Synthetic, Spectroscopic, and *X*-Ray Studies on Methylmercury(II) and Dimethylthallium(III) Complexes with Cyclopentanone Thiosemicarbazone†

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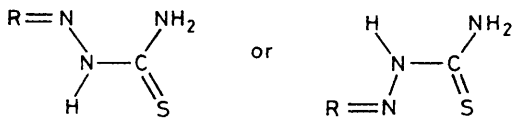
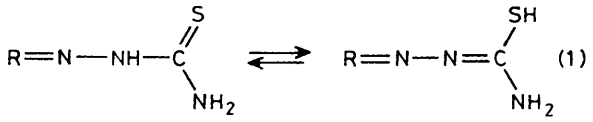
Compounds of cyclopentanone thiosemicarbazone (HL) have been prepared from methylmercury(II) chloride or dimethylthallium(III) hydroxide. The crystal structure of $TlMe_2(L)\cdot HL$ has been determined. The compound crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with a = 12.088(4), b = 13.656(3), c = 13.271(4) Å, β = 108.68(2)°, and Z = 4 (R = 0.069, R' = 0.076). Two different types of ligand molecules are present in the lattice. One, L, deprotonated and chelated to Tl and the other one, HL, weakly bonded to Tl and hydrogen bonded to L. The i.r., ^1H and ^{13}C n.m.r. spectra of the compounds are discussed in the light of the crystallographic data.

The co-ordination chemistry of thiosemicarbazones (HL) has been explored as regards the transition metals[1,2] but much less attention has been paid to the elements of the main groups.[3] In the solid state, thiosemicarbazones adopt a configuration in which the sulphur atom is *trans* with respect to the R=N nitrogen atom (configuration *E* about the N–C bond; see ref. 4 and references therein). They may therefore be represented as shown though other canonical forms in which the π charge is



redistributed must also be considered in order to obtain a realistic idea of the system.[5] In solution, they probably exist as an equilibrium mixture of tautomers [equation (1)]. The



(1)

predominant form in basic media is the deprotonated thiol. Both forms can act as bidentate ligands *via* the S and R=N nitrogen atoms, and more rarely, as unidentate ligands *via* the sulphur atom. The formation of chelates necessarily involves a configurational change from *E* to *Z*.[1]

The present study was undertaken to compare the properties of the above two co-ordination modes of cyclopentanone thiosemicarbazone (HL) in complexes with 'soft' cations such as MMe_n^+ (n = 1 or 2, M = Hg or Tl respectively), in which the thiosemicarbazone was expected to be present in deprotonated thiol form. In the case of HgMe(L), unidentate co-ordination *via* the sulphur atom was expected, possibly together with weak secondary bonds involving the R=N nitrogen atom,[6] whereas it was thought that TlR_2 compounds would form N,S-bidentate chelates.[7] Unexpectedly, a $Tl^{III}Me_2$ complex was isolated in which there were two molecules of cyclopentanone thiosemicarbazone, one of which was not deprotonated and was only very weakly bound to the metal atom. We have thus been able to compare different forms of the thiosemicarbazone.

Experimental

Merck thiosemicarbazide, EGA cyclopentanone, and ALFA methylmercury(II) chloride were used as received. Dimethylthallium(III) hydroxide was prepared as before.[7] Analytical data were obtained from Galbraith Lab. Inc., Knoxville, Tennessee [for the methylmercury(II) compound] or using a Perkin-Elmer Model 240B analyser. Melting points were determined in a Büchi apparatus. Infrared spectra were recorded using Nujol mulls or KBr discs in a Perkin-Elmer 180 spectrometer, ^1H and ^{13}C n.m.r. spectra on a Bruker WM250 or Varian FT80A instrument.

Preparation of HL.—Glacial acetic acid (5 cm^3) was added to thiosemicarbazide (9.11 g, 0.1 mol) in refluxing ethanol. To the resulting mixture was added cyclopentanone (8.41 g, 0.1 mol) dissolved in ethanol (25 cm^3). The solution was refluxed for 1 h and on cooling a yellowish white solid was formed, m.p. 150 °C (from EtOH) (Found: C, 45.4; H, 7.2; N, 26.6. Calc. for $C_6H_{11}N_3S$: C, 45.8; H, 7.0; N, 26.7%).

