

Synthesis, structure and spectral properties of [(HgPh)₂TbSMe]; a dinuclear 2-*S*-methylthiobarbiturate of phenylmercury(II) exhibiting linkage isomerism

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Abstract

The reaction of 2-*S*-methylthiobarbituric acid (H₂TbSMe) with phenylmercury(II) acetate in ethanol afforded the title complex, which crystallizes in the space group *P*2₁/*c* (No. 14). The asymmetric unit consists of two independent [(HgPh)₂TbSMe] molecules: in molecule 1, the two organometallic moieties are bound primarily to the nitrogen atoms of the ligand ring (N(1) and N(3)); in molecule 2, one phenylmercury(II) is N(1)-bound but the other is bound to the exocyclic oxygen contiguous to N(3). Hence molecules 1 and 2 are linkage isomers. Several weak intra- and intermolecular interactions are also observed. In DMSO solution, ¹H, ¹³C and ¹⁹⁹Hg NMR measurements suggest fast exchange of phenylmercury(II) between N- and O-coordination, with prevalence of the former.

Keywords: Mercury; X-ray structure; Phenylmercury(II) complexes; Linkage isomerism

1. Introduction

Several dinuclear mono-organomercury(II) compounds have been isolated and structurally characterized by X-ray diffraction [1]. Many of them derived from dimetallation reactions of nucleobases or amino acids with methylmercury(II). Surprisingly, reports of similar compounds with phenylmercury(II) are scarce [1] (only one example appears to have been described prior to 1992 [2]). However, in the course of a comprehensive study of the influence of deprotonation and metallation with organometallic cations on the keto–enolic tautomerism of heterocyclic compounds [3–7] we have prepared several dinuclear complexes of phenylmercury(II) [3], and we recently reported the crystal structure of an interesting complex of PyPhHg(II) with the ligand 2-thiouracil [7]. In continuance of this work, we have now prepared a dinuclear complex derived from PhHg(II) and 2-*S*-methylthiobarbituric acid (H₂TbSMe;

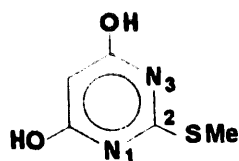
Scheme 1). This article describes the synthesis and structure of the new complex, [(HgPh)₂TbSMe], which presents some interesting and unusual coordination features.

2. Experimental details

2.1. Synthesis of [(HgPh)₂TbSMe]

A solution of 1.0 g (2.97 mmol) of phenylmercury acetate in 110 ml of ethanol was added to a solution of 0.47 g (2.97 mmol) of H₂TbSMe in 50 ml of the same solvent. The small amount of pale pink solid produced after several hours gentle heating with stirring was filtered out, and the mother liquor was concentrated until a colourless crystalline solid appeared. Elemental analysis of this compound suggested that the bimetallic, not the monometallic complex had been prepared, as was later confirmed by the X-ray study (*vide infra*). (Anal. Found: C, 28.1; H, 2.1. C₁₇H₁₄Hg₂N₂O₂S. Calc.: C, 28.7; H, 2.0%.)

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Scheme 1.

2.2. Measurements

H_2TbSMe and phenylmercury acetate were obtained from commercial sources and used without further purification. Elemental analysis was performed by Galbraith Lab., Knoxville, TN, USA. ^1H , ^{13}C and ^{199}Hg NMR spectra in either $\text{DMSO-}d_6$ or a $\text{DMSO-DMSO-}d_6$ mixture were recorded at room temperature on a Bruker WM-250 spectrometer at 250.13 MHz, 62.83 MHz and 44.70 MHz respectively. ^1H and ^{13}C NMR shifts were referred to TMS using the solvent signal and ^{199}Hg shifts to neat HgMe_2 .

2.3. Crystal data

$\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_2\text{SHg}_2$, $M = 711.54$, monoclinic, space group $P2_1/c$ (No. 14), $a = 17.830(5)$, $b = 10.3811(4)$, $c = 20.847(5)$ Å, $\beta = 112.505(10)^\circ$, $V = 3564.8(12)$ Å³, $Z = 8$, $D_c = 2.652$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 17.334$ mm⁻¹, $F(000) = 2576$.

