

Interaction of methyl- and phenyl-mercury(II) with the tripod ligand tris(2-dimethylaminoethyl)amine

Carlo A. Ghilardi, Stefano Midollini, Annabella Orlandini and Alberto Vacca

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi, 39, 50132 Firenze (Italy)

(Received date September 8, 1993)

Abstract

Reactions of $[(\text{HgR})(\text{CF}_3\text{SO}_3)]$ ($\text{R} = \text{CH}_3$ or C_6H_5) with tris(2-dimethylaminoethyl)amine (trenMe_6) give the complexes $[(\text{trenMe}_6)\text{HgR}](\text{CF}_3\text{SO}_3)$. These have been characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and the complex formation equilibria in aqueous solution between methylmercury(II) ion and trenMe_6 have been investigated. A complete X-ray analysis of the phenylmercury derivative has been carried out. The complexes appear to be five-coordinate both in the solid state and in organic solvents; potentiometric investigations also support strongly the total coordination of trenMe_6 to methyl-mercury(II) in aqueous solution.

Key words: Mercury; Polydentate

1. Introduction

Interest in organomercury(II) coordination chemistry has recently been renewed because of investigations of the mechanism of cleavage of the mercury-carbon bond in biological mercury detoxification processes. In particular a coordination number higher than 2 has been suggested in the initial uptake of the organomercurial by the enzyme active site [1].

We have recently reported that the tripod-like tris(2-diphenylphosphinoethyl)amine, np_3 , is capable of stabilizing a tetrahedral complex with methylmercury(II), in which the apical nitrogen atom of the np_3 is uncoordinated [2]. We report the syntheses and the structural characterization of the methyl- and phenylmercury(II) complexes of the related tris(2-dimethylaminoethyl)amine trenMe_6 [3], and the thermodynamic stability of the complexes it forms with methylmercury(II) ions in aqueous solution.

2. Results and discussion

Colourless crystals of $[(\text{trenMe}_6)\text{HgR}](\text{CF}_3\text{SO}_3)$ ($\text{R} = \text{Me}$, **1**; $\text{R} = \text{Ph}$, **2**), were prepared by simple reaction

of $[(\text{HgR})(\text{CF}_3\text{SO}_3)]$ with trenMe_6 (molar ratio 1:1). The complexes, which are air-stable, decompose slowly in the light, producing elemental mercury.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** and **2** (see Experimental section) in acetone solution at room temperature are quite similar, apart from the signals due to the Hg–R groups, indicating analogous structures. Both ^1H and ^{13}C resonances of the trenMe_6 show satellites arising from coupling with the ^{199}Hg nucleus. In the spectra of previously reported methylmercury(II) complexes with polydentate nitrogen-donors the spin correlations with ^{199}Hg were generally not observed, because of a rapid equilibrium $\text{HgCH}_3^+ + \text{L} \rightleftharpoons [(\text{LHgCH}_3)]^+$ [4]. The three $\text{N}(\text{CH}_3)_2$ groups of the trenMe_6 appear equivalent in **1** and **2**; moreover the values of the $J(\text{HgC})$ involving the two different CH_2 and the CH_3 carbon atoms are comparable. These findings suggest that all four nitrogen atoms are linked to the mercury. The high value of $^2J(\text{HgH})$ in the spectrum of **1** (242 compared with 265 Hz for $[(\text{HgCH}_3)(\text{CF}_3\text{SO}_3)]$ acetone as solvent) indicates that the contribution of the mercury s orbital to the nitrogen-mercury bonds is negligible [5].

The molecular structure of **2**, established by X-ray analysis, consists of complex cations $[(\text{trenMe}_6)\text{HgPh}]^+$ and CF_3SO_3^- anions. A perspective view of the cation is given in Fig. 1. Selected bond distances and angles are in Table 1.

Correspondence to: Dr. C.A. Ghilardi.