Preparation of $TlMe_2(L)\cdot HL$.—The compound $TlMe_2(OH)$ (0.79 g, 3.2 mmol) dissolved in water (40 cm^3) was slowly added, with stirring, to HL (0.50 g, 3.2 mmol) dissolved in ethanol (25 cm^3). The yellowish white crystalline solid formed after stirring was isolated and dried under vacuum, m.p. 140 °C (Found: C, 30.2; H, 4.9; N, 15.2. $C_{14}H_{27}N_6S_2Tl$ requires C, 30.7; H, 4.9; N, 15.3%).

Preparation of HgMe(L).—The compound HgMe(Cl) (1.11 g, 4.5 mmol) dissolved in dichloromethane (50 cm^3) was added to the sodium salt of the ligand (0.70 g, 4.5 mmol) (prepared *in situ* by reaction between equimolar quantities of HL and aqueous NaOH) in water (50 cm^3). Stirring the two phases together for 2 h produced a blackish product that tended to accumulate at the interface between the phases. The organic layer was decanted off, filtered until colourless, and concentrated until

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

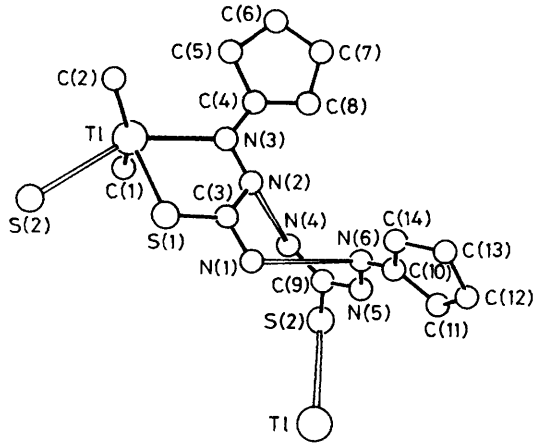


Figure 1. ORTEP drawing of $TlMe_2(L)$·HL showing the atomic numbering scheme

Table 1. Positional parameters for $TlMe_2(L)$·HL with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c
Tl	0.242 5(1)	0.240 9(1)	0.437 7(1)
S(1)	0.130 8(4)	0.095 8(3)	0.492 3(3)
S(2)	0.044 9(4)	0.344 3(3)	0.519 9(3)
N(1)	0.095(1)	−0.082(1)	0.406(1)
N(2)	0.249(1)	−0.002(1)	0.376(1)
N(3)	0.322(1)	0.079(1)	0.394(1)
N(4)	−0.111(1)	0.432(1)	0.353 7(9)
N(5)	−0.091(1)	0.261 6(9)	0.346(1)
N(6)	−0.167(1)	0.265(1)	0.246(1)
C(1)	0.158(3)	0.262(2)	0.277(2)
C(2)	0.371(3)	0.285(2)	0.582(2)
C(3)	0.165(2)	−0.002(1)	0.419(1)
C(4)	0.413(1)	0.065(1)	0.364(1)
C(5)	0.497(2)	0.154(2)	0.379(1)
C(6)	0.597(2)	0.104(2)	0.347(2)
C(7)	0.567(3)	0.010(3)	0.310(2)
C(8)	0.448(2)	−0.021(2)	0.319(1)
C(9)	−0.061(2)	0.348(1)	0.399(1)
C(10)	−0.192(1)	0.185(1)	0.194(1)
C(11)	−0.150(2)	0.084(1)	0.229(1)
C(12)	−0.211(2)	0.011(2)	0.135(2)
C(13)	−0.297(3)	0.077(2)	0.062(2)
C(14)	−0.270(2)	0.180(2)	0.081(2)

there emerged a white, apparently crystalline solid that was isolated and dried under vacuum. Unfortunately, no monocrystals suitable for *X*-ray diffraction studies could be located, and the compound's instability prevented recrystallization, m.p. 129 °C (Found: C, 22.7; H, 3.8. $C_7H_{13}HgN_3S$ requires C, 22.6; H, 3.5%).