2.4. Data collection, structure analysis and refinement

A colourless prismatic crystal of approximate dimensions $0.30 \times 0.20 \times 0.10$ mm³ was selected and analysed at 203 K with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation. Cell parameters were obtained from the setting angles of 25 reflections (θ range $7\text{--}13^\circ$). 9381 reflections were collected in the θ range $3\text{--}30^\circ$ ($-1 \leq h \leq 23$, $0 \leq k \leq 13$, $-27 \leq l \leq 25$) by the $\omega/2\theta$ scan tech-

nique. Of 8574 independent reflections ($R_{\text{int}} = 0.0353$), after Ψ -scan absorption correction (max./min. factor corrections 0.999/0.711) 5643 with $I > 2\sigma(I)$ were considered as observed.

The structure was solved by direct methods. All non-H atoms were anisotropically refined. The H atoms bound to C(5) and C(51) (H(5) and H(51)) were refined at positions obtained from difference Fourier techniques with a common temperature factor ($U_{\text{eq}} = 0.048$ Å²). All other hydrogen atoms were included in the model in geometrically calculated positions [8]. Full-matrix least squares refinement on F^2 of 8571 reflections led to the final indices $R_1 = 0.0537$ (for observed reflections), $R_w = 0.0877$ and $\text{GoF} = 1.141$ for all reflections.

Most calculations were performed with SHELXS86 [8] and SHELXL93 [9]. Figures were plotted with ORTEP [10] and SCHAKAL [11]. Scattering factors and anomalous dispersion corrections were taken from Ref. [12].

3. Results and discussion

3.1. Crystal structure

A view of the structure is shown in Fig. 1. Atomic positions, interatomic distances and angles are listed in Tables 1–3.

The asymmetric unit consists of two independent [(HgPh)₂TbSMe] molecules which are linkage isomers (Fig. 1): in molecule 1, the two HgPh^+ moieties are coordinated to N(1) and N(3) ($\text{Hg}(1)\text{--N}(1) = 2.117(10)$, $\text{Hg}(2)\text{--N}(3) = 2.105(10)$ Å) while in molecule 2 the organometallic cations are bound to N(11) and O(41) ($\text{Hg}(3)\text{--N}(11) = 2.091(11)$, $\text{Hg}(4)\text{--O}(41) = 2.088(10)$ Å). The $\text{Hg}(4)\text{--O}(41)$ bond, which is rather uncommon in mono-organomercury(II) compounds other than carboxylates, is very short, so molecules 1

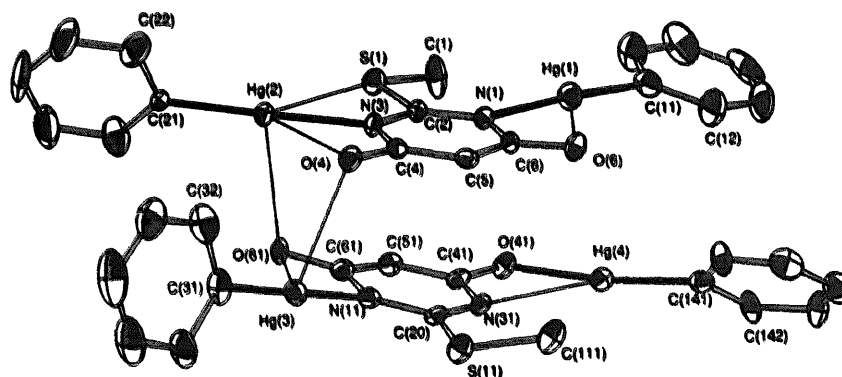


Fig. 1. ORTEP plot showing the structure of [(HgPh)₂TbSMe] with the atom-numbering scheme used. The thermal ellipsoids correspond to 30% probability.

and 2 are true linkage isomers, not the more common distortion isomers [1,13]. The average Hg–C distance (2.04 Å) is a little shorter than, but not significantly different from, the mean reported for phenylmercury(II) compounds, 2.06 Å [1]. The primary bonds of each Hg cation (Hg–C and Hg–N or Hg–O) are roughly collinear, as usual for mercury atoms; the largest deviations affect the Hg(4) and Hg(1) (C(141)–Hg(4)–O(41) = 171.4(5)°, C(11)–Hg(1)–N(1) = 172.9(6)°).

