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Complexes derived from 4-amino-3-methyl-5-thione-1,2,4-triazole and monoorganomercury moieties. Crystal structure of (4-amino-5-mercapto-3-methyl-1,2,4-triazolato)methylmercury(II)

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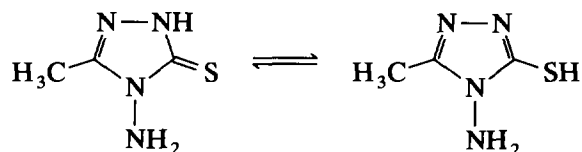
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Abstract

The compounds [HgR(L)] (R = Me or Ph; L = 4-amino-5-mercapto-3-methyl-1,2,4-triazolate) have been prepared and the crystal structure of the methylmercury(II) compound determined. This compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 5.087(1)$, $b = 10.102(1)$, $c = 16.167(2)$ Å, $\beta = 98.56(1)^\circ$, $Z = 4$ ($R = 0.027$; $R_w = 0.030$). It is formed of molecules in which the triazolate anion is bound to mercury strongly via the S atom and weakly via the amine N; there is also a weak intermolecular interaction between the endocyclic N and the Hg atom of a neighbouring unit.

1. Introduction

The desire to understand the toxicological behaviour of organomercury cations and to find effective chemical antidotes to them has increased the amount of research into their coordination chemistry. Being interested in the residual Lewis acidity of complexes [HgMe(SR)] which leads to the formation of secondary bonds [1], we have studied the interaction of the cations HgMe^+ and HgPh^+ with several S-donors which also have available N-donor atoms. X-Ray studies of the complexes [HgMe(L)] showed intramolecular Hg–N distances of 2.537(8), 2.980(5), 3.065 (mean) and 3.15(3) Å when the unbound donor (HL) was cyclopentanethiosemicarbazone [2], 2-mercaptopyridine [3], bismutiol I [4] or 2-mercaptobenzoxazole [5], respectively. Weak intermolecular Hg–S and Hg–N interactions were also detected in these compounds. In continuance of this research, we have selected the potentially multidonor 4-amino-3-methyl-5-thione-1,2,4-triazole (HL), which is capable of undergoing thione–thiol tautomerism and we have studied its inter-



action with the HgR^+ cations (R = Me or Ph) determining the crystal structure of (4-amino-5-mercapto-3-methyl-1,2,4-triazolato)methylmercury(II). The latter was found to have a secondary Hg–N (amino) bond 2.7167(6) Å long.

2. Experimental details

2.1. Reagents

The ligand was prepared by published methods [6]. [HgMe(Ac)] and [HgPh(Ac)] were commercial products.

2.2. Synthesis of compounds

[HgMe(L)]: solid [HgMe(Ac)] (1 g, 3.8 mmol) was added to HL (0.5 g, 3.8 mmol) dissolved in ethanol (*ca.* 50 ml). The white solid formed after stirring was filtered off and vacuum dried. Anal Found: C, 13.9; H, 2.5; Calc.: C, 13.9; H, 2.3%.

[HgPh(L)]: HL (0.5 g, 3.8 mmol) in ethanol was added to solid HgPh(Ac) (1.3 g, 3.8 mmol). The solid formed after 24 h stirring was filtered off and dried under vacuum over CaCl_2 . Anal. Found: C, 26.6; H, 2.8. Calc.: C, 26.2; H, 2.9%.

2.3. Physicochemical measurements

Elemental analyses were performed by Galbraith Lab. Inc., Knoxville, TN, USA. IR spectra were

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recorded in Nujol mulls or as KBr pellets on a Perkin–Elmer 180 spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Varian FT-80A or a Bruker WM 250 spectrometer.

2.4. Crystal structure determination

A colourless crystal with approximate dimensions $0.20 \times 0.24 \times 0.28 \text{ mm}^3$ was mounted on an Enraf–Nonius CAD-4 four-circle diffractometer. All constants were determined from setting angles for 25 reflections. The systematic absences observed suggested the space group to be $P2_1/n$. Reflections were measured by the ω – θ scan technique with variable scan width and scan speed. The hkl range was $h < 5$, $k < 11$ and $-18 < l < 18$ with θ varying between 3 and 24. Of 1539 reflections measured, 1248 were unique with $R_{\text{int}} = 0.019$ and 1038 with $I_o > 3\sigma(I_o)$ were considered as observed and used for refinement. Lorentz polarization corrections and an empirical absorption correction [7] were performed (max. and min. transmission factors 1.610 and 0.802). The standard reflections varied by +5.8% in mean intensity during the course of data collection.

