and potassium hydroxide were purchased from Mallinckrodt. Literature methods[21] served as a guide for the preparation of the elusive $K_2B_5O_8(OH)\cdot 2H_2O$. It is difficult to prepare; we found it necessary to introduce seed crystals to the supersaturated "K_2B_5" solution to prevent formation of a glass. Even this was not always successful. Identification and purity of the microcrystalline product were checked by X-ray powder crystallography.[22] The infrared spectrum is distinct from those of other potassium borates and not previously reported in the literature: 3513 m, br; 1636 w; 1445 m, sh; 1385 s; 1361 s; 1237 s; 1182 w; 1090 m; 1056 m; 979 vs; 928 s; 848 m; 820 w; 752 w; 745 w; 729 w; 702 w; 630 w; 610 w; 596 vw; 555 vw; 498 vw; 463 vw cm^{-1} (KBr disk).

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Registry No. $B(OH)_4^-$, 15390-83-7; $B_3O_3(OH)_4^-$, 17927-68-3; $B_5O_6(OH)_4^-$, 17927-69-4; ^{11}B, 14798-13-1.

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[21] (a) Carpêni, G. *C. R. Hebd. Seances Acad. Sci.* **1954**, *239*, 1500. (b) Carpêni, G.; Haladjian, J.; Pilard, M. *Bull. Soc. Chim. Fr.* **1960**, 1634.

[22] Tolédano, P. *Bull. Soc. Chim. Fr.* **1966**, 2302.

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Crystal Structure and Vibrational Spectra of $(TePh_2)HgI_2$

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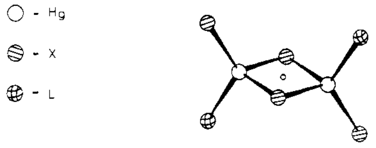
The structure of $(TePh_2)HgI_2$ has been determined by single-crystal X-ray crystallography. The compound crystallizes in the space group $P2_1/c$ with $a = 14.827$ (2) Å, $b = 13.438$ (3) Å, $c = 15.245$ (2) Å, $\beta = 90.32$ (1)°, $Z = 8$, $d_{calcd} = 3.220$ g cm^{-3}, and $d_{obsd} = 3.19$ g cm^{-3}. Intensities were measured for 3987 independent reflections ($2\theta \le 45°$), of which 2734 were classed as observed [$I \ge 2.3\sigma(I)$] and used in subsequent structure determination and refinement ($R = 0.043$). The molecule was found to exhibit a novel tetrameric structure involving two different types of iodine bridges. Low-wavenumber vibrational data for the $(TePh_2)HgX_2$ series (where X = Cl, Br, or I) were also collected and are discussed in relation to the $(TePh_2)HgI_2$ structure.

Introduction

The literature contains numerous reports of 1:1 complexes formed between mercuric halides, HgX_2 (X = Cl, Br, or I), and neutral donor ligands (L) containing group 5B (N, P, As, or Sb) and group 6B (S, Se, or Te) donor atoms.[1-29] For many years the solid-state structure of these compounds was thought to be that of a discrete dimeric halogen-bridged molecule in which Hg atoms lie in a tetrahedral environment and donor ligands lie mutually trans with respect to one another (i).



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More recent studies have indicated that in addition to the discrete dimeric arrangement[15,17,19-23] other more associated structures also occur.[15-18,24-28]

The $(2,4,6\text{-}Me_3py)HgCl_2$[24] and $(PEt_3)HgCl_2$[15,18] molecules exist as continuous chlorine-bridged chains in which mercury atoms lie in trigonal-bipyramidal environments (ii). The compounds $(C_4H_8S)HgCl_2$[27] and $(PMe_3)HgCl_2$[15,18] have "pseudoionic" structures in which $[L\text{-}Hg\text{-}Cl]^+$ and Cl^- "ions" are alternately arranged giving rise to continuous chlorine-bridged chains (iii). The α-form of $(P\text{-}n\text{-}Bu_3)HgCl_2$, in the

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[1] Dean, P. A. W. *Prog. Inorg. Chem.* **1978**, *24*, 109.

[2] Evans, R. C.; Mann, F. G.; Peiser, H. S.; Purdie, D. *J. Chem. Soc.* **1940**, 1209.

[3] (a) Ahuja, I. S.; Rastogi, P. *J. Chem. Soc. A* **1970**, 2161. (b) Ahuja, I. S.; Singh, R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1505.

[4] Bernard, M. A.; Busnot, F.; Lequerler, J. F. *Thermochim. Acta* **1975**, *12*, 387.

[5] Moers, F. G.; Langhout, J. P. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 996.

[6] Coates, G. E.; Ridley, D. *J. Chem. Soc.* **1964**, 166.

[7] Deacon, G. B.; Green, J. H. S.; Harrison, D. J. *Spectrochim. Acta, Part A* **1968**, *24A*, 1921.

[8] Schmidbaur, H.; Rathlein, K. H. *Chem. Ber.* **1973**, *106*, 2491.

[9] Alyea, E. C.; Skelton, D. A.; Goel, R. G.; Ogini, W. G. *Can. J. Chem.* **1977**, *55*, 4227.