Determination of the Crystal Structure of $TlMe_2(L)$·HL.—A transparent white parallelepiped monocrystal measuring 0.25 × 0.20 × 0.10 mm was used. Since the compound's crystallinity deteriorated when in contact with the atmosphere, the crystal was placed in a capillary tube for measurement, which was carried out at 20 °C. Unit-cell dimensions were determined on an Enraf-Nonius CAD4 automated four-circle diffractometer by least-squares refinement of 25 reflections. Systematic extinctions were characteristic of the space group $P2_1/c$.

Crystal data. $C_{14}H_{27}N_6S_2Tl$, M = 547.92, monoclinic, a = 12.088(4), b = 13.656(3), c = 13.271(4) Å, β = 108.68(2)°, U = 2075.3 Å^3, space group $P2_1/c$ (no. 14), Z = 4, D_c = 1.750 g cm^{-3}, $F(000)$ = 1 060, μ(Cu-K_α) = 168.60 cm^{-1}, 209 parameters, 293 K.

Table 2. Bond distances (Å) for $TlMe_2(L)$·HL *

Tl–S(1)	2.627(5)	N(6)–C(10)	1.28(2)
Tl–S(2)	3.249(5)	C(4)–C(5)	1.56(3)
Tl–N(3)	2.55(1)	C(4)–C(8)	1.44(3)
Tl–C(1)	2.07(3)	C(5)–C(6)	1.56(4)
Tl–C(2)	2.13(3)	C(6)–C(7)	1.38(5)
S(1)–C(3)	1.78(2)	C(7)–C(8)	1.54(4)
S(2)–C(9)	1.70(2)	C(10)–C(11)	1.49(3)
N(1)–C(3)	1.36(2)	C(10)–C(14)	1.50(3)
N(2)–N(3)	1.39(2)	C(11)–C(12)	1.58(3)
N(2)–C(3)	1.31(2)	C(12)–C(13)	1.48(4)
N(3)–C(4)	1.30(2)	C(13)–C(14)	1.45(4)
N(4)–C(9)	1.35(2)	N(1)–N(6^{I})	3.21(2)
N(5)–N(6)	1.35(2)	N(2)–N(4^{I})	3.10(2)
N(5)–C(9)	1.36(2)		

* Numbers in parentheses are e.s.d.s in the least significant digits. Symmetry code: I $-x, y - 0.5, 0.5 - z$.

Table 3. Bond angles (°) for $TlMe_2(L)$·HL *

S(1)–Tl–S(2)	74.8(1)	N(3)–C(4)–C(5)	115(1)
S(1)–Tl–N(3)	70.9(3)	N(3)–C(4)–C(8)	130(1)
S(1)–Tl–C(1)	105.2(7)	C(5)–C(4)–C(8)	115(1)
S(1)–Tl–C(2)	104.9(7)	C(4)–C(5)–C(6)	99(1)
S(2)–Tl–N(3)	145.5(3)	C(5)–C(6)–C(7)	111(1)
S(2)–Tl–C(1)	96.4(7)	C(6)–C(7)–C(8)	112(1)
S(2)–Tl–C(2)	88.7(7)	C(4)–C(8)–C(7)	102(1)
N(3)–Tl–C(1)	89.1(8)	S(2)–C(9)–N(4)	123(1)
N(3)–Tl–C(2)	103.3(8)	S(2)–C(9)–N(5)	117(1)
C(1)–Tl–C(2)	150(1)	N(4)–C(9)–N(5)	120(1)
N(3)–N(2)–C(3)	118(1)	N(6)–C(10)–C(11)	129(1)
N(2)–N(3)–C(4)	113(1)	N(6)–C(10)–C(14)	123(1)
N(6)–N(5)–C(9)	118(1)	C(11)–C(10)–C(14)	108(1)
N(5)–N(6)–C(10)	118(1)	C(10)–C(11)–C(12)	108(1)
S(1)–C(3)–N(1)	115(1)	C(11)–C(12)–C(13)	101(1)
S(1)–C(3)–N(2)	126(1)	C(12)–C(13)–C(14)	114(1)
N(1)–C(3)–N(2)	119(1)	C(10)–C(14)–C(13)	105(1)

* Numbers in parentheses are e.s.d.s in the least significant digits.