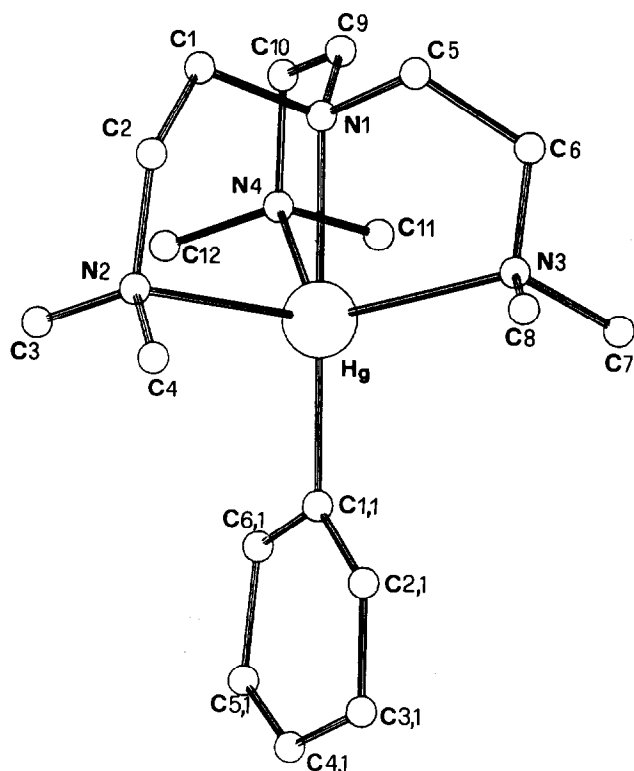


Fig. 1. PLUTO drawing of the perspective view of the complex cation [(trenMe₆)HgPh]⁺.

The mercury atom, in accordance with its tendency to linear digonal coordination, has two strong axial links (Hg–N_{ax} and Hg–C), and three considerably weaker equatorial bonds (Hg–N_{eq}). The resulting geometry can be described as an approximate trigonal bipyramid with the N_{ax}–Hg–C angle being 179.5(9)° and the N_{eq}–Hg–C angle averaging 105.7(1.5)°. The Hg–N_{ax} bond distance is consistent with the sum of covalent radii (2.27(2) versus 2.24 Å) and the Hg–C bond, somewhat shorter than expected (2.09(3) versus 2.26 Å), compares perfectly with literature data: 2.09 in [(PPh₃)HgPh] [6], 2.08 in [HgPh₂] [7], 2.09 Å in [Hg(C₆F₅)₂] [8]. The Hg–N_{eq} bond distances (av. 2.71(2) Å), much larger than the sum of covalent radii, are significantly less than the sum of the van der Waals radii (3.0 Å) [9].

TABLE 1. Selected bond distances (Å) and angles (deg)

Hg–N1	2.27(2)	Hg–N4	2.74(3)
Hg–N2	2.70(3)	Hg–C1,1	2.09(3)
Hg–N3	2.68(3)		
N1–Hg–N2	77.4(9)	N2–Hg–N4	111.0(9)
N1–Hg–N3	74.0(9)	N2–Hg–C1,1	102.8(9)
N1–Hg–N4	71.5(9)	N3–Hg–N4	122.0(9)
N1–Hg–C1,1	179.5(9)	N3–Hg–C1,1	106.2(9)
N2–Hg–N3	105.1(9)	N4–Hg–C1,1	108.0(9)

TABLE 2. Stepwise basicity constants of trenMe₆ (L) and selected formation constants of the complexes with the methylmercury(II) ion at 25°C in 0.15 mol dm⁻³ NaClO₄ (uncertainty limits are three times the standard deviations)

Reaction	log K
L + H ⁺ ⇌ HL ⁺	9.68 ± 0.01
HL ⁺ + H ⁺ ⇌ H ₂ L ²⁺	8.80 ± 0.01
H ₂ L ²⁺ + H ⁺ ⇌ H ₃ L ³⁺	7.57 ± 0.01
H ₃ L ³⁺ + H ⁺ ⇌ H ₄ L ⁴⁺	< 1.5
HgCH ₃ ⁺ + L ⇌ [LHgCH ₃] ⁺	7.62 ± 0.11
[LHgCH ₃] ⁺ + H ⁺ ⇌ [(HL)HgCH ₃] ²⁺	8.45 ± 0.06
[(HL)HgCH ₃] ²⁺ + H ⁺ ⇌ [(H ₂ L)HgCH ₃] ³⁺	8.45 ± 0.09

