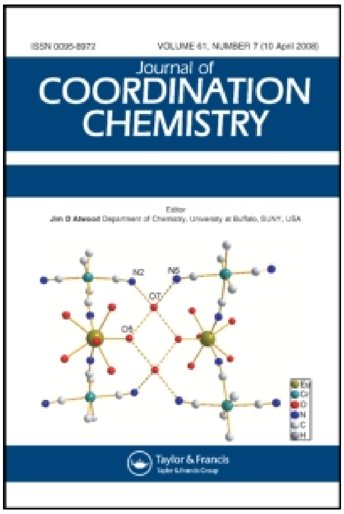

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The Crystal and Molecular Structure of Methyl(Cyclopentanone-Thiosemicarbazonato)Mercury(II)

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THE CRYSTAL AND MOLECULAR STRUCTURE OF METHYL(CYCLOPENTANONE-THIOSEMICARBAZONATO)MERCURY(II)

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The crystal structure of HgMe(L) (L = Cyclopentanonethiosemicarbazonato) has been determined. The compound, which crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.973(2)$, $b = 15.247(3)$, $c = 7.511(2)$ Å, $\beta = 101.90(2)°$, and $Z = 4$ ($R = 0.040$, $R' = 0.041$), is formed from molecules in which the thiosemicarbazonato anion forms a bond with mercury with the sulphur atom as well as a particularly strong secondary bond with nitrogen N(1). Molecules in the unit cell pack in pairs through weak hydrogen bonds.

Keywords: Mercury(II), methylmercury(II), cyclopentanonethiosemicarbazone, X-ray structure

INTRODUCTION

The coordination chemistry of dimethylthallium(III) ($TlMe_2$) and methylmercury(II) (HgMe) ions with the anion derived from cyclopentanonethiosemicarbazone (L^-) has already been compared in a previous paper.[1] From a structure determination of $TlMe_2(L).HL$ by X-ray diffraction, it was observed that the L^- anion coordinates to the metal *via* S and one of its N atoms, whereas the HL molecule weakly interacts with thallium through the S, and with L^- *via* hydrogen bonds.[1] Spectroscopic analysis of the compound HgMe(L) suggested a number of analogies between it and the thallium complex concerning the coordination of the thiosemicarbazonato ligand.[1] The solution of the structure of HgMe(L) has confirmed this and has demonstrated the presence of a rather strong secondary[2] nitrogen–mercury bond.

EXPERIMENTAL

Synthesis of HgMe(L) was as previously reported.[1] Crystals suitable for X-ray diffraction measurements were isolated in one of the syntheses on cooling the appropriate organic solution.

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Determination of the Crystal Structure of HgMe(L)

A colourless crystal of approximate dimensions 0.08 × 0.24 × 0.32 mm was selected for the X-ray analysis.

Crystal data

$C_7H_{13}HgN_3S$, $M = 371.86$, monoclinic, $a = 8.973(2)$, $b = 15.247(3)$, $c = 7.511(2)$ Å, $\beta = 101.90(2)°$, $U = 1005.5(8)$ Å^3, (by least-squares refinement of the setting angles of 25 reflections, $\lambda = 0.71069$ Å), space group $P2_1/c$, $Z = 4$, $D_c = 2.456$ g cm^{-3}, $F(000) = 688$, μ(Mo-Kα) $= 154.59$ cm^{-1}.

Data collection and structure analysis

Data were obtained at room temperature using a CAD-4 diffractometer, ω/θ scan mode with scan width $= 0.85 + 0.35 \tan\theta$ and scan speed 2.7–6.8° min^{-1}; graphite-monochromated Mo–Kα radiation; 2461 reflections measured ($3 \leq \theta \leq 30°$, $-12 < h < 12$, $0 < k < 21$, $0 < l < 9$); 2307 unique (merging $R = 0.02$), giving 1519 with $I > 3\sigma(I)$. Absorption corrections were applied at a later stage in the refinement[3] (max. and min. transmission factors = 1.55, 0.77). Heavy atom methods (Hg atom) followed by subsequent Fourier difference techniques were used. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic[4] and hydrogens at fixed positions with one, overall refined U_{iso} [$=0.04(1)$ Å^2] was employed. Final $R\,[=\Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ and $R'\,\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}, w = [\sigma^2(F_o) + 0.00085F_o^{\,2}]^{-1}\}$ values were 0.040 and 0.041, respectively. Scattering factors and anomalous dispersion corrections were taken from ref. 5. Calculations were performed on a DECMICRO VAX II computer. Positional parameters are given in Table I. Additional material including thermal parameters, bond lengths and angles and observed and calculated structure factors are available from J.S.C.

