X-Ray Crystallographic Determination of the Infinite, Helical, Polymeric Structure Formed from Acetylacetonato(trichloroacetato)copper(II) Chemical Units

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Summary The infinite, left-handed, helical structure of catena-μ-trichloroacetato-acetylacetonatocopper(II) has been determined by *X*-ray methods: each copper atom is surrounded by six oxygen atoms; two from a bidentate acetylacetonato-ligand, two from separate trichloroacetato-ligands which bridge to neighbouring copper atoms in the spiral, and two which are atoms of ligands bidentate to these neighbouring copper atoms.

AN addition complex, formed when copper acetylacetonate is added to an excess of trichloroacetic acid, has been found to act as a catalyst in initiating the graft copolymerization of acrylonitrile inside wool fibre.[1] As a possible aid to understanding the mechanism of polymerization, we have carried out an *X*-ray structure analysis of the catalyst complex.

The predominant compound, in catalyst samples supplied by the Wool Research Organization of New Zealand, had crystallized as long, fibrous, blue-green needles of hexagonal habit. The hexagonal crystal system was confirmed with unit cell constants $a = 11{\cdot}143(2)$ and $c = 17{\cdot}917(4)$ Å, and conditions limiting possible reflections were consistent with the enantiomorphous pair of space groups $P6_1$ and $P6_5$. Single crystals, more suitable for *X*-ray intensity measurements, were prepared by recrystallization from dichloromethane, and from benzene, and also by direct synthesis in this laboratory. Calculated and measured densities (1·68 g/cm^3) were consistent with six $[Cu(C_5H_8O_2)(Cl_3CCO_2)]$ chemical units in the crystallographic unit cell. This study shows that the compound is properly described by the name catena-μ-trichloroacetato-acetylacetonatocopper(II).

Intensity data were collected on a Hilger and Watts 4-circle automatic diffractometer using nickel-filtered Cu-K_α *X*-radiation. Two equivalent forms of both *hkl* and the corresponding non-equivalent $\bar{h}\bar{k}\bar{l}$ reflections, were collected at room temperature (25°) up to a maximum Bragg angle of 40°. These yielded the 731 unique intensities, greater than their estimated standard deviations based on counting statistics, which were used for this analysis.

Co-ordinates of the copper atom were readily obtained by inspection of Harker sections from three-dimensional Patterson calculations. The remaining 14 non-hydrogen atoms were obtained with difficulty using difference Fourier techniques. Ultimately, all atoms were refined by full-matrix least-squares procedures until the conventional agreement factor $R = 8{\cdot}0\%$ for a completely anisotropic model in space group $P6_5$. In $P6_1$ refinement converged to the significantly higher value of $R = 8{\cdot}3\%$.[2]

The Figure shows the polymer coiled around the six-fold screw axis. There is a 3 Å pitch between adjacent symmetry related atoms. The helical axes are 11·14 Å apart so that closest contact between the infinite chains is 3·7 Å [Cl(1) to Cl(3)]. The terminal chlorine atoms undergo extreme anisotropic thermal vibrations in this empty region of crystal space. This structural feature, which hindered the *X*-ray analysis, may increase the known potential of trichloroacetate groups to yield ions and free radicals. Fragments such as CCl_3^- have been mentioned in discussions of the catalysis mechanism.[3]

One section of the helix has been enlarged to show important details of the environment around each copper atom. The acetylacetonate ligand, the central copper atom, and the oxygen atoms of the two bridging trichloroacetato-ligands are approximately coplanar. The Cu–O bond lengths in this plane presently range from 1·85—1·94 Å but co-ordination about the copper atom can be considered distorted octahedral since the Cu–O distances to oxygen atoms of acetylacetonato-ligands above and below this plane indicate further bonding interactions. The normal to the approximate plane is tilted 22° from the 6-fold screw axis. Cu · · · Cu distances are 3·19 Å.

Strong bonding along the helix combined with very weak van der Waals attractions between helices is consistent with the extreme fibrous nature of the crystals. Provided the helices persist in solution they are potentially large catalytic surfaces or sources of CCl_3^- fragments.

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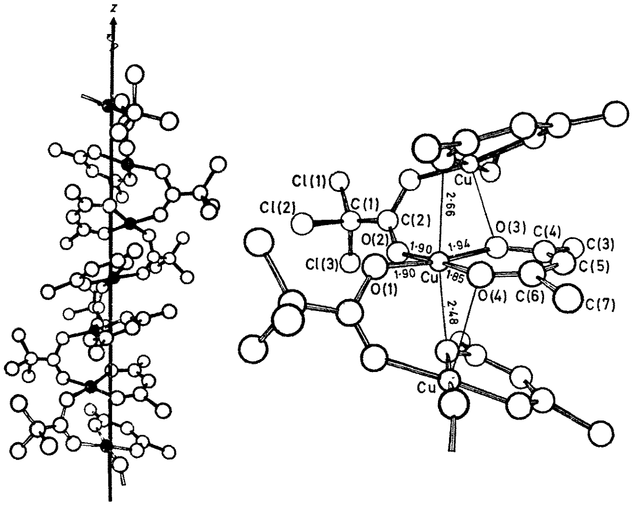

FIGURE. *Catena-μ-trichloroacetato-acetylacetonatocopper*(II).

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