated large thermal parameters on the chloride ions, while EPR spectroscopy results were consistent with a low-symmetry compressed tetrahedral geometry. Thus the possibility that the tetragonal phase was disordered, with a phase transition to an ordered phase occurring below room temperature, had to be considered. Crystalline samples of $(2\text{tbpo}\cdot\text{H})_2\text{CuCl}_4$ were obtained from the previous study.¹ Preliminary X-ray studies at room temperature indicated that,

in contrast to the above results, the crystals of these samples were triclinic, space group $P\bar{1}$ with $a = 13.471(4)$, $b = 14.685(5)$, $c = 19.875(4)$ Å, $\alpha = 82.31(2)$, $\beta = 78.03(2)$, $\gamma = 86.56(2)^\circ$, $U = 3810(1)$ Å³, $Z = 2$, and $\rho_c = 1.30$ g cm^{−3}. Thus, a thorough reinvestigation of the system was begun.

The DSC data were taken on a Perkin Elmer DSC-7. A powdered sample was packed into a volatile sample pan. The sample was scanned from 30 to 200 °C at a scan rate of 10 °C min^{−1}. This study exhibited a single feature at T 196 °C, due to the melting of the sample. The melting point recorded for the corresponding tetragonal phase was 176 °C. No evidence was seen for a triclinic to tetragonal phase change.

The EPR spectra were recorded on a Varian Model E-3 spectrometer at various temperatures. At liquid nitrogen temperature, an axial spectrum was obtained which gave g_\perp 2.08 and g_\parallel 2.40; at room temperature a much broader ($\Delta H \sim 200$ Oe), isotropic spectrum was superimposed on this spectrum. Heating to 100 °C yielded a still broader spectrum ($\Delta H \sim 250$ Oe). Subsequent cycling between high temperature (approximately 100 °C) and room temperature led us to believe that the dynamics between the liquid nitrogen spectra and the broad superimposed spectra are dictated by domains and are not indicative of any structural phase transition. The situation is very different for the tetragonal phase where even though the site symmetry was found to be D_{2d} , the EPR spectrum exhibited a rhombic distortion with three different g values (g_1 2.196, g_2 2.140, g_3 2.046).

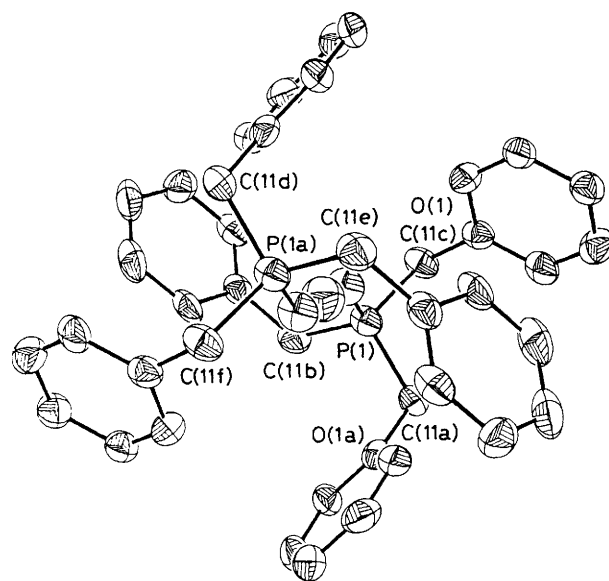
Table 1. Table of selected short O...O distances.

Compound	O—O pair	O...O distances	Ref.
(2tbpo·H ⁺) ₂ CuCl ₄ triclinic	O(1)—O(1A)	2.364(6)	— ^a
	O(2)—O(2A)	2.404(6)	
	O(3)—O(3A)	2.394(6)	
	O(4)—O(4A)	2.295(6)	
(2tbpo·H) ₂ CuCl ₄ tetragonal phase		2.324	1
(2Ph ₃ AsO·H ⁺) ₂ Hg ₂ Br ₆		2.40	7
H ₃ O ₂ [−] anion in Na ₂ (Me ₃ EtN)·(CrC ₂₁ H ₁₅ S ₃ N ₃ O ₃)·(H ₃ O ₂)1/2·18 H ₂ O		2.29	2
Pyridine-2,3-dicarboxylic acid		2.398	8
HBr·2H ₂ O		2.40	9
[(Me ₂ SO) ₂ H]RhCl ₄ (Me ₂ SO) ₂		2.42	10

^a This work.

A preliminary structure determination at room temperature revealed large thermal parameters for all atoms, although no discernable disorder was found. Hence a low temperature structure determination was done.[†] The structure of the triclinic phase consists of discrete CuCl₄^{2−} anions and four crystallographically independent 2tbpo·H⁺ cations. The copper ion has a distorted tetrahedral geometry with an average Cu—Cl distance of 2.256(3) Å and an average *trans* Cl—Cu—Cl angle of 133.0(3.3)°. The phosphorus atoms all have near tetrahedral co-ordination in which the largest deformations exist between the oxygen atoms and at least one of the carbon atoms. The three benzyl groups on each tbpo fragment fold back over the oxygen atom. The dihedral angles between each ring and the plane defined by P—C(*n*1)—C(*n*2) (*n* being the number label of the cation) are all close to 90°. This, in conjunction with the inversion centre in the cation, produces a unique type of cage structure with the proton at the centre of the cage (Figure 1).