TABLE I

Final atomic positional coordinates with e.s.d.s. in parentheses for HgMe(L).

Atom	*x/a*	*y/b*	*z/c*
Hg	0.1769(1)	0.3731(1)	0.6718(1)
S	0.0288(4)	0.3203(2)	0.3926(4)
N(1)	0.1874(9)	0.4937(5)	0.442(1)
N(2)	0.091(1)	0.4854(5)	0.273(1)
N(3)	−0.076(1)	0.3958(6)	0.087(1)
C(1)	0.021(1)	0.4106(7)	0.247(2)
C(2)	0.270(1)	0.5611(6)	0.466(2)
C(3)	0.385(1)	0.5782(7)	0.642(2)
C(4)	0.493(1)	0.6476(7)	0.582(2)
C(5)	0.385(2)	0.7020(7)	0.445(2)
C(6)	0.272(2)	0.6350(7)	0.332(2)
C(7)	0.308(2)	0.3912(9)	0.933(2)

RESULTS AND DISCUSSION

The structure of the complex HgMe(L) is shown in Figure 1 with the atomic numbering scheme. The most significant bond distances and angles are given in Table II. The mercury is coordinated by the methyl carbon and by the ligand S and N(1) atoms, giving rise to a distorted T-shaped stereochemistry around the metal. The Hg–C(7) distance (2.09(1) Å) is at the upper limit of the accepted range[2] for an unperturbed mercury–carbon bond (2.05–2.09 Å). The Hg–S bond length (2.380(3) Å), although within the range of values for truly two-coordinate Hg atoms,[6] is slightly longer than is observed for methylmercury compounds with very weak Hg–N secondary bonds.[7,8] The Hg–N bond (2.537(8) Å), even though much longer than a covalent bond[9] (approx. 2.1 Å) or the bonds observed in neutral methylmercury compounds whose main bond is mercury–nitrogen,[10] is rather short when compared with the usual lengths of so-called secondary bonds.[2] The importance of this bond is also suggested by the obvious non-linearity (167.7°) of the S–Hg–C(7) angle, suggesting that the mercury *sp* hybridization changes to accommodate the bond with nitrogen. Coordination is similar when the ligand is the dithizonato[6] ion, although the Hg–N bond is slightly longer in this case.

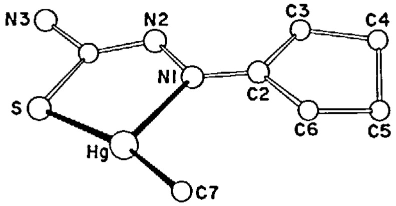

FIGURE 1 View of the structure of HgMe(L) with the atomic numbering scheme.

TABLE II

Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for HgMe(L).

Hg-S	2.380(3)
Hg-N(1)	2.537(8)
Hg-C(7)	2.09(1)
S-C(1)	1.75(1)
N(1)-N(2)	1.39(1)
N(1)-C(2)	1.26(1)
N(2)-C(1)	1.30(1)
N(3)-C(1)	1.35(1)
S-Hg-N(1)	74.8(2)
S-Hg-C(7)	167.7(4)
N(1)-Hg-C(7)	116.8(4)
Hg-S-C(1)	103.2(4)
Hg-N(1)-N(2)	116.9(6)
Hg-N(1)-C(2)	126.7(7)
N(2)-N(1)-C(2)	116.3(9)
N(1)-N(2)-C(1)	114.2(9)
S-C(1)-N(2)	129.9(9)
S-C(1)-N(3)	111.1(8)
N(2)-C(1)-N(3)	119(1)
N(1)-C(2)-C(3)	122.6(9)
N(1)-C(2)-C(6)	127(1)
C(3)-C(2)-C(6)	110.6(9)