A comparison can be made with the related complex [(np₃)HgCH₃]⁺ [2], in which the np₃ can be regarded as derived from “trenMe₆” by replacing the equatorial amino-groups by phosphorus-groups. It has been recently described as the first example of a tetrahedrally coordinated methylmercury(II) complex because the nitrogen atom in axial position is definitely not coordinated, being 3.50 Å away [2].

Since substitution of the phenyl by the methyl group leaves the coordination polyhedron of the complexes 1 and 2 [10*] substantially unchanged, the differences between the [(np₃)HgCH₃]⁺ and [(trenMe₆)HgPh]⁺ moieties (Hg–N_{ax} 3.50 versus 2.27 Å and L_{eq}–Hg–C (av.) 118.0 versus 105.7°) seem due mainly to the different equatorial donor atoms. The better σ-donor capabilities of the phosphines play a significant role in involving the available metal orbitals in bonding/antibonding interactions.

There is therefore evidence that the tripod-like trenMe₆ is able to bind the organomercury(II) ion using all four nitrogen donor atoms, both in the solid state and in aprotic solvents. In order to determine its coordinating ability in aqueous solution as well, the formation equilibria of complexes of methylmercury(II) and trenMe₆ have been investigated using the potentiometric technique. The basicity constants of trenMe₆ were first determined. Then, using a well tested speciation procedure [11], the presence at equilibrium of three different complex species was detected: the ‘simple’ complex [(trenMe₆)HgCH₃]⁺ and two protonated complexes, [(HtrenMe₆)HgCH₃]²⁺ and [(H₂trenMe₆)HgCH₃]³⁺. No evidence of polymetal species was obtained, even in experiments with a threefold excess of methylmercury(II) with respect to trenMe₆. Selected stepwise equilibrium constants for the system are in Table 2.

As expected, trenMe₆, which contains four tertiary amine groups, is a weaker base in aqueous solution

* Reference number with an asterisk indicates a note in the list of references.

than the corresponding unsubstituted compound tris(2-aminoethyl)amine (tren) ($\log K_1 = 10.14$, $\log K_2 = 9.43$ and $\log K_3 = 8.41$ at 25° in 0.10 mol dm⁻³) [12].

The formation constant of the simple complex [(trenMe₆)HgCH₃]⁺ (7.62) is higher than that for the corresponding complex of other tertiary amines such as trimethylamine (5.03) [13]. The large difference in stability can be explained by supposing that the metal forms more than one coordinate bond with the potentially tetradentate trenMe₆.

The protonation constants of the simple and mono-protonated complexes are equal, within the calculated error limits. These values are quite high, being only about one order of magnitude smaller than the first protonation constant of the uncomplexed polyamine. Such a result is usually ascribed to the fact that the amine group which undergoes protonation is either uncoordinated or only weakly bound to the metal. Anyway, as no evidence has been found for a triprotonated complex species, it can be assumed that at least two amine groups are strongly bound to the methylmercury in all complex species. Moreover, as reported above, it was not possible to detect any poly-metal species. This further supports the assumption of complete coordination of the trenMe₆ to the methylmercury.

3. Experimental details

The compound trenMe₆ was prepared as previously described [3]. The reactions were carried out under dinitrogen. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker ACP200 spectrometer, at 200.13 and 50.33 MHz, respectively. Chemical shifts are relative to internal TMS, with down-field values reported as positive. DEPT experiments were performed to assign the ¹³C resonances.