Also, as usual, there are several short intra- and intermolecular interactions which may be imposed or facilitated by the stereochemistry of the ligand and/or the molecular packing in the lattice. The four mercury atoms differ as regards these weak interactions. Hg(1) has only an intramolecular secondary bond with O(6) (Hg(1)–O(6) = 2.627(10) Å; sum of the van der Waals radii, 3.23 Å [14,15]). Hg(2) has two intramolecular interactions, with O(4) (2.833(10) Å) and S(1)

Table 1
Atomic coordinates ($\times 10^6$) and equivalent isotropic displacement ($\text{\AA}^2 \times 10^3$) parameters for [(HgPh)₂TbSMe]

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Hg(1)	1930(1)	922(1)	1482(1)	39(1)
Hg(2)	–1562(1)	–1513(1)	548(1)	31(1)
S(1)	368(2)	–1586(4)	1547(2)	34(1)
N(1)	657(6)	682(10)	992(5)	24(2)
N(3)	–645(6)	–178(11)	617(6)	27(3)
O(4)	–1721(6)	779(10)	–232(5)	35(2)
O(6)	935(6)	2511(9)	569(5)	36(2)
C(1)	1388(9)	–1424(18)	2137(10)	58(5)
C(2)	137(8)	–216(13)	1020(6)	22(3)
C(4)	–973(8)	855(14)	135(7)	27(3)
C(5)	–432(9)	1805(14)	131(7)	29(3)
C(6)	378(8)	1727(12)	550(6)	24(3)
C(11)	3131(9)	1130(19)	2065(8)	49(5)
C(12)	3562(11)	2226(20)	2111(11)	64(6)
C(13)	4370(12)	2345(24)	2558(11)	71(6)
C(14)	4759(10)	1313(30)	2946(10)	82(8)
C(15)	4343(12)	189(27)	2923(11)	79(7)
C(16)	3542(10)	105(20)	2494(10)	62(6)
C(21)	–2478(8)	–2812(13)	417(8)	30(3)
C(22)	–2802(11)	–3447(19)	–203(10)	64(5)
C(23)	–3426(14)	–4308(23)	–315(15)	92(8)
C(24)	–3683(13)	–4589(22)	188(21)	112(12)
C(25)	–3349(13)	–3952(24)	811(15)	86(8)
C(26)	–2743(11)	–3107(21)	912(11)	65(6)
Hg(3)	–2529(1)	1738(1)	583(1)	34(1)
Hg(4)	1496(1)	3673(1)	2265(1)	33(1)
S(11)	–1330(2)	4318(4)	805(2)	41(1)
O(41)	981(6)	2106(9)	2575(5)	34(2)
O(61)	–1569(6)	45(9)	1662(5)	31(2)
N(11)	–1368(7)	2060(11)	1335(6)	27(3)
N(31)	–104(7)	3089(11)	1778(6)	27(3)
C(20)	–883(8)	3069(12)	1379(7)	28(3)
C(41)	214(9)	2072(13)	2220(6)	26(3)
C(51)	–264(9)	1047(13)	2240(7)	29(3)
C(61)	–1075(9)	980(13)	1762(7)	32(3)
C(111)	–459(10)	5182(15)	779(8)	46(4)
C(31)	–3675(9)	1316(16)	–103(9)	45(4)
C(32)	–3775(11)	525(21)	–651(9)	62(6)
C(33)	–4544(15)	204(22)	–1106(12)	77(7)
C(34)	–5214(14)	650(32)	–994(14)	101(11)
C(35)	–5105(13)	1456(26)	–452(16)	92(9)
C(36)	–4353(10)	1826(20)	2(12)	68(6)
C(141)	2150(9)	5033(15)	2001(7)	34(3)
C(146)	1973(9)	5412(17)	1313(8)	43(4)
C(142)	2789(8)	5608(16)	2515(9)	43(4)
C(143)	3253(10)	6524(18)	2364(10)	53(5)
C(145)	2394(11)	6357(20)	1164(9)	57(5)
C(144)	3957(11)	6916(18)	1685(10)	55(5)