As in $TlMe_2(L).HL$,[1] the ligand adopts a *Z* configuration about the C(1)–N(2) bond. The thiosemicarbazone fragment (N(3)–C(1)(S)–N(2)–N(1)) is planar (χ^2 = 0), while the Hg atom lies 0.309(0) Å outside this plane. In common with the dimethylthallium compound, the C(1)–S bond also lengthens, while the C(1)–N(2) distance is reduced, as compared to these bonds in the HL molecule. The cyclopentanone ring make an angle of 13(1)° with the plane defined by N(1), C(1) and S. The five-membered chelate rings (Fig. 2) of the $TlMe_2$ and HgMe complexes are surprisingly similar, the bond angles not differing by more than 4°. With regard to the lengths of the M–S and M–N(1) bonds that close the ring, there are some differences however. The mercury–sulphur bond is considerably shorter than the thallium–sulphur (by about 0.25 Å), while, although the metal–nitrogen bond seems shorter in the mercury derivative as compared to the thallium compound, the difference lies within the standard errors obtained. With these data it is difficult to compare the characteristics of these bonds in the compounds, since the smaller covalent (and also van der Waals[2,11]) radius[9] of mercury (1.30 Å) as compared with thallium and the imprecise estimation of the covalent radius of the latter[12] (1.45–1.55 Å), complicates the analysis.

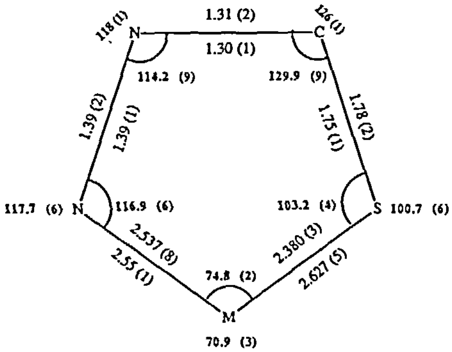

FIGURE 2 Structure parameters of the HgMe(L) chelate rings (data inside the pentagonal ring) and $TlMe_2(L).HL$ (data outside the pentagonal ring). Bond lengths (light type) are in Å and bond angles (in heavy type) are given in degrees.

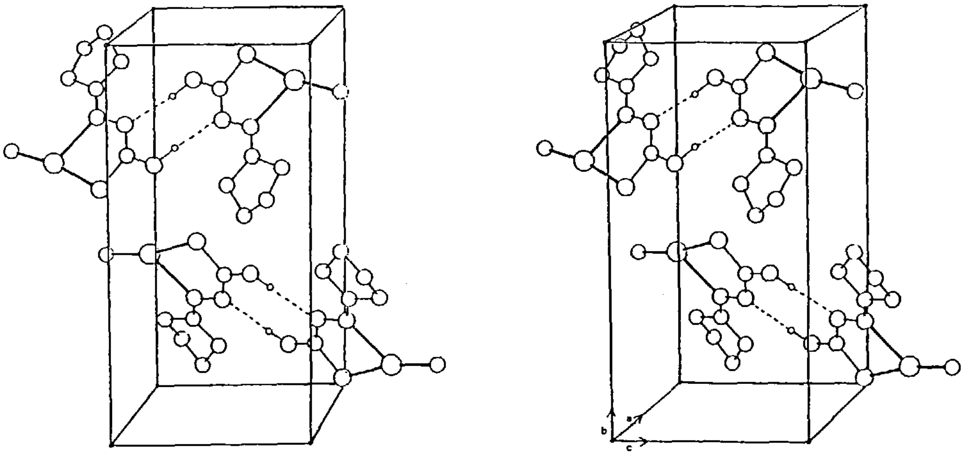

FIGURE 3 Stereoview of the packing arrangement of HgMe(L) units within the unit cell, showing proposed hydrogen bonds.

The molecular packing is shown in Figure 3. The distance N(3)...N(2)* (3.23(1) Å), where N(2)* is generated by the symmetry operation $(-x, 1-y, -z)$, is of the order of that separating N(1) and N(6) in $TlMe_2(L).HL$.[1] This suggests that the presence of two hydrogen bonds between neighbouring molecules determines the final packing arrangement.

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