Intensity data in the range 5 < θ < 50° were collected in ω—θ scan mode using graphite-monochromated Cu-K_α radiation: hkl ranges, $-11 < h < 11$, $k < 13$, $l < 13$. The intensities of the standards 802 and 413 varied by ± 1.2% of their means over the period of data collection. Lorentz and polarization corrections and an empirical absorption correction[8] (maximum and minimum transmission factors 1.8179 and 0.6056) were applied to the 2 379 reflections measured. Averaging equivalent reflections gave 2 026 unique reflections (R_{int} = 0.057), of which 1 759 with $I > 3\sigma(I)$ were used for all subsequent calculations. The position of the Tl atom was taken as that exhibited in the Patterson map. Subsequent Fourier difference synthesis revealed the positions of the S, N, and C atoms. The H atoms were not found and were not included in the model. In final cycles of full-matrix least-squares refinement all atoms were treated as anisotropic. The function minimized was $w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + 0.0079F_o^2]^{-1}$; 209 parameters were refined. Inspection of F_c and F_o values indicated that a correction for secondary extinction was required: $F_{corr} = F_c(1.0 - \chi F_c^2/\sin\theta)$ was χ refined to 2.037×10^{-7} in the final run (R = 0.069, R' = 0.076; maximum shift/error 0.01). Scattering factors and anomalous dispersion corrections were taken from refs 9 and 10. Programs used: SHELX 76[11] and SDP[12]. Calculations were performed on a DECMicro VAX II computer.

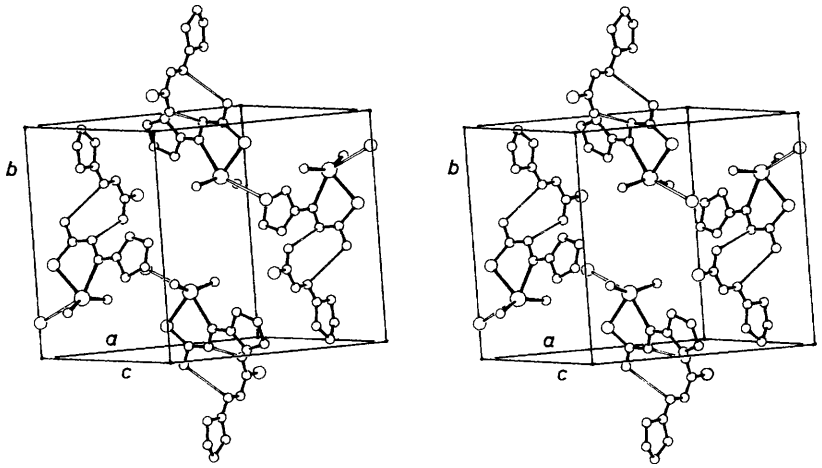


Figure 2. A stereoscopic view of the unit cell of $TlMe_2(L)\cdot HL$

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

Description of the Structure.—The atomic numbering of $TlMe_2(L)\cdot HL$ is shown in Figure 1, and atomic positions, bond lengths and angles are listed in Tables 1, 2, and 3 respectively. Figure 1 also shows the two different types of ligand molecules present in the lattice, L and HL. The long Tl–S(2) distance, though less than the sum of the van der Waals radii (3.76 Å),[13] means that the ligand molecule HL is co-ordinated to the thallium atom only very weakly. The deprotonated ligand molecule co-ordinates *via* N(3) and S(1): the Tl–N(3) distance is the same as in a similar complex of thiouracil[14] suggesting quite a strong bond, while the other co-ordination bond seems to be singularly strong since the Tl–S(1) distance appears to be the shortest yet observed in dimethylthallium(III) compounds.[7,15–17] The Tl–C(1) and Tl–C(2) bond lengths are quite normal, and the difference between them is not very significant in view of the large estimated standard deviations (e.s.d.s). The C(1)–Tl–C(2) angle, though far from linear, is much wider than in the thiouracil complex[14] and faces the region with least steric hindrance. If the weak Tl–S(2) bond is ignored, the metal atom has a trigonal-bipyramidal environment with one vacant equatorial position: if the Tl–S(2) bond is not ignored, the co-ordination geometry of the thallium atom may be described as a deformed octahedron with one vacant position.

