The Structure of Bis-(toluene-*p*-sulphinato)copper(II) Tetrahydrate

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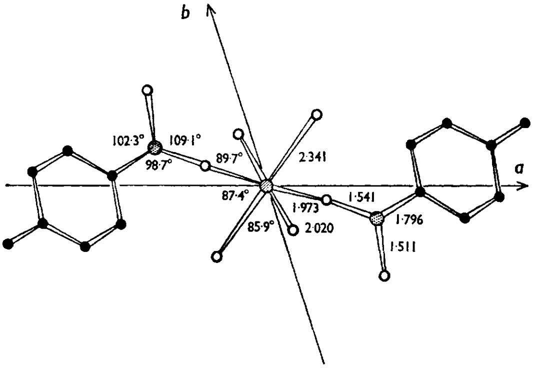
THE visible and infrared spectra of bis-(toluene-*p*-sulphinato)copper(II) tetrahydrate and the dihydrate of bis(benzenesulphinato)copper(II) dihydrate suggest that the copper ion is co-ordinated to the oxygen of the sulphinate. This observation is based on the lowering of the S–O stretching frequency and the typical oxygen-bonded visible absorption band at 12,500 cm.$^{-1}$. Previously, the structure of only one sulphinate salt, Na(HO·CH$_2$-SO$_2$),2H$_2$O, has been determined.[1] In view of the current interest in the binding site of similar ligands such as dimethyl,[2] sulphoxide SO$_3^{2-}$,[3] and SO$_2$,[4] and the lack of structural information on the sulphinates, a complete structural determination of Cu(CH$_3$·C$_6$H$_4$·SO$_2$)$_2$,4H$_2$O was undertaken.

Crystal data: light green, monoclinic prisms, space group $P2_1/b$ (No. 14), $a = 15{\cdot}789$, $b = 11{\cdot}911$, $c = 5{\cdot}086$ Å, $\gamma = 108{\cdot}13°$, $Z = 2$ $D_m = 1{\cdot}635$, $D_c = 1{\cdot}635$. The intensities of 1990 independent reflections were measured using a G.E.C. XRD6 diffractometer. The use of Cu-K_α radiation necessitated that an absorption correction ($\mu = 40{\cdot}8$ cm.$^{-1}$) be applied to the data. The co-ordinates of the sulphur and oxygen atoms were obtained from two-dimensional Fourier synthesis using only the *hk*0 and *h*0*l* reflections, and the carbon atoms were located by three-dimensional Fourier synthesis. The residual was reduced by least-squares refinement including anisotropic temperature factors to 7·7%.



FIGURE

The results of this work show that the sulphinate ligand is monodentate and oxygen bonded to the copper ion in Cu(CH$_3$·C$_6$H$_4$·SO$_2$)$_2$,4H$_2$O. The copper ion occupies the origin of the unit cell (C_i symmetry) and is co-ordinated to six oxygen atoms as shown in the Figure.† The relevant bond distances and angles are also given in the Figure. The ligand field of the copper ion is nearly a tetragonally elongated octahedron. A water molecule and the sulphinate oxygen form the approximate tetragonal plane of the centrosymmetric complex with bond distances† of 2·020 (4) and 1·973 (4) Å,

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† The standard deviations in the bond distances and angles given in the Figure are ±0·004 Å and 0·2°, respectively. In the text the standard deviation of the last significant figure is given in parentheses.

respectively, and the apical position is occupied by a water molecule at 2·347 (4) Å. The water molecules serve the role of both a ligand and a means of joining the $Cu(CH_3\cdot C_6H_4\cdot SO_2)_2,4H_2O$ units together through hydrogen bonding.

The toluenesulphinate group is nonplanar and the bonds about the S atom are disposed in a trigonal pyramidal array. The S–O bond length directed to the copper ion is 1·541(4) Å which is longer than the one which is not [1·511(4) Å]. An increased bond length is consistent with a lowering of the bond order on co-ordination. The C–C bond lengths of the aromatic ring are identical within the estimated standard deviation and are in good agreement with an accepted average value of 1·39 Å. The aromatic carbon atoms 2, 3, 5, and 6 lie in a plane, and carbon atoms 1 and 4 lie 0·036(5) and 0·031(7) Å above this plane, respectively. The methyl carbon atom is 0·207(8) Å above the plane, while the sulphur atom lies 0·137(7) Å below. This distortion can be partially accounted for by the steric interaction of the methyl groups of the sulphinate ligands on neighbouring complexes occurring in the hydrophobic region of the unit cell. This methyl–methyl interaction is 3·86 Å which is the limit of the sum of the van der Waals radii of the methyl group.[5]

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