Table 2
Selected interatomic distances (Å) in [(HgPh)₂TbSMe]

Molecule 1		Molecule 2	
Hg(1)–C(11)	2.029(14)	Hg(3)–C(31)	2.043(14)
Hg(1)–N(1)	2.117(10)	Hg(3)–N(11)	2.091(11)
Hg(2)–C(21)	2.054(3)	Hg(4)–C(141)	2.04(2)
Hg(2)–N(3)	2.105(10)	Hg(4)–O(41)	2.088(10)
S(1)–C(1)	1.77(2)	S(11)–C(20)	1.728(14)
S(1)–C(2)	1.746(13)	S(11)–C(111)	1.81(2)
N(1)–C(2)	1.33(2)	O(41)–C(41)	1.28(2)
N(1)–C(6)	1.39(2)	O(61)–C(61)	1.26(2)
N(3)–C(2)	1.32(2)	N(11)–C(20)	1.43(2)
N(3)–C(4)	1.43(2)	N(11)–C(61)	1.40(2)
O(4)–C(4)	1.26(2)	N(31)–C(20)	1.32(2)
O(6)–C(6)	1.27(2)	N(31)–C(41)	1.37(2)
C(4)–C(5)	1.38(2)	C(41)–C(51)	1.37(2)
C(5)–C(6)	1.38(2)	C(51)–C(61)	1.41(2)
Intramolecular interactions		Intermolecular interactions	
Hg(1)–O(6)	2.627(10)	Hg(1)···Hg(4)	3.5190(9)
Hg(2)–O(4)	2.833(10)	Hg(3)···O(4)	2.797(10)
Hg(2)–S(1)	3.270(4)	Hg(2)···O(61)	2.829(10)
Hg(3)–O(61)	2.85(6)	Hg(4)···O(61')	2.617(9)
Hg(4)–N(31)	2.707(11)		

' = -x, y + 0.5, -z + 0.5.

(3.270(4) Å; sum of the van der Waals radii 3.53 Å [15]), and an intermolecular interactions with O(61) (2.829(10) Å) in molecule 2. Hg(3) has the same secondary bonds as Hg(2) except for Hg···S; the angle S(11)–C(20)–N(11) (115.4(10)°) is wider than N(3)–C(2)–S(1) (111.2(9)°) (which shows there is some flexibility in the exocyclic part of the ligand skeleton), and the Hg(3)–S(11) distance is consequently greater than the sum of the van der Waals radii. This lack of interaction with a thioether sulphur was previously found in similar systems [3]. Hg(4) has an intramolecular secondary Hg···N bond (Hg(4)···N(31) = 2.707(11) Å) and also an intermolecular Hg···O interaction with a neighbouring type 2 molecule (Fig. 2, Hg(4)···O(61') = 2.617(9) Å; ' = -x, y + 0.5, -z + 0.5). Overall, molecules 1 and 2 are connected in pairs by the Hg(2)···O(61) and Hg(3)···O(4) interactions with their pyrimidine rings (dihedral angle 6.19°) practi-

cally eclipsing each other (Fig. 3), while the Hg(4)···O(61') interactions assemble the pairs in a helicoidal arrangement along the *b* axis. O(61) is a triple-bridging atom connecting Hg(2), Hg(3) and Hg(4'') ('' = -x, y - 0.5, -z + 0.5).