The chelating ligand molecule is almost planar, with the virtually planar cyclopentane ring ($\chi^2 = 1$) making an angle of 170(1)° with the plane defined by C(3), N(2), N(3), and C(4). To achieve chelation the molecule adopts a *Z* configuration about the C(2)–N(3) bond. Though the two canonical forms shown in equation (1) are insufficient to describe the delocalization of the π electrons, it is clear that the thione–thiol transition must reduce the order of the C(3)–S(1) bond and increase that of the C(3)–N(2) bond: this is confirmed by the observed shortening of the C(3)–N(2) bond and the lengthening of the C(3)–S(1) bond to a value close to single bond lengths [d(C–S) = 1.81 Å].[18] The ligand molecule HL is very different, with the sulphur atom *trans* with respect to N(6) of Figure 1, *i.e.* the molecule retains the arrangement typical of free thiosemicarbazones.[1] Overall, the compound may therefore be described as having one deprotonated thiol molecule chelating to the metal atom and one neutral molecule with the thione form that is normal for free thiosemicarbazones.

Consideration of intermolecular distances suggests that the HL molecules are held in the crystal lattice not only by the weak Tl–S(2) bonds, but probably also by hydrogen bonds formed with the L molecules of the neighbouring complex molecule. Though it was unfortunately impossible to locate the hydrogen atoms, the N(2)–N(4) and N(1)–N(6) distances [3.10(2) and 3.21(2) Å; open bonds in Figure 1] are within, or at least close to, the accepted range for N–H ··· N bonds (2.94—3.15 Å),[19] and since the species involved are metallic chelates may be assumed to be indicative of hydrogen bonding.

Figure 2 shows a stereoscopic view of the unit cell of the crystalline compound.

I.r. Spectra.—The i.r. spectrum obtained for the free ligand is essentially identical with that published by Puniyani and Srivastava[20] as regards the position of the main bands, and has been interpreted following the ideas of these and other authors.[21–23] The bands at 3 390, 3 220, 3 180, and 3 140 cm^{-1} are assigned to N–H stretching in the N–H and NH_2 groups. That some of these bands are slightly shifted in $TlMe_2(L)\cdot HL$ to 3 410, 3 300, and 3 140 cm^{-1} (positions that confirm the absence of co-ordination *via* the NH_2 group) is explicable in terms of the effects which the deprotonation of one of the ligand molecules and its co-ordination to the metal produce on the hydrogen bonds present in the free ligand. The shift to 1 665 cm^{-1} of the medium-intensity $\delta(NH_2)$ band at 1 660 cm^{-1} for the free ligand is in keeping with this interpretation. The change wrought in the strong ν(C=N) band at 1 590 cm^{-1} for the free ligand, which appears as two bands at 1 625 and 1 580 cm^{-1} for the complex, reflects the difference between the co-ordinated and unco-ordinated C=N groups of the solid complex. The band at 1 030 cm^{-1} for the free ligand, to which a degree of ν(C=S) influence has been attributed, shifts to 1 040 cm^{-1} in the complex (HL molecule), while the second ν(C=S) band, which lies at 750 cm^{-1} for the free ligand, shifts to 740 (HL molecule) and 690 cm^{-1} (L molecule). With respect to the organometallic part, the bands at 780, 520, and 470 cm^{-1} are assigned to $\rho(CH_3)$, ν_{asym}(C–Tl–C) and ν_{sym}(C–Tl–C) respectively, while those at 440 and 270 cm^{-1} are tentatively assigned[7,23] to ν(Tl–N) and ν(Tl–S), though as in other complexes it is possible that these bands also have other components.

The proximity of the HgMe(L) bands at 3 460, 3 280, and 1 650 cm^{-1} to the corresponding $TlMe_2(L)\cdot HL$ bands suggests that in HgMe(L), too, the NH_2 group is not co-ordinated to the

Table 4. Proton n.m.r. data (p.p.m. from $SiMe_4$)