3.1. Synthesis of 1

A solution of trenMe₆ (230 mg, 1 mmol) in 10 ml of dichloromethane was added, at room temperature, to a solution of (HgCH₃)(CF₃SO₃) (365 mg, 1 mmol) in 10 ml of the same solvent. Addition of 20 ml of heptane and evaporation of the solvent precipitated colourless crystals. These were filtered off, washed with heptane and dried in a current of dinitrogen. Yield: 480 mg (81%). Anal. Found: C, 28.15; H, 5.40; N, 9.30; Hg, 33.90; Calcd. for C₁₄H₃₃F₃HgN₄O₃S: C, 28.31; H, 5.43; N, 9.43; Hg, 33.77%. ¹H-NMR (acetone-*d*₆, 296 K): δ 3.2–3.6 (m, 12H, CH₂CH₂), 2.23 (s with sat., 18H, J(HgH) = 6.2 Hz, CH₃N), 0.60 (s with sat., 3H, ³J(HgH) = 241 Hz, HgCH₃) ppm. ¹³C{¹H}-NMR (acetone-*d*₆, 296 K): δ 122.24 (q, J(CF) = 342 Hz, CF₃), 54.3 (s with satellites, J(HgC) = 18.7 Hz,

CH₂CH₂), 54.25 (s with sat., J(HgC) = 14.5 Hz, CH₂CH₂), 44.46 (s with sat., J(HgC) = 17 Hz, CH₃N), -8.9 (s, HgCH₃) ppm.

3.2. Synthesis of 2

Complex 2 was prepared analogously using [Hg(C₆H₅)](CF₃SO₃) and a 1:1 mixture of THF and acetone in the place of (HgCH₃)(CF₃SO₃) and dichloromethane. Yield: 84%. Anal. Found: C, 34.95; H, 5.45; N, 8.40; Calcd. for C₁₉H₃₅F₃HgN₄O₃S: C, 34.72, H, 5.37, N, 8.52%. ¹H-NMR (acetone-*d*₆, 296 K): δ 8.1–6.8 (m, 5H, C₆H₅), 3.6–2.9 (m, 12H, CH₂CH₂), 2.54 (s with sat., 18H, J(HgH) = 4.6 Hz, CH₃N) ppm. ¹³C{¹H}-NMR (acetone-*d*₆, 296 K): δ 150.0 [s [14 *], C₆H₅(C_α)], 138.8 [s with sat., ²J(HgC) = 112.3 Hz, C₆H₅(C₀)], 129.7 [s with sat., ³J(HgC) = 227 Hz, C₆H₅(C_m)], 128.7 (s with sat., ⁴J(HgC) = 42.5 Hz, C₆H₅(C_p)], 122.24 (q, ¹J(CF) = 342 Hz, CF₃), 55.7 (s with sat., J(HgC) = 16.7 Hz, CH₂CH₂), 55.6 (s with sat., J(HgC) = 19.5, CH₂CH₂), 46.4 (s with sat., J(HgC) = 14 Hz, CH₃N) ppm.

3.3. Crystallography

Crystal data for 2: C₁₉H₃₅F₃HgN₄O₃S, M = 657.16, monoclinic, space group *P*2₁, *a* = 8.296(4), *b* = 14.166(6), *c* = 11.093(6) Å, β = 92.99(3)°, *U* = 1301.9 Å³, *Z* = 2, *d*_{calc} = 1.676 g cm⁻³, Mo K α radiation, λ = 0.71069 Å, μ (Mo K α) = 60.3 cm⁻¹, *F*(000) = 648; white prism (0.12 × 0.30 × 0.40 mm). Cell constants were determined from 25 carefully measured reflections. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer in the ω -2 θ scan mode to a maximum 2 θ of 45°; a scan width equal to 0.80 + 0.35 tan θ was used with a scan speed of 8.24° min⁻¹. The intensities of three standard reflections measured every two h were used to check the stability of the crystal. Of a total of 1906 measured reflections 1453 were considered observed with *I* ≥ 3 σ (*I*). The standard deviations of the observed intensities σ (*I*) were calculated by using the value of 0.03 for the instability factor *k* [15]. The intensities were corrected for Lorentz-polarization effects and for absorption [16].