The TbSMe ligands are almost planar in both molecules, with the main deviations from the best plane at C(1), O(4) and S(1) (0.25(2), -0.05(2) and 0.01(2) Å) in molecule 1 and C(111), O(61) and S(11) (0.02(2), -0.175(9) and 0.444(8) Å) in molecule 2. In molecule 1 the mercury atoms deviate 0.131 (Hg(1)) and 0.030 Å (Hg(2)) from the ligand plane, which forms dihedral angles of 12° and 65° respectively with the phenyl planes (C(11), C(12), C(13), C(14), C(15), C(16)) and (C(21), C(22), C(23), C(24), C(25), C(26)). In molecule 2, Hg(3) and Hg(4) respectively deviate 0.157 Å and 0.163 Å from the ligand plane, while the dihedral angles between the phenyl rings and this plane are 80° (C(31),

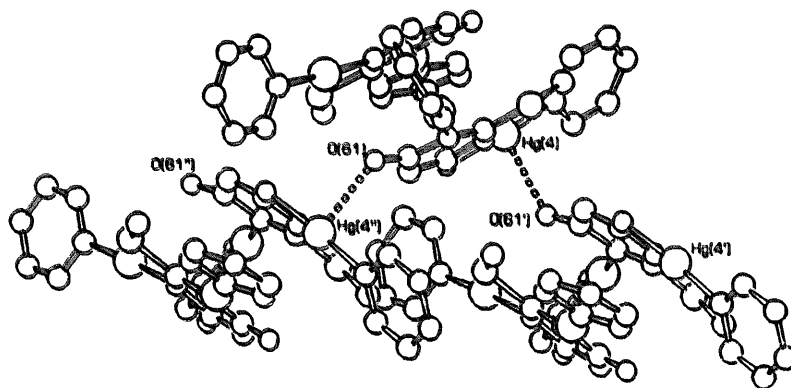


Fig. 2. SCHAKAL plot showing the intermolecular Hg···O interactions between type 2 molecules.

Table 3
Selected interatomic bond angles (deg) in [(HgPh)₂TbSMe]

Molecule 1		Molecule 2	
C(11)–Hg(1)–N(1)	172.9(6)	C(31)–Hg(3)–N(11)	175.6(5)
C(11)–Hg(1)–O(6)	129.2(6)	C(31)–Hg(3)–O(4)	96.2(6)
N(1)–Hg(1)–O(6)	54.7(3)	N(11)–Hg(3)–O(4)	85.5(4)
C(11)–Hg(1)–Hg(4)	90.3(5)	C(31)–Hg(3)–O(61)	124.1(5)
N(1)–Hg(1)–Hg(4)	86.2(3)	N(11)–Hg(3)–O(61)	51.8(4)
O(6)–Hg(1)–Hg(4)	67.6(2)	O(4)–Hg(3)–O(61)	87.9(3)
C(21)–Hg(2)–N(3)	176.6(5)	C(141)–Hg(4)–O(41)	171.4(5)
C(21)–Hg(2)–O(61)	103.6(4)	C(141)–Hg(4)–O(61')	90.7(5)
N(3)–Hg(2)–O(61)	79.1(4)	O(41)–Hg(4)–O(61')	92.3(3)
C(21)–Hg(2)–O(4)	125.1(5)	C(141)–Hg(4)–N(31)	133.2(5)
N(3)–Hg(2)–O(4)	52.5(4)	O(41)–Hg(4)–N(31)	54.2(3)
O(61)–Hg(2)–O(4)	87.7(3)	O(61')–Hg(4)–N(31)	97.9(3)
S(1)–Hg(2)–N(3)	51.1(3)	C(141)–Hg(4)–Hg(1)	100.8(4)
S(1)–Hg(2)–O(4)	103.6(2)	O(41)–Hg(4)–Hg(1)	73.3(3)
S(1)–Hg(2)–C(21)	131.1(4)	O(61')–Hg(4)–Hg(1)	153.2(2)
S(1)–Hg(2)–O(61)	79.7(2)	N(31)–Hg(4)–Hg(1)	91.8(2)
C(2)–S(1)–C(1)	107.0(7)	C(20)–S(11)–C(111)	102.4(7)
C(2)–N(1)–C(6)	120.0(11)	C(41)–O(41)–Hg(4)	110.0(8)
C(2)–N(1)–Hg(1)	134.1(9)	C(61)–O(61)–Hg(2)	111.1(8)
C(6)–N(1)–Hg(1)	105.9(8)	Hg(4'')–O(61)–Hg(2)	112.1(3)
C(6)–O(6)–Hg(1)	85.6(8)	C(61)–O(61)–Hg(3)	80.0(8)
C(2)–N(3)–C(4)	121.1(11)	Hg(4'')–O(61)–Hg(3)	145.4(4)
C(2)–N(3)–Hg(2)	128.6(9)	Hg(2)–O(61)–Hg(3)	84.0(3)
C(4)–N(3)–Hg(2)	110.3(8)	C(20)–N(11)–Hg(3)	126.7(9)
C(4)–O(4)–Hg(3)	106.3(8)	C(61)–N(11)–Hg(3)	111.7(9)
C(4)–O(4)–Hg(2)	81.6(8)	C(20)–N(31)–C(41)	118.9(12)
Hg(3)–O(4)–Hg(2)	85.0(3)	C(20)–N(31)–Hg(4)	160.3(9)
N(3)–C(2)–N(1)	122.1(12)	C(41)–N(31)–Hg(4)	79.3(8)
N(3)–C(2)–S(1)	111.2(9)	N(31)–C(20)–N(11)	122.9(12)
N(1)–C(2)–S(1)	126.7(10)	N(31)–C(20)–S(11)	121.6(10)
O(4)–C(4)–C(5)	128.3(14)	N(11)–C(20)–S(11)	115.4(10)
O(4)–C(4)–N(3)	115.6(12)	O(41)–C(41)–N(3)	116.2(12)
C(5)–C(4)–N(3)	116.1(12)	O(41)–C(41)–C(51)	122.7(12)
C(6)–C(5)–C(4)	121.4(13)	N(31)–C(41)–C(51)	120.9(12)
O(6)–C(6)–C(5)	126.9(12)	C(41)–C(51)–C(61)	119.8(12)
O(6)–C(6)–N(1)	113.8(11)	O(61)–C(61)–N(11)	116.4(13)
C(5)–C(6)–N(1)	119.2(12)	O(61)–C(61)–C(51)	127.4(13)
		N(11)–C(61)–C(51)	116.2(12)