Compound	Solvent	MR_n	H(5), H(8)	H(6), H(7)	NH_2	NH
HL	$CDCl_3$	—	2.41(t) 2.30(t)	1.73—1.96(m)	6.80(d,br)	8.34(s)
	$(CD_3)_2SO$	—	2.27—2.37(m)	1.62—1.75(m)	7.72(d)	9.83(s)
HgMe(L)	$(CD_3)_2SO$	0.73 [a]	2.62—2.46(m)	1.75(m) [b]	6.48(s)	—
$TlMe_2(L)$·HL	$CDCl_3$	1.09 [a]	2.59(m) 2.40(m) 2.27(m)	1.76—1.92	4.93(s) 7.02(s,br)	—
	$(CD_3)_2SO$	c	2.38—2.29(m)	1.62—1.76(m)	7—8(vbr) 5.87(s)	9.84(s)

[a] ^2J(M–H) = 179.7 (M = Hg), 357.8 Hz (M = Tl). [b] Partially overlapped with the $(CD_3)_2SO$ signal. [c] One of the $TlMe_2$ doublet peaks is masked by the H(6) and H(7) signals making it impossible to establish the chemical shift and the coupling constant.

Table 5. Carbon-13 n.m.r. data (p.p.m. from $SiMe_4$) in $(CD_3)_2SO$

Compound	MR_n	C(6), C(7)	C(5), C(8)	C(4)	C(3)
HL	—	24.20, 24.46	28.30, 32.97	163.63	178.34
HgMe(L)	*a*	24.16, 24.31	30.37, 32.58	—	170.87
$TlMe_2(L)$·HL	19.8 [b]	24.17, 24.44	28.30, 32.84 29.96, 32.49	163.63 167.75	176.88 172.62

[a] Very weak signal (saturated solution). [b] ^1J(Tl–C) = 2 929 Hz.

metal. A strong band at 1 610 cm^{-1} is assigned to ν(C=N). The co-ordination of the C=S group is confirmed by the disappearance of the free-ligand band at 1 030 cm^{-1} and the shift of the band at 750 to 700 cm^{-1}. Among the other vibrations of interest, the positions of $\delta_{sym}(CH_3)$, ν(Hg–C), and ν(Hg–S) (1 175, 535, and 350 cm^{-1} respectively) are all close to those found for other compounds with Hg–S bonds.[6,24]

Proton and ^{13}C *N.M.R. Spectra.*—Table 4 lists the ^1H n.m.r. signals of the free ligand and the complexes. The two NH_2 resonances show that rotation about the C(3)–NH_2 bond is hindered, possibly due to its being partially double.[20,25] The location of the bands in $(CD_3)_2SO$ agrees quite well with published precedents.[20] For the complex HgMe(L) the NH signal disappears as the result of the ligand's deprotonation; the coupling constant $^2J(^{199}Hg–^1H)$ suggests that metal and ligand are bonded *via* a thiole sulphur atom.[26] The spectrum of $TlMe_2(L)$·HL is in keeping with the *X*-ray diffraction results for the crystalline solid: the NH signal is clearly visible in $(CD_3)_2SO$ and so too are both NH_2 groups, one resonating at high field as for the methylmercury(II) complex, and the other in the same region as for the free ligand. In $CDCl_3$ the region featuring H(5) and H(8) exhibits three multiplets in positions similar to those observed for HgMe(L) and HL. The combined results for $TlMe_2(L)$·HL show the presence of one deprotonated ligand molecule co-ordinated to the metal atom, together with another ligand molecule similar to the free ligand. It may be pointed out that the signals of both types of ligand molecule are clearly visible in spite of the spectra having been obtained at room temperature.

The ^{13}C n.m.r. spectra (Table 5) confirm the situation described above. The dimethylthallium(III) complex exhibits four signals for C(5) and C(8), two of which are in practically the same positions as for the free ligand. The signals attributed to the strongly co-ordinated ligand molecule are closer together than for the free ligand because co-ordination slightly shields the lower-field signal and deshields the higher-field signal. This difference between the two carbon atoms may be due to the conformational change undergone by the ligand upon co-ordination, in which case the alterations in the spectrum of the ligand derive not only from the induction effect of the new metal–ligand bonds but also from modification of the anisotropic effect of N(2).[27] If so, the configuration of the ligand in HgMe(L) is the same as that of the molecule in $TlMe_2(L)$·HL, since the C(5) and C(8) signals of the two compounds appear at very similar positions. It may be noted that for HgMe(L) the position of the methyl signal is rather low for a methylmercury(II) group bound to a deprotonated thiol.[26]

Acknowledgements

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