The four crystallographically independent cationic tbpo pairs are bridged by hydrogen ions restricted to lie at the centres of inversion at 0, 0, 0; 0, 0, 0.5; 0.5, 0.5, 0; and 0.5, 0.5, 0.5. This produces apparent symmetric hydrogen bonds that bridge the tbpo pairs with extremely short O—H—O distances ranging from 2.295(6) to 2.404(6) Å (Table 1). Such hydrogen bonded systems were previously proposed by Hadzi¹¹ and were reported in the tetragonal phase of the 2tbpo·H⁺ salt, (O...O 2.324 Å),¹ as well as in the (2Ph₃AsO·H⁺)₂Hg₂Br₆ salt (O...O 2.40 Å).⁷ All of the O...O distances in the

**Figure 1.** Illustration of the 2tbpo·H⁺ cation located at 0.5, 0.5, 0.

triclinic phase of the tbpo salt are shorter than the normal range of symmetric hydrogen bridges (2.40–2.50 Å).¹² The 2.295 Å distance for the O(4)...O(4A) bridge is essentially the same as the shortest O...O distance known (2.29 Å), reported in the bihydroxide ion,² and more than 0.5 Å shorter than the sum of two oxygen van der Waals radii. The differences in O—H—O distances appears to be related to packing forces which influence the geometry of the P—O—H—O—P linkage. In the two longer hydrogen bonds [involving O(2) and O(3)], the P—O—O' angles are 135.1(3) and 133.8(3)°, while for the shorter hydrogen bonded cations [involving O(1) and O(4)] these angles are larger, 143.0(3) and 143.9(3)°. This causes the P...P distances to be longer [5.065(4), 5.032(4) Å] for the two shorter hydrogen bonded systems than in the longer ones [5.004(4), 4.987(4) Å].

The source of the extreme shortening of the O—H—O distances in (2tbpo·H)₂CuCl₄ certainly lies in the unique way the six phenyl rings in the 2tbpo·H⁺ cation surround the O—H—O moiety. This prohibits any further electrostatic interactions, which would only weaken the hydrogen bonding and lengthen the O—H—O bond. The cage type structure produces short contacts between the positive ring protons and the negative π electron cloud on other phenyl groups within the cage. It has been argued that this type of interaction leads to stability in the structure of proteins.¹³ It would appear to be the driving force for stabilizing the hydrophobic cage about the hydrophilic O—H—O core. This cage structure cannot form for the 2Ph₃AsO·H⁺ salts,⁷ thus accounting for the longer (2.40 Å) O—H—O distance in that cation.

Short O—H—O interaction between Ph₃PO and various organic species have also been noted.¹⁴ In particular, a distance of 2.504 Å has been found for its complex with an enolized sulphamide.¹⁵ Short hydrogen bonding distances involving related sulphur oxide species are also known, e.g., the O...O distance of 2.42 Å found for the (Me₂SO)₂H⁺ species present in [(Me₂SO)₂H][RhCl₄(MeSO)₂].¹⁰

A preliminary investigation of (2tbpo·H)₂CuBr₄ confirms that it is isomorphous with the chloride salt, and also contains very short O—H—O interactions.

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[†] Crystal data for [(PhCH₂)₃PO]₂H₂CuCl₄: *M* = 1488.92, triclinic, space group *P* $\bar{1}$, *a* = 13.398(6), *b* = 14.522(4), *c* = 19.676(7) Å, α = 82.08(3), β = 78.52(3), γ = 87.56(3)° at −130 °C, *U* = 3714(2)°, *D*_c = 1.30 g cm^{−3}, *F*(000) = 1558, μ = 29.8 cm^{−1}. Data were collected out to 2 θ = 110° on a Nicolet R3m diffractometer system, with Cu-K α radiation (λ = 1.5418 Å) and a graphite monochromator.⁵ 9751 unique reflections, with 6509 reflections \geq 3 σ . Empirical absorption corrections, *T*_{min} = 0.545, *T*_{max} = 0.947. The triclinic unit cell and orientation matrix were defined by least-squares refinement of 25 accurately centred high angle (40 < 2 θ < 55°) reflections. Refinement, with anisotropic thermal parameters for the non-hydrogen atoms and rigid body constraints (C—C = 1.38 Å) for all phenyl rings, gave a final value of *R* = 0.0761 and *R*_w = 0.0890 for all observed reflections with intensity greater than 3 σ , where *R* = $\sum ||F_o| - |F_c|| / \sum |F_o|$ and *R*_w = $\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$ and *w* = $[\sigma^2(F_o) + g|F_o|^2]^{-1}$, *g* = 0.00177.⁶ 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.

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