a = -x, y + 0.5, -z + 0.5; *b* = -x, y - 0.5, -z + 0.5.

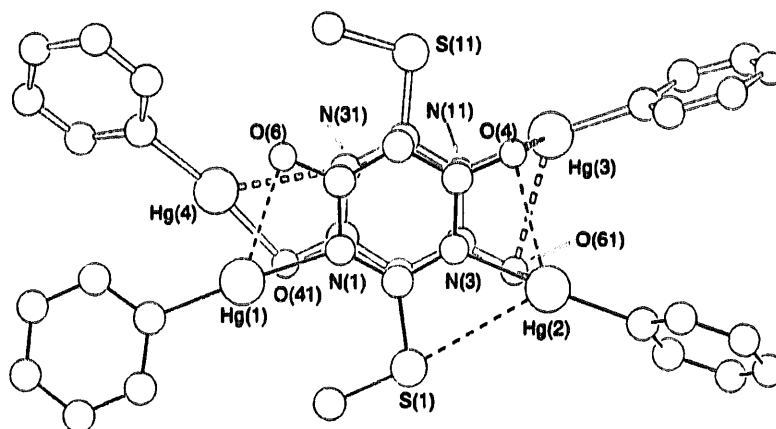


Fig. 3. SCHAKAL plot showing the relative positions of molecules 1 and 2: fine line, molecule 1; double line, molecule 2.

Table 4
 ^1H , ^{13}C and ^{199}Hg NMR parameters of H_2TbSMe and $[(\text{HgPh})_2\text{TbSMe}]$ in $\text{DMSO}-d_6$ ^a

Compound	NH	C(5)-H	S-CH ₃	H(Ph)	$^3J(^1\text{H}-^{199}\text{Hg})$		
H_2TbSMe	11.45b	5.15s	2.47s				
$[(\text{HgPh})_2\text{TbSMe}]$		4.93s	2.51s	7.45dd, <i>H_o</i> 7.30t, <i>H_m</i> 7.23tt, <i>H_p</i>	188.5		
	C(4), C(6)	C(2)	C(5)	S-CH ₃	C(Ph)	$^nJ(^{13}\text{C}-^{199}\text{Hg})$	$\delta(^{199}\text{Hg})$
H_2TbSMe	167.4	163.7	85.7	12.7			
$[(\text{HgPh})_2\text{TbSMe}]$	170.8	163.9	85.9	13.8	147.7, <i>C_i</i> 137.3, <i>C_o</i> 128.4, <i>C_m</i> 128.2, <i>C_p</i>	118.8 197.2 39.9	-1311(426) ^b

^a Values of J in Hz; b = broad, s = singlet, dd = doublet of doublets, t = triplet, tt = triplet of triplets.