The structure was solved by Patterson techniques, which showed the position of the Hg atom, and subsequent difference Fourier maps, which revealed the positions of all other non-H atoms. The possible H atoms found in the Fourier maps converged poorly under refinement by least-squares and were not included in the model. Refinement was carried out minimizing the function $\sum w([F_o] - [F_c])^2$ with $w^{-1} = \sigma^2(F_o)$, and in final least-squares cycles all atoms were treated anisotropically. A correction for secondary extinction was also made: $F_{\text{corr}} = F_c(1.0 + kF_c^2/\sin 2\theta)^{0.25}$, where k refined to 2.6987×10^{-7} in the final run. A total of 92 parameters were refined. At that stage, $R = 0.027$ and $R_w = 0.030$. Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-Ray Crystallography* [8]. Calculations were performed with SHELX-86 [9] and the SDP program system [10] on a DECMICRO VAXII computer. The main diffraction data and the final atomic coordinates are listed in Tables 1 and 2, respectively.

3. Results and discussion

3.1. X-Ray structure of [HgMe(L)]

The structure of this complex is shown in Fig. 1 with the atomic numbering scheme. The most significant bond distances and angles are listed in Table 3. The mercury atom is coordinated to the methyl carbon and to the triazolate S and N(7) atoms in a distorted T-shaped pattern. The triazole ring is planar ($\chi^2 = 0$) and the distances of the extra-annular atoms from this

TABLE 1. Crystal data for [HgMe(L)]

Molecular formula	$\text{C}_4\text{H}_8\text{N}_4\text{SHg}$
Molecular weight	344.79
Crystal class	Monoclinic
Space group	$P2_1/n$ (non-standard No. 14)
Lattice constants	
a (Å)	5.087(1)
b (Å)	10.102(1)
c (Å)	16.167(2)
β (°)	98.56(1)
Cell volume, V (Å ³)	821.9
Formula units, Z	4
Density, D_x (g cm ⁻³)	2.786
Absorption coefficient, μ (Mo K α) (cm ⁻¹)	189.05
Temperature (K)	296
R , R_w	0.027, 0.030

TABLE 2. Positional parameters and their estimated standard deviations for [HgMe(L)]

Atom	x	y	z	B_{eq}^a
Hg	0.22529(9)	0.14747(4)	0.05714(3)	3.326(8)
S	0.3402(5)	-0.0779(3)	0.0898(2)	3.46(6)
N(1)	0.167(2)	-0.2329(8)	0.2064(5)	3.0(2)
N(2)	0.006(2)	-0.2245(9)	0.2685(5)	3.0(2)
N(4)	0.006(1)	-0.0331(7)	0.2075(5)	2.0(1)
N(7)	-0.046(1)	0.1007(8)	0.1867(5)	2.5(2)
C(1)	0.183(3)	0.338(1)	0.0103(9)	5.8(3)
C(3)	-0.090(2)	-0.103(1)	0.2684(6)	2.4(2)
C(5)	0.164(2)	-0.1178(9)	0.1703(6)	2.4(2)
C(6)	-0.267(2)	-0.048(1)	0.3246(7)	4.1(3)

$$^a B_{\text{eq}} = 4/3 \sum_{ij} B_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j).$$

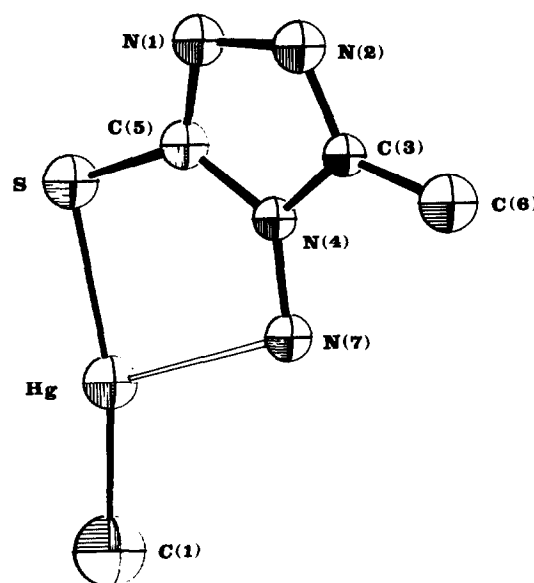


Fig. 1. View of the structure of [HgMe(L)], with the atomic numbering scheme (thermal ellipsoids at the 80% probability level).

