Tetrakis(triphenylarsine oxide)copper(II) Bis[dichlorocuprate(I)]

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Abstract. [Cu(C₁₆H₁₅AsO)₄]²⁺·2[CuCl₂]⁻, monoclinic, P2₁/c, a = 13.315(2), b = 20.162(4), c = 17.761(2) Å, β = 134.25(3)°, V = 3415(1) Å³, Z = 2, Dₐ = 1.59 (flotation), Dₓ = 1.577 Mg m⁻³. The final R was 0.045 for 3357 observed reflections. The Cuᴵᴵ is coordinated to four O in a square-planar arrangement and the Cuᴵ is coordinated to two Cl in a linear structure.

Introduction. The preparation and the spectral properties of a yellow-brown complex with empirical formula [Cu(tpaso)₂Cl₂] (tpaso = triphenylarsine oxide) have been reported (Goodgame & Cotton, 1961; Rodley, Goodgame & Cotton, 1965). In an attempt to prepare this compound according to the procedure described by Goodgame & Cotton a yellow-brown complex was in fact obtained, but it analysed as 2CuCl₂·3(tpaso). On the other hand, recrystallization of this complex from anhydrous acetone yields blue crystals of a new complex with empirical formula Cu₃Cl₄·4(tpaso). A complex with the same colour and empirical formula was studied by Nyholm (1951) starting from CuCl₂ and methyldiphenylarsine. The complex was formulated as [Cu(mdpaso)₄][CuCl₂]₂, where mdpaso is methyldiphenylarsine oxide, suggesting that copper would be present as Cuᴵ and Cuᴵᴵ. Although this formulation seems plausible and could also apply to the Cu₃Cl₄·4(tpaso) complex it was felt that more conclusive evidence should be obtained concerning the copper coordination. Hence, an X-ray investigation of the latter complex was undertaken to elucidate its structural situation and to confirm the presence of copper in two oxidation states.

A crystal 0.2 × 0.3 × 0.15 mm was mounted at random on an automatic CAD-4 diffractometer. Cell dimensions were determined by a least-squares fit of settings for 25 reflections (±hkI). Intensity measurements were carried out up to θ = 75° using the ω/2θ scan mode and graphite-monochromated Cu Kα radiation. 4345 unique reflections were measured, of which 3357 were considered observed [I > 3σ(I)] and retained for use in the structure analysis.

Lorentz and polarization corrections were applied but no absorption correction [μ(Cu Kα) = 4.02 mm⁻¹] was made.

The structure was solved by application of the multi-solution weighted tangent formula (Germain, Main & Woolfson, 1971) to the reflections with E > 1.70. An E map based on the solution with the highest absolute figure of merit (1.008) and the lowest residual index (25.88) revealed the positions of one Cu and two As atoms.

The remaining non-hydrogen atoms of the organic-ligand molecules were located by successive difference-Fourier calculations. At this point, a difference-Fourier synthesis unambiguously showed the dichlorocuprate ion.

The refinement was by minimization of Σw(kI[Fo] - |Fc|)² through iterative full-matrix least-squares calculations including all data. Weights wᵢ = [σ₀²ᵢ + (0.05Fₐ)²]⁻¹ (where σ₀ᵢ was the variance based on counting statistics) were assigned to observed reflections (wᵢ = 0 for unobserved).

The refinement was conducted until all atomic-parameter shifts were smaller than their standard deviations. The final unweighted R factor omitting unobserved reflections was 0.045, and including them, 0.048.*

Anisotropic temperature factors were assigned to all non-hydrogen atoms. Neutral-atom complex scattering factors were used (International Tables for X-ray Crystallography, 1974). Table 1 gives the heavy-atom coordinates.

* Lists of structure factors, anisotropic thermal parameters and bond distances and angles in the organic-ligand molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35598 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates ($\times 10^5$ for As and Cu, $\times 10^4$ for Cl, O and C) with their e.s.d.'s in parentheses
The $B_{eq}$ values are the equivalent isotropic temperature factors (Hamilton, 1959).