^b Value of $W_{\frac{1}{2}}$ in parentheses.

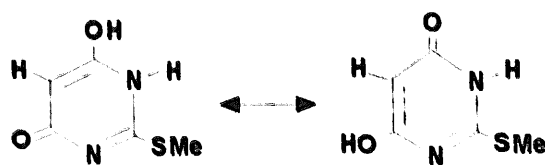
C(32), C(33), C(34), C(35), C(36)) and 38° (C(141), C(142), C(143), C(144), C(145), C(146)). This orientation of the phenyl rings must be a compromise between packing efficiency and the maximization of the intermolecular $\text{Hg}(4) \cdots \text{O}(61')$ interactions.

The large standard deviations of the bond lengths of the TbSMe moiety hinder analysis of the influence of coordination mode on the charge distribution in the ligand. It is, nevertheless, clear: that the bond lengths in the intra-annular N-C-N and C-C-C substructures (N(1)-C(2)-N(3), N(11)-C(20)-N(31), C(4)-C(5)-C(6) and C(41)-C(51)-C(61)) are those characteristic of the pyrimidine ring (unweighted mean distances (d) 1.333 Å and 1.387 Å respectively [16]); that the N-C(O) bonds (N(1)-C(6), N(3)-C(4), N(11)-C(61) and N(31)-C(41)) are longer than in the C=N-C substructures of the pyrimidine (1.339 Å [16]); and, that the C=O distances are shorter than in phenols ($d = 1.362$ Å [16]) but longer than in γ -lactams (C^{*}-NH-C=O groups, C^{*} = Csp³ with only additional C or H bonds; $d = 1.235$ Å [16]). All this means that the TbSMe rings do not attain total charge delocalization, as in pyrimidine, but instead retain some lactam character.

3.2. NMR study

Both H_2TbSMe and $[(\text{HgPh})_2\text{TbSMe}]$ are very poorly soluble in CHCl_3 , but very soluble in DMSO. Their main NMR parameters in the latter solvent are listed in Table 4.

As has already been reported [4] the ^1H and ^{13}C NMR spectra of H_2TbSMe suggest that in DMSO solution the distribution of charge in this molecule is mainly determined by the two keto-enol forms (Scheme 2).



Scheme 2.

although minor contributions by other forms cannot be ruled out. These keto-enol forms can undergo both -OH and -NH deprotonation, and both O- and N-coordination. The ^1H NMR spectrum of $[(\text{HgPh})_2\text{TbSMe}]$ does not feature the NH signal observed in the spectrum of the free ligand, and the signal attributed to C(5)-H (Scheme 1) appears at 4.93 ppm, 0.22 ppm upfield of its position in the spectrum of the free ligand (Table 4). In the ^{13}C NMR spectrum of the complex, the C(5) and C(2) signals are practically in the same positions as in the free ligand, and the SCH₃ signal is only slightly deshielded, showing that the double deprotonation and bimetalation only induces minimal changes in the electronic charge distribution at these carbon atoms. The carbon signals most affected by metallation are, as expected, those of C(4) and C(6), suggesting that coordination to N and/or O atoms must persist in DMSO. The $^nJ(^{13}\text{C}-^{199}\text{Hg})$ values and the ^{13}C chemical shifts for the phenyl ring carbons are mostly consistent with coordination to nitrogen atoms; however, the fact that ^{199}Hg is slightly more shielded than in N-bound phenylmercury complexes with similar ligands [3] may be indicative of some O-metallation [17], in which case HgPh cations would be coordinated to both N and O atoms as in the solid state.

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