TABLE 3. Bond lengths (Å) and angles (°) for [HgMe(L)]

Hg-S	2.391(2)	N(1)-C(5)	1.301(8)
Hg-N(2) ⁱ	3.216(5)	N(2)-C(3)	1.319(8)
Hg-N(7)	2.717(6)	N(4)-N(7)	1.408(7)
Hg-C(1)	2.071(9)	N(4)-C(3)	1.361(8)
S-C(5)	1.735(7)	N(4)-C(5)	1.375(8)
N(1)-N(2)	1.388(7)	C(3)-C(6)	1.478(9)
S-Hg-N(2) ^{i a}	97.6(1)	N(7)-N(4)-C(5)	126.4(6)
S-Hg-N(7)	78.5(1)	C(3)-N(4)-C(5)	106.8(5)
S-Hg-C(1)	167.5(3)	N(2)-C(3)-N(4)	108.1(5)
N(2) ⁱ -Hg-N(7)	66.0(2)	N(2)-C(3)-C(6)	127.5(6)
N(2) ⁱ -Hg-C(1)	87.3(3)	N(4)-C(3)-C(6)	124.4(6)
N(7)-Hg-C(1)	114.0(4)	S-C(5)-N(1)	124.9(5)
N(2)-N(1)-C(5)	107.5(5)	S-C(5)-N(4)	126.0(5)
N(1)-N(2)-C(3)	108.4(5)	N(1)-C(5)-N(4)	109.2(6)
N(7)-N(4)-C(3)	126.9(6)		

^a i indicates symmetry code 0.5 - x, 0.5 + y, 0.5 - z.

TABLE 4. Significant IR bands (cm⁻¹) for the ligand and the complexes prepared ^a

	HL	[HgMe(L)]	[HgPh(L)]
$\nu(\text{NH}_2)$	3280m,b 3180m,b 3120m,b	3260m 3080m	3320m 3240m
$\delta(\text{NH}_2)$	1630s 1610s	1630s,b	1620s
Thioamide I	1580s	1570m	1575m
Thioamide II	1320s	1370m	1380m
Thioamide III	1110m 1045m	1080m 1020w	1080m 1025m 1015m
Thioamide IV	750m	700m	730s

^a s, strong; m, medium; w, weak; b, broad.

plane are negligible [the farthest, C(1), is 0.05 Å away]. The [HgMe(L)] molecule can thus be considered as planar. The Hg-C(1) distance (2.071(9)Å) is within the accepted range for an Hg-C bond (2.05–2.09 Å) [1] and the Hg-S distance (2.391(2)Å) is close to the values found in other sulfhydrylated methylmercury(II) complexes with secondary bonds [2–5]. The secondary bond in this case is formed via the amino nitrogen N(7); the Hg-N distance (2.717(6)Å) is shorter than those found in compounds in which the mercury atom is involved in a four-membered ring Hg-S-C-N [3–5], but slightly longer than the distance found in (cyclopentanethiosemicarbazonato) methylmercury(II) [2], the five-membered ring of which has the same atoms in different groups. As in this latter molecule, the C(1)-Hg-S fragment is non-linear [167.5(3)], suggesting that

the mercury sp hybridization changes to bind the nitrogen.

Comparison of the HgSCNN rings of [HgMe(L)], of the thiosemicarbazone studied previously [2] and of the dithiazonate [11] shows that in spite of certain differences (*e.g.* the Hg-N distance is greatest in [HgMe(L)]), the ring bond lengths and angles are similar.

The packing of the [HgMe(L)] molecules (Fig. 2) seems to suggest a very weak additional intermolecular interaction between Hg and N(2)ⁱ, the distance between these atoms (3.216(5)Å) being at the upper limit of the sum of their van der Waals radii (3.2 Å) [12].

3.2. IR spectra

Table 4 lists the assignments [13,14] of the main IR bands of the triazole and the complexes. A weak free triazole band near 2500 cm⁻¹, due to a small propor-

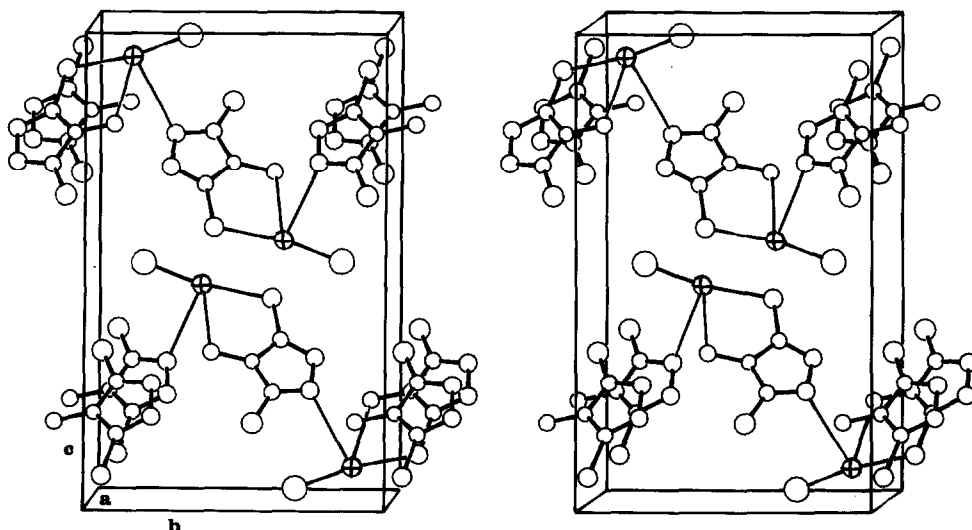
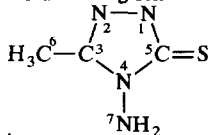


Fig. 2. Stereoview of the structure of [HgMe(L)], showing weak intermolecular interactions.

