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CRYSTAL STRUCTURE OF DICHLORO-TETRAKIS(DIETHYLDITHIOCARBAMATO)-TRIMERCURY, $Hg_3Cl_2(S_2CNEt_2)_4$

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The reaction of mercury dichloride with sodium diethyldithiocarbamate gave triclinic crystals of the title compound in addition to two monoclinic forms of mercury diethyldithiocarbamate. An X-ray investigation has revealed that the mercury atoms are linked together by bridging carbamate groups and chlorine atoms to form an infinite linear chain.

Polymorphism of mercury diethyldithiocarbamate was observed in the course of a series of X-ray studies of dithioacid compounds of heavy metals. Mercury dichloride ($HgCl_2$) and sodium diethyldithiocarbamate (NaS_2CNEt_2) were mixed in an aqueous solution, and yellowish fine powder was precipitated. By recrystallization from acetone, three different kinds of crystals, named α-, β- and γ-forms respectively, were obtained from the same solution.[1] The crystal structures of α- and β-forms have already been determined, and the α-form consists of dimeric molecules of tetrakis(diethyldithiocarbamato)dimercury whereas the β-form has isolated monomeric units of bis(diethyldithiocarbamato)mercury.[2] This paper reports the structure of the γ-form.

The structure analysis of the γ-form revealed that the crystal contained chlorine atoms, and corresponded to the title compound, which were later confirmed by chemical analysis (found: S 20.15, Cl 5.55, N 4.41 %; calcd. for $Hg_3Cl_2S_8N_4C_{20}H_{40}$: S 20.27, Cl 5.60, N 4.43 %). Existence of chlorine atoms was rather unexpected, since so many metal-diethyldithiocarbamates had been prepared so far in a similar way from sodium carbamate and metal chloride.

The lattice constants were obtained from Weissenberg photographs using Straumanis type cassette, taken with the CuKα radiation ($\lambda(K\alpha_1)$=1.54051 Å).

Crystal data: $Hg_3Cl_2(S_2CN(C_2H_5)_2)_4$, M.W.=1265.8; triclinic needles (elongated along the c-axis), pale-yellow in color and transparent; space group $P\bar{1}$; a=18.562 (2), b=10.157 (8), c=11.012 (4) Å, α=113.06 (5), β=97.06 (2), γ=91.24 (3) °, V=1890.2 (1.5) A^3; D_o=2.2 $g.cm^{-3}$, D_x=2.223 $g.cm^{-3}$, Z=2.

The intensities were measured with an equi-inclination type automatic diffractometer, around the c-axis up to the 14th layer. MoKα radiation was used with a graphite monochromator. About 3550 independent reflections were obtained. The structure was solved by Patterson and Fourier techniques. At the present stage the conventional R factor is 0.069, and the refinement is still in progress.

Mercury atoms are linked together by bridging carbamate ligands and chlorine atoms to form an infinite linear chain, as schematically shown in Fig. 1. The chains are arranged spirally along the c-axis, and the dipole possessed by a chain is compensated by that on its neighboring chain. The Hg-S bond distances range from 2.41 to 2.60 Å, while the Hg-Cl bonds are about 2.7 Å and not so strong. Two Hg-Cl-Hg bond angles are around 90°. Since four independent Hg-Cl distances are almost equal in length, it is inadequate to describe this substance as a simple addition compound between mercury dichloride and dimeric mercury diethyldithiocarbamate.

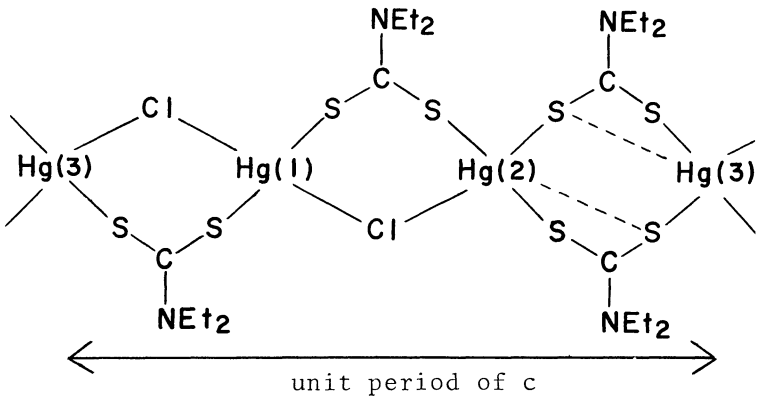

Fig. 1.

The coordination polyhedron around each mercury atom is a distorted tetrahedron. As is seen in Fig. 1, the polymeric chain contains eight membered rings comprised of Hg(2), Hg(3), four sulphur and two carbon atoms. Within the ring, there are relatively short Hg---S contacts of about 3.16 Å as shown with dotted lines. Therefore, Hg(2) and Hg(3) atoms can also be regarded as five-coordinate. These features are remarkably similar to those found in the molecular structure of the dimeric form of mercury diethyldithiocarbamate.[2)]

As for the Hg(1) atom, two Hg-S bonds are about 2.41 Å, and the S-Hg-S bond angle is 155°, showing a linear bicovalent character to some extent. This situation can be compared with the molecular structure of monomeric mercury diethyldithiocarbamate, which involves a strong linear S-Hg-S bond with Hg-S distances of 2.40 Å and a weak S-Hg-S bond with 2.96 Å.

A detailed discussion on this structure and polymorphism in mercury diethyldithiocarbamate will appear elsewhere.

References

1) H. Iwasaki, Paper read at the 26th Annual Meeting of the Chemical Society of Japan, Hiratsuka, April 1972.
2) H. Iwasaki, Paper read at the 9th International Congress of Crystallography, Kyoto, September 1972; Abstract in Acta Cryst., A28, S85 (1972).

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