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Crystallographic report

Bis(pyrrolinedithiocarbamato)mercury(II)

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The mononuclear structure of $Hg(S_2CN(CH_2)_4)_2$ has crystallographically imposed twofold symmetry and features chelating dithiocarbamate ligands that form asymmetric Hg—S bond distances leading to a heavily distorted tetrahedral geometry. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; mercury; dithiocarbamate

COMMENT

Five distinct structural motifs are known for the mercury(II) bis-dithiocarbamates, $Hg(S_2CNR_2)_2$, ranging from isolated mononuclear entities to dinuclear oligomers and two-dimensional arrays.[1,2] The X-ray structure of the title compound, $Hg(S_2CN(CH_2)_4)_2$ (**I**), a known species (e.g. see Ref. 3), was determined as a part of a systematic evaluation of such structures. Direct reaction of ammonium pyrrolidinedithiocarbamate with mercury(II) salts inevitably resulted in the formation of an insoluble precipitate. Crystals (see below) of **I** were isolated from an acetonitrile/chloroform (1/1) solution containing equimolar amounts of $Hg(S_2CNEt_2)_2$ and $Zn(S_2CN(CH_2)_4)_2$,[4] evidently via ligand exchange. The mercury atom in **I** is situated on a crystallographic twofold axis of symmetry and is coordinated by two anisobidentate dithiocarbamate ligands forming distinct Hg—S(1), S(2) bond distances of 2.4015(14) Å and 2.7840(13) Å, respectively. There are considerable distortions from the ideal tetrahedral geometry, as seen in the range of angles about mercury from 69.89(4)°, i.e. the chelate angle, to 160.79(8)°, i.e. involving the more strongly bound S(1) atoms. The structure reported here has four precedents in the literature, namely $Hg(S_2CN^iPr_2)_2$,[5] $Hg(S_2CN^iBu_2)_2$,[2] Hg $(S_2CN(^iPr)Cy)_2$,[2] and $Hg(S_2CNCy)_2$.[6]

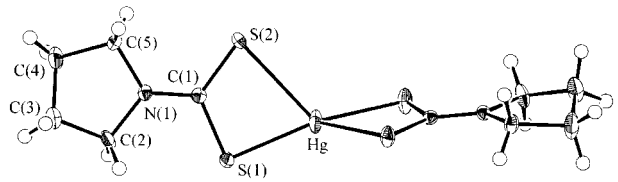

Figure 1. Molecular structure of **I**. Key geometric parameters: Hg—S(1) 2.4015(14), Hg—S(2) 2.7840(13), S(1)—C(1) 1.745(5), S(2)—C(1) 1.697(5), C(1)—N(1) 1.328(6) Å; S(1)—Hg—S(2) 69.89(4), S(1)—Hg—S(1)^i 160.69(8), S(1)—Hg—S(2)^i 121.47(5), S(2)—Hg—S(2)^i 115.78(6)°. Symmetry operation *i*: $-x$, y, $1/2-z$.

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CRYSTALLOGRAPHY

Crystals were isolated from an acetonitrile/chloroform (1/1) solution containing equimolar amounts of $Hg(S_2CNEt_2)_2$ and $Zn(S_2CN(CH_2)_4)_2$;[4] m.p. 235–239 °C. IR (KBr): ν(C—S) 991 and ν(C—N) 1439 cm^{-1}. Intensity data for **I** were collected at 183 K on a Bruker AXS SMART CCD diffractometer for a yellow needle $0.07 \times 0.10 \times 0.47$ mm^3. $C_{10}H_{16}HgN_2S_4$, M = 493.1, monoclinic, $C2/c$, a = 18.5533(16), b = 8.3322(7), c = 11.1692(10) Å, β = 122.542(1)°, V = 1455.6(2) Å^3, Z = 4, 2115 unique data (θ_{max} 30.0°), R = 0.054 (all data), wR = 0.126 (all data), ρ_{max} = 3.61 e$^-$ Å^{-3} (near Hg). Programs used: teXsan, DIRDIF, SHELXL, and ORTEP. CCDC deposition number: 191094.

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REFERENCES

1. Cox MJ, Tiekink ERT. *Rev. Inorg. Chem.* 1997; **17**: 1.
2. Cox MJ, Tiekink ERT. *Z. Kristallogr.* 1999; **214**: 571.
3. Cavalheiro ETG, Ionashiro M, Marino G, Breviglieri ST, Chierice GO. *Transition Met. Chem.* 2000; **25**: 69.
4. Jie Q, Tiekink ERT. *Main Group Met. Chem.* 2002; **25**: 317.
5. Ito M, Iwasaki H. *Acta Crystallogr. Sect. B* 1979; **35**: 2720.
6. Cox MJ, Tiekink ERT. *Main Group Met. Chem.* 2000; **23**: 793.