The structure was solved by the heavy atom method and refined by full-matrix least-squares, the function minimized during the refinement being $\sum w(|F_o| - |F_c|)^2$, with *w* set equal to 1/ σ^2 (*F*_o); anisotropic thermal parameters were assigned to mercury and nitrogen atoms. Owing to the polarity of *P*2₁ space group, the absolute configuration of the structure was determined. At the convergence the *R* and *R*_w factors were 0.051 and 0.050 respectively. All the crystallographic calculations were performed on an HP 486 PC using the SHELX76 [17] and PLUTO [18] programs. Atomic scattering factors were taken from ref. 19. Both the

TABLE 3. Final atomic parameters

	x	y	z	U or U_{eq}
Hg	577(1)	2500	2313(1)	61(1) ^a
N1	-105(3)	376(2)	192(3)	83(18) ^a
N2	-241(3)	177(2)	253(3)	85(20) ^a
N3	104(4)	366(2)	421(3)	117(27) ^a
N4	99(3)	308(2)	0(3)	93(20) ^a
C1	-282(6)	346(4)	153(5)	123(16)
C2	-336(4)	267(4)	236(3)	102(12)
C3	-254(7)	113(5)	158(6)	151(24)
C4	-248(6)	139(3)	364(5)	134(16)
C5	-108(5)	443(3)	288(4)	120(14)
C6	48(5)	451(3)	367(4)	105(12)
C7	283(5)	381(3)	440(4)	114(15)
C8	46(6)	344(3)	538(5)	133(16)
C9	-51(6)	429(4)	90(5)	136(16)
C10	-12(7)	390(4)	-14(5)	155(18)
C11	267(5)	341(3)	-7(4)	104(12)
C12	69(7)	233(3)	-94(5)	163(23)
S	555(2)	92(1)	825(1)	140(5)
O1	419(3)	89(3)	907(3)	183(14)
O2	719(2)	69(3)	876(3)	193(15)
O3	514(5)	41(4)	703(3)	264(27)
C13	547(5)	196(4)	743(4)	385(68)
F1	609(5)	240(5)	849(3)	320(26)
F2	417(4)	248(6)	693(4)	361(27)
F3	665(5)	187(3)	660(4)	261(21)

Thermal parameters multiplied by 1000, coordinates of the mercury atom by 10000, all the others by 1000.

^a U_{eq} defined as one third of the trace of the orthogonalized thermal tensor.

$\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included in F_c calculations [20]. Final atomic parameters are reported in Table 3.

3.4. EMF measurements

All reagents were of analytical grade (Merck and BDH) and solutions were prepared with water obtained from a Millipore Milli-Q system. Potentiometric titrations were carried out with an automatic titration system consisting of an Orion digital pH meter fitted with an Orion combined glass electrode, a Hamilton motor driven automatic syringe, and a thermostatted cell, under the control of an appropriate program running on a PC [21]. Calibration of the potentiometric cell in terms of hydrogen ion concentrations was obtained from strong acid-strong base titrations using the Gran method [22]. In all measurements the titrant used was $0.100 \text{ mol dm}^{-3} \text{ NaOH}$; the temperature was maintained at $25.0 \pm 0.1^\circ\text{C}$, and the ionic strength adjusted to 0.15 mol dm^{-3} by adding NaClO_4 . The value of the ionic product of water was found to be $K_w = 1.70 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ ($\text{p}K_w = 13.770$). In a typical measurement 20 ml of a solution containing 0.1–0.2 mmol of $\text{trenMe}_6 \cdot 3\text{HClO}_4$, 0.2–0.8 mmol of an excess of HClO_4 , and variable quantities of HgCH_3OH (0–0.4

mmol) were titrated in the pH interval from 2.5 to 10.3. The potentiometric titration curves show in the absence of metal two distinct buffer regions with a sharp inflection between pH 3 and 6, resulting from the different basicities of the inequivalent amino groups of the trenMe_6 . The data were processed with the computer program SUPERQUAD [23] to obtain the equilibrium constants associated with the stepwise protonation equilibria. The titration curves obtained using varying amounts of the methylmercury(II) hydroxide exhibit evident buffer regions where complex formation occurs. The experimental data have been processed with SUPERQUAD, in order to select the best model for the complexation equilibria and to calculate the best values of the stability constants of the complexes.