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\begin{array}{cccc}
 x & y & z & B_{eq} (\text{Å}^2) \\
\hline
\text{As(1)} & 11510 (7) & 5075 (5) & 21946 (5) & 2.4 \\
\text{As(2)} & 27997 (7) & 5764 (5) & 6625 (5) & 2.3 \\
\text{Cu(1)} & 0 & 0 & 0 & 2.2 \\
\text{Cu(2)} & 80410 (10) & 16588 (8) & 33116 (9) & 4.5 \\
\text{Cl(1)} & 9579 (2) & 933 (1) & 4212 (2) & 5.2 \\
\text{Cl(2)} & 6499 (3) & 2380 (2) & 2382 (2) & 7.8 \\
\text{O(1)} & 1426 (4) & 277 (3) & 1445 (3) & 2.7 \\
\text{O(2)} & 1271 (4) & 151 (3) & -142 (3) & 2.6 \\
\text{Cl(1)} & 2854 (7) & 924 (5) & 3450 (5) & 3.2 \\
\text{Cl(2)} & 2762 (8) & 1494 (5) & 3841 (6) & 4.0 \\
\text{Cl(3)} & 4010 (9) & 1771 (5) & 4759 (6) & 4.9 \\
\text{Cl(4)} & 5290 (9) & 1493 (5) & 5246 (5) & 4.8 \\
\text{Cl(5)} & 5367 (8) & 922 (6) & 4830 (6) & 4.8 \\
\text{Cl(6)} & 4128 (7) & 625 (5) & 3918 (6) & 3.7 \\
\text{Cl(7)} & -301 (7) & 1172 (4) & 1469 (5) & 2.6 \\
\text{Cl(8)} & -1000 (7) & 1331 (5) & 1773 (6) & 3.7 \\
\text{Cl(9)} & -2035 (8) & 1831 (5) & 1203 (7) & 4.5 \\
\text{Cl(10)} & -2368 (9) & 2134 (5) & 353 (7) & 5.0 \\
\text{Cl(11)} & -1643 (9) & 1965 (5) & 61 (7) & 4.8 \\
\text{Cl(12)} & -598 (8) & 1477 (5) & 626 (6) & 3.7 \\
\text{Cl(13)} & 844 (7) & -254 (4) & 2664 (5) & 2.6 \\
\text{Cl(14)} & 927 (8) & -878 (5) & 2380 (6) & 3.8 \\
\text{Cl(15)} & 734 (10) & -1428 (5) & 2747 (7) & 5.5 \\
\text{Cl(16)} & 459 (9) & -1348 (6) & 3365 (7) & 5.8 \\
\text{Cl(17)} & 402 (8) & -722 (6) & 3645 (6) & 3.2 \\
\text{Cl(18)} & 618 (7) & -165 (5) & 3307 (5) & 3.9 \\
\text{Cl(19)} & 4325 (7) & 75 (4) & 1916 (5) & 2.7 \\
\text{Cl(20)} & 3908 (7) & -555 (4) & 2005 (5) & 3.1 \\
\text{Cl(21)} & 4968 (9) & -935 (5) & 2902 (6) & 4.4 \\
\text{Cl(22)} & 6337 (8) & -674 (5) & 3678 (6) & 4.6 \\
\text{Cl(23)} & 6658 (8) & -34 (6) & 3559 (6) & 4.7 \\
\text{Cl(24)} & 5388 (7) & 344 (5) & 2654 (6) & 3.4 \\
\text{Cl(25)} & 5393 (7) & 681 (4) & -116 (5) & 2.4 \\
\text{Cl(26)} & 3993 (7) & 1252 (5) & 9 (6) & 3.8 \\
\text{Cl(27)} & 4302 (8) & 1320 (6) & -589 (6) & 5.1 \\
\text{Cl(28)} & 3921 (7) & 831 (6) & -1304 (6) & 5.0 \\
\text{Cl(29)} & 3245 (8) & 251 (6) & -1404 (6) & 5.1 \\
\text{Cl(30)} & 2939 (7) & 1873 (5) & 125 (7) & 5.0 \\
\text{Cl(31)} & 1711 (8) & 1365 (6) & 300 (8) & 6.3 \\
\text{Cl(32)} & 1527 (9) & 2515 (6) & 1993 (5) & 4.3 \\
\end{array}
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Discussion. The structure consists of discrete $[\text{Cu}^{II}\text{OAs(C_6H_{13})_4}]^{2+}$ cations and $[\text{Cu}^\text{II}\text{Cl}_2]^{-}$ anions, as can be seen in Fig. 1.

