X-Ray Crystal and Molecular Structure of the Adduct of Mercury(II) Chloride with Dehydrodithizone

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Summary The structure of the 1:1 adduct formed between mercury(II) chloride and dehydrodithizone has been shown, by a single crystal *X*-ray diffraction study, to be a sulphur bridged polymer containing five-co-ordinate mercury atoms.

MERCURY(II) can form complexes in which the co-ordination number of the mercury atom can assume any value from 2 to 6. In complexes of mercury(II) chloride, the co-ordination polyhedron around the mercury atom is usually a distorted octahedron in which the linear structure of the

$HgCl_2$ molecule is retained.[1] Elemental analyses on the product of the reaction between $HgCl_2$ and dehydrodithizone,[2] have proved that its empirical formula was $C_{13}H_{10}N_4S{\cdot}HgCl_2$. Thus, either an addition or a substitution reaction had occurred to form an adduct or a substitution compound of the type $C_{13}H_{10}N_4S{\cdot}HgCl^+Cl^-$. In view of the variety of structures that have been reported for the products of the reaction between mercury(II) chloride and ligands containing sulphur donor atoms, a structure determination of the complex was undertaken.

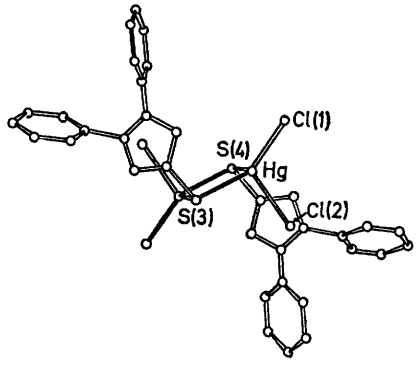

FIGURE 1. *A perspective view of two units of the molecule,* $C_{13}H_{10}N_4S{\cdot}HgCl_2$.

The addition of an aqueous solution of mercury(II) chloride to dehydrodithizone in ethanol and slow evaporation gave a 1:1 adduct. Pale yellow, needle-shaped, monoclinic crystals of the adduct were obtained from acetone. Space group $C2$, $a = 25{\cdot}717(10)$, $b = 6{\cdot}476(6)$, $c = 11{\cdot}476(8)$ Å, $\beta = 102{\cdot}79(3)°$, $U = 1864{\cdot}0$ Å^3, $D_m = 1{\cdot}97 \pm 0{\cdot}05$ g cm^{-3} (by the density gradient method), $D_c = 1{\cdot}89$ g cm^{-3}. The unit cell contained four units with the formula, $C_{13}H_{10}N_4S{\cdot}HgCl_2$. Intensity data were collected on a Picker FACS I diffractometer equipped with a graphite monochromator and Mo-K_α radiation ($\lambda = 0{\cdot}70962$ Å). Approximately 1430 reflections were collected out to $2\theta = 45°$, and 1134 reflections which had intensities $> 3\sigma$ were used for the structure determination. The measured intensities were corrected for Lorentz and polarization effects and also for absorption and anomalous scattering by the Hg, S, and Cl atoms. The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares technique in which the phenyl groups were treated as rigid bodies. Anisotropic temperature factors were used for the Hg, S, and Cl atoms, and isotropic temperature factors were used for the rest of the atoms. After the last refinement cycle, the conventional value of R that was obtained was 6·2%.

The complex is an adduct of mercury(II) chloride and dehydrodithizone and is a sulphur bridged polymer. A perspective view of two units of the polymer is shown in Figure 1. The co-ordination polyhedron around the mercury atom is a trigonal bipyramid and is shown in Figure 2.

Each mercury atom is co-ordinated to three sulphur atoms and two chlorine atoms. The equatorial plane of the trigonal bipyramid contains the mercury atom, the two chlorine atoms and one sulphur atom. The longer Hg–Cl distance may be attributed to the location of the Cl(1) atom between two tetrazole rings with residual positive charges.[2] The two sulphur atoms that are at the apices of the bipyramid are equidistant from the mercury atom. These two long Hg–S bonds are perpendicular to the plane of the trigonal bipyramid. The sulphur–carbon distance is 1·68 Å and is essentially the same as that found in dehydrodithizone.[2] The rest of the distances in the dehydrodithizone moiety are the same as the values reported previously.[2]

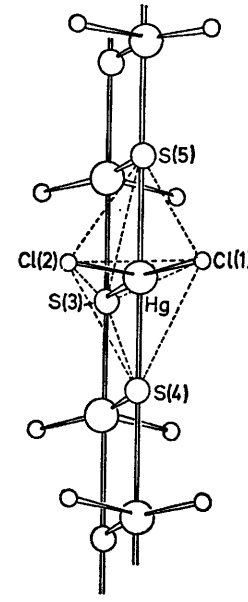

FIGURE 2. *The infinite chains of alternating mercury and sulphur atoms and the co-ordination polyhedron around the mercury atom.* Hg–Cl(1) = 2·35(1), Hg–Cl(2) = 2·56(1), Hg–S(3) = 2·40(1), *and* Hg–S(4) = Hg–S(5) = 3·24(1) Å; Cl(1)–Hg–Cl(2) = 111·4(4), Cl(2)–Hg–S(3) = 96·5(3), and S(3)–Hg–Cl(1) = 152·0(3)°.

The polymeric structure therefore, consists of two parallel infinite chains of alternating mercury and sulphur atoms. The two chains are 2·40 Å apart and are parallel to the crystallographic b-axis. There are two types of sulphur bridges in the structure: a long bridge in which the sulphur and mercury atoms are collinear, S(4)–Hg–S(5), and a much shorter bridge in which the Hg–S distance is 2·40 Å and the S–Hg–S angle is 90°. The structure of mercury t-butyl mercaptide[3] was also found to be a sulphur bridged polymer but the mercury atoms were tetrahedral and the S–Hg–S angle in the sulphur bridge was approximately 90°.

We thank Dr. L. L. Reed for assistance in the initial stages of this work.

(*Received, 20th March* 1972; *Com.* 456.)

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