TABLE 5. ^1H and ^{13}C NMR parameters (in $\text{DMSO}-d_6$, δ in ppm from TMS and J in Hz) for the triazole ^a and its complexes

Compound	C(6)-H	N(1, 2)-H	N(7)-H	HgR	$^2J(^1\text{H}-^{199}\text{Hg})$	C(3)	C(5)	C(6)	HgR	$^1J(^{13}\text{C}-^{199}\text{Hg})$
HL	2.23 (s) ^b	13.39 (s)	5.51 (s)	—	—	149.2	165.5	10.4	—	—
[HgMe(L)]	2.24 (s)	—	6.15 (s)	0.69 (t)	186.1	151.6	154.2	10.3	9.0	1445.0
[HgPh(L)]	2.28 (s)	—	6.40 (s)	7.46 (Ho, dd) 7.33 (Hm, t) 7.22 (Hp, m)	164.7	151.7	154.3	10.4	159.1 (Ci) 137.1 (Co) 128.4 (Cm) 127.8 (Cp)	— 106.2 175.6 —

^a Numbering scheme^b s, singlet; dd, doublet of doublets; t, triplet; m, multiplet.

tion of the thiol form, is absent from the spectra of the complexes, consistent with the ligand being deprotonated. This deprotonation also reduces the intensity of the thioamide bands I and II, both with $\delta(\text{NH})$ contributions. Coordination via the sulfur atom shifts the thioamide III band to slightly lower wavenumbers and reduces its intensity, and thioamide IV is also slightly shifted to lower wavenumbers. The fact that all the above bands have similar positions in the spectra of the methyl- and phenylmercury derivatives suggests that both compounds have a similar S-coordination.

Coordination via the NH_2 group in [HgMe(L)] shifts $\nu(\text{NH}_2)$ to slightly lower wavenumbers. This shift does not occur in the phenyl derivative, probably due to weaker NH_2 coordination.

In [HgMe(L)], bands typical of the organometallic fragment, $\rho(\text{Me})$ at 790 and $\nu(\text{Hg}-\text{C})$ at 540 cm^{-1} , are near the positions reported for other S-bonded methylmercury complexes [12]. In the phenylmercury complex, the t mode is at 265 cm^{-1} . Both complexes show a medium band near 350 cm^{-1} which may be contributed to by $\nu(\text{Hg}-\text{S})$ [12].

3.3. NMR spectra

Despite the basically molecular nature of [HgMe(L)] (see the X-ray results above), its solubility in chloroform is very poor, due possibly to the weak intermolecular $\text{Hg} \cdots \text{N}(2)^1$ interaction. Both methyl- and phenylmercury(II) derivatives are nevertheless soluble in $\text{DMSO}-d_6$, and their main NMR signals in this medium are listed in Table 5. For [HgMe(L)], the values of $^2J(^1\text{H}-^{199}\text{Hg})$ and the ^{13}C chemical shift of the HgMe group are in keeping with the mercury atom being bound to a thiolate [15]. In the spectra of both complexes, the triazole resonances show that deprotonation of the N(1,2)-H group occurs upon metallation, and confirms that the triazole shifts from the thione form towards the thiol form, increasing the shielding of

C(5) [16]. There are no significant differences between the triazolate resonances of the two complexes, suggesting that, as in the solid state, they have similar coordination. However, the persistence of the N(7)-Hg intramolecular interaction in $\text{DMSO}-d_6$ solution cannot be ascertained directly from the spectra because, although the protons of the amino group are deshielded by metallation, this might be due to the direct inductive influence of the mercury atom, or to the rearrangement of ring charge after the thione-to-thiol conversion or to the influence of hydrogen bonding that probably occurs between the $-\text{N}(7)\text{H}_2$ group and the solvent. Indeed, the fact that the coupling constant $^2J(^1\text{H}-^{199}\text{Hg})$ has a very similar value in [HgMe(L)] and in the methylmercury(II) complex with 2-thione-1,2,4-triazole [17], a donor similar to HL but lacking the $-\text{NH}_2$ group, seems to rule out $\text{N}(7) \cdots \text{Hg}$ interaction in $\text{DMSO}-d_6$ solution.

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