The Cu$^{II}$ ions are located at centres of inversion. Four organic ligands are coordinated to the metal, via oxygen, in a square-planar geometry, according to symmetry conditions. The rings of the organic part are planar within standard deviations. All distances and angles are normal. The most important bond distances and angles are indicated in Fig. 2.

The dichlorocuprate ion is practically linear. The Cu–Cl distance is 2.079 (2) Å for the two bonds and the central angle is 178.65 (8)°.

The occurrence of this kind of ion in the solid state has been definitely established in chloro[dodeca-kis(dimethylamino)cyclohexa(phosphazene)-N1,N2,N4,N5]copper(II) dichlorocuprate(I) where the Cu–Cl bond length is 2.06 (1) Å and the Cl–Cu–Cl angle is 179.5 (9)° (Marsh & Trotter, 1971).

All computer calculations were performed using the Enraf-Nonius structure determination package. The figures were drawn with the ORTEP program (Johnson, 1965).

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Abstract. \([\text{Cu(C}_{18}\text{H}_{15}\text{AsO})_{4}]^{2+}: 2[\text{CuCl}_{2}]^{-}\)  

Cyano[3,3′-(1,3-propanediamino)bis(3-methyl-2-butanone oximato)copper(II)—\(\frac{1}{2}\)-Acetonitrile

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Introduction. The deep-purple crystals (Murmann & Monzyk, 1978) were consistently twinned when grown from aqueous media but gave satisfactory crystals from anhydrous acetonitrile. They crystallize with primarily \{010\}, \{011\}, and \{110\} facial development. The crystal selected was semi-spherical and had a volume of about 0.023 mm\(^3\). The space group and cell dimensions were first determined by precession film data, and the final cell dimensions were obtained with a Picker diffractometer from a least-squares refinement of the setting angles of 18 manually centered reflections. Intensity data were collected for 4094 reflections by the \(θ-2θ\) scan method using Mo \(Kα\) radiation (\(λ = 0.7107 \text{ Å}\)) filtered with Nb. The data were corrected for background, Lp and absorption (\(μ = 1.27 \text{ mm}^{-1}\)).* The transmission factor ranged from 0.89 to 0.73. Standards monitored about every 75 reflections showed no significant systematic variation with time.

The structure was solved by Patterson and Fourier methods. The acetonitrile was revealed by a difference Fourier map and its occupancy factor refined to 0.5. After a few cycles of least-squares refinement with all non-hydrogen atoms present, a difference Fourier map revealed most of the H atoms. When ambiguities occurred, idealized positions for these H atoms were calculated and were found to be consistent with difference Fourier peaks. Refinement was made using anisotropic temperature factors for all non-hydrogen atoms, with fixed H atoms. H atoms on the CH\(_2\)CN molecule were treated as disordered around the twofold axis. Full-matrix refinement minimizing \(Σ_{} w(F_2^2 - F_0^2)^2\), using 2600 independent reflections, 213 variables, scattering factors of Cromer & Waber (1962), and anomalous scattering for Cu (Cromer, 1962), gave

References