A complete list of thermal parameters and bond lengths and angles has been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

This work was partially supported by the Progetto Finalizzato Chimica Fine, CNR, Rome. We are grateful to Mr. F. Cecconi and P. Innocenti for technical assistance.

References and notes

- M.J. Moore, M.D. Distefano, L.D. Zydowsky, R.J. Cummings, C.T. Walsh, *Acc. Chem. Res.*, 23 (1990) 301 and references therein.
- C.A. Ghilardi, P. Innocenti, S. Midollini, A. Orlandini and A. Vacca, *J. Chem. Soc., Chem. Commun.*, (1992) 1691.
- M. Ciampolini and N. Nardi, *Inorg. Chem.*, 5 (1966) 41; M. Ciampolini and N. Nardi, *Inorg. Chem.*, 5 (1966) 1150; M. Ciampolini, *J. Chem. Soc., Chem. Commun.*, (1966) 47.
- A.J. Canty, N. Chaichit, B.M. Gatehouse and E.E. George, *Inorg. Chem.*, 20 (1981) 4293; A.J. Canty and A. Marker, *Inorg. Chem.*, 15 (1976) 425.
- H.F. Enneke, *J. Am. Chem. Soc.*, 94 (1972) 5945.
- T.S. Lobana, M.K. Sandhu, D.C. Povey and G.W. Smith, *J. Chem. Soc., Dalton Trans.*, (1988) 2913.
- D. Grdenic, B. Kamenar and A. Nagl, *Acta Crystallogr., B*, 33 (1977) 587.
- N.R. Kunchur and M. Mathew, *J. Chem. Soc., Chem. Commun.*, (1966) 71.
- D. Grdenic, *Quart. Rev.*, 19 (1965) 303.
- A preliminary X-ray analysis on $[(\text{trenMe}_6)\text{HgCH}_3][\text{CF}_3\text{SO}_3]$ established that the conformation of $[(\text{trenMe}_6)\text{HgCH}_3]^+$ is very similar to that of the phenylmercury derivative, described in this paper. Unfortunately the crystallographic data are not of sufficient quality to allow publication of the results.
- A. Vacca, A. Sabatini and M.A. Gristina, *Coord. Chem. Rev.*, 8 (1972) 45; L. Bologni, A. Sabatini and A. Vacca, *Inorg. Chim. Acta*, 69 (1983) 71.
- J.E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, 33 (1950) 963; P. Paoletti and M. Ciampolini, *Ric. Sci.*, 33 (II-A) (1963) 405.

- 13 D.L. Rabenstein, R. Ozubko, S. Libich, C.A. Evans, M.T. Fairhurst and C. Suvanprakorn, *J. Coord. Chem.*, 3 (1974) 263; D.L. Rabenstein, *Acc. Chem. Res.*, 11 (1978) 100.
- 14 ¹⁹⁹Hg satellites were not detected due to the low intensity of the signal.
- 15 P.W.R. Corfield, R.J. Doedens and J.A. Ibers, *Inorg. Chem.*, 6 (1967) 197.
- 16 N. Walker and D. Stuart, *Acta Crystallogr. A*, 39 (1983) 158.
- 17 G.M. Sheldrick, SHELX, System of Computing Programs, University of Cambridge, UK, 1976.
- 18 S. Motherwell, PLUTO, Plotting Program for Molecular Packing Diagram, University of Cambridge, UK, 1978.
- 19 D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, UK, 1974, p. 99.
- 20 D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, UK, 1974, p. 149.
- 21 M. Fontanelli and M. Micheloni, *Proceedings of the I Spanish-Italian Congress on Thermodynamics of Metal Complexes, Peniscola, 3-6 June, 1990*.
- 22 G. Gran, *Analyst*, 77 (1952) 661.
- 23 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, (1985) 1195.