APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 141–142
DOI:10.1002/aoc.391

Crystallographic report

Chloro(*N,N*-diethyldithiocarbamato)(4,7-dimethyl-1,10-phenanthroline)mercury(II) hemi-chloroform solvate

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Received 21 August 2002; Revised 30 August 2002; Accepted 25 September 2002

The X-ray crystal structure of Hg(S_2CNEt_2)(4,7-Me_2-phen)Cl features an essentially four-coordinate geometry for mercury within a ClN_2S donor set that defines a distorted tetrahedral arrangement.

KEYWORDS: crystal structure; mercury; dithiocarbamate; imine adduct

COMMENT

A motivation for preparing adducts of the zinc-triad 1,1-dithiolates is the disruption of the often observed polymeric arrays[1] to yield smaller aggregates as precursors for the chemical vapour deposition of, for example, ZnS.[2] In this connection we have explored the adduct chemistry of zinc[3] and cadmium[4] 1,1-dithiolates. It appears that the analogous chemistry with mercury is not straightforward, as revealed in the present study and consistent with an earlier report.[5] The reaction between an authenticated sample of Hg(S_2CNEt_2)$_2$ and 4,7-Me_2-phen in chloroform solution resulted in the deposition of crystals that were characterized crystallographically (see below) as Hg(S_2CNEt_2)(4,7-Me_2-phen)Cl (**I**, Fig. 1). The product presumably arises from the loss of one dithiocarbamate ligand and chloride extraction from the solvent. The mercury atom exists in a ClN_2S donor set that defines a highly distorted tetrahedral geometry with a range of angles from 66.18(12)°, i.e. the chelate angle, to 149.74(5)° for S(1)—Hg—Cl. There is a close intramolecular Hg···S(2) interaction of 3.0138(12) Å of note.

CRYSTALLOGRAPHY

Bright-yellow crystals were obtained from the slow evaporation of an acetonitrile–chloroform solution of a solid that had precipitated from the refluxing (1 h) of equimolar amounts of Hg(S_2CNEt_2)$_2$ and 4,7-Me_2-phen in chloroform solution; m.p. 127–129 °C. IR (KBr, cm^{-1}): ν(C—S) 985, 1072 and ν(C—N) 1424. Intensity data for **I** were collected at 183 K on a Bruker AXS SMART CCD diffractometer for a block $0.08 \times 0.08 \times 0.21\ mm^3$. $C_{19}H_{22}ClHgN_3S_2 \cdot 0.5\ CHCl_3$, M = 652.2, monoclinic, $C2/c$, a = 19.7145(15), b = 10.5893(8), c = 24.0361(18) Å, β = 114.076(2)°, V = 4581.3(6) Å^3, Z = 8, 6619 unique data (θ_{max} 30.0°), R = 0.073 (all data), wR =

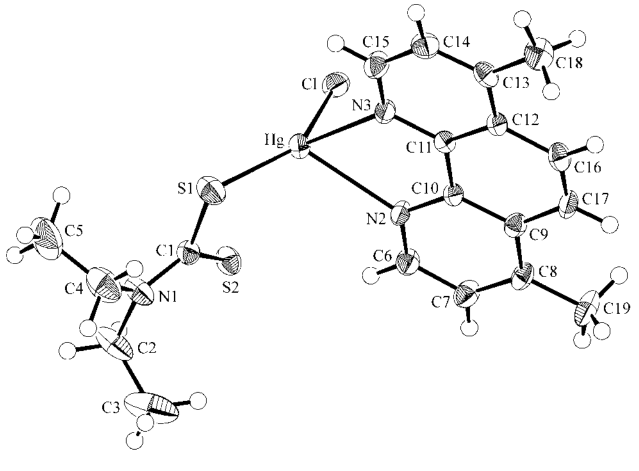

Figure 1. Molecular structure of **I**. Key geometric parameters: Hg—S(1) 2.4102(13), Hg···S(2) 3.0138(12), Hg—Cl 2.4243(13), Hg—N(2) 2.465(4), Hg—N(3) 2.511(4), S(1)—C(1) 1.746(5), S(2)—C(1) 1.696(5), C(1)—N(1) 1.323(6) Å; S(1)—Hg—Cl 149.74(5), S(1)—Hg—N(2) 115.41(9), S(1)—Hg—N(3) 104.41(9), Cl—Hg—N(2) 90.37(9), Cl—Hg—N(3) 100.32(9), N(2)—Hg—N(3) 66.18(12)°.

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Contract/grant sponsor: National University of Singapore; Contract/grant number: R-143-000-151-112.

0.091 (all data), $\rho_{max} = 1.91\ e^- \ Å^{-3}$ (near Hg). A disordered molecule of $CHCl_3$ was modelled (0.5 weight for C and 0.375 for each of four Cl atoms) situated around a crystallographic twofold axis with isotropic displacement parameters. Programs used: teXsan, DIRDIF, SHELXL, and ORTEP. CCDC deposition number: 191092.

Acknowledgement

The National University of Singapore is thanked for support (R-143-000-151-112).

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