[10] Biscarni, P.; Nivellini, G. D. *J. Chem. Soc. A* **1969**, 2206.

[11] Ferguson, J. E.; Loh, K. S. *Aust. J. Chem.* **1973**, *26*, 2615.

[12] (a) Marcotrigiano, G.; Battistuzzi, R. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 969. (b) Marcotrigiano, G.; Peyronel, G.; Battistuzzi, R. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1675. (c) Marcotrigiano, G. *Z. Anorg. Allg. Chem.* **1975**, *417*, 75. (d) Marcotrigiano, G. *Ibid.* **1976**, *422*, 80. (e) Marcotrigiano, G.; Battistuzzi, R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 3719.

[13] Aitken, G. B.; Duncan, J. L.; McQuillan, G. P. *J. Chem. Soc., Dalton Trans.* **1972**, 2103.

[14] Dance, N. S.; Jones, C. H. W. *J. Organomet. Chem.* **1978**, *152*, 175.

[15] Bell, N. A.; Goldstein, M.; Jones, T.; Nowell, I. W. *J. Chem. Soc., Chem. Commun.* **1976**, 1039.

[16] Bell, N. A.; Goldstein, M.; Jones, T.; Nowell, I. W. *Inorg. Chim. Acta* **1978**, L169.

[17] (a) Bell, N. A.; Goldstein, M.; Jones, T.; Nowell, I. W. *Inorg. Chim. Acta* **1980**, *43*, 87. (b) The weakness of interdimer interaction in α-$(P\text{-}n\text{-}Bu_3)HgCl_2$ is perhaps confirmed by the fact that the β-form reported in ref 19 exists as a discrete centrosymmeric dimer of similar geometry.

[18] (a) Bell, N. A.; Goldstein, M.; Jones, T.; Nowell, I. W. *Inorg. Chim. Acta* **1981**, *48*, 185. (b) It has been established for the $(PR_3)HgCl_2$ series (where R = Ph, *n*-Bu_3, Et, or Me) that the P-Hg-Cl_s angle is dependent mainly upon donor strength of the PR_3, rather than on secondary packing effects.

[19] Bell, N. A.; Goldstein, M.; Jones, T.; March, L. A.; Nowell, I. W. *Inorg. Chim. Acta* **1982**, *61*, 83.

[20] Glasser, L. S.; Ingram, L.; King, M. G.; McQuillan, G. P. *J. Chem. Soc. A* **1969**, 2501.

[21] Brotherton, P. D.; Epstein, J. M.; White, A. H.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1974**, 2341.

[22] Holy, N. L.; Baenziger, N. C.; Flynn, R. M.; Swenson, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 7823.

[23] Authier-Martin, M.; Beauchamp, A. L. *Can. J. Chem.* **1977**, *55*, 1213.

[24] Kulpe, S. *Z. Anorg. Allg. Chem.* **1967**, *349*, 314.

[25] Bell, N. A.; Goldstein, M.; Jones, T.; Nowell, I. W. *Acta Crystallogr., Sect. B* **1980**, *B36*, 710.

[26] Authier-Martin, M.; Hubert, J.; Rivest, R.; Beauchamp, A. L. *Acta Crystallogr., Sect. B* **1978**, *B34*, 273.

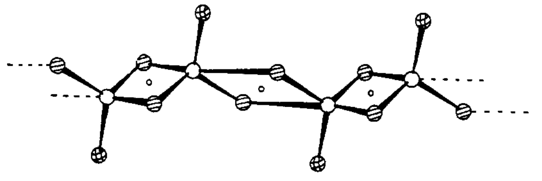
[27] Branden, C. I. *Ark. Kemi* **1964**, *22*, 495.

[28] Kozarek, J.; Fernando, Q. *Inorg. Chem.* **1973**, *12*, 2129.

[29] Dalziel, J. A. W.; Holding, A. F. C.; Watts, B. E. *J. Chem. Soc. A* **1967**, 358.

[30] Beurskens, P. T.; Bosman, W. P. J. H.; Cras, J. A. *J. Cryst. Mol. Struct.* **1972**, *95*, 157.

[31] White, J. G. *Acta Crystallogr.* **1963**, *16*, 397.



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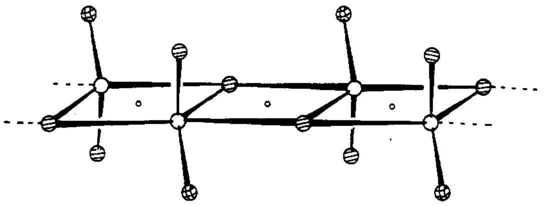
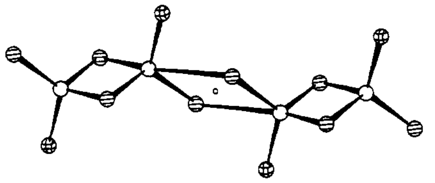


iii

strict crystallographic sense, is a tetramer consisting of two weakly held unsymmetric dimers[16,17] (iv), (guanosine-N^7)-$HgCl_2$ gives rise to a continuous $[Cl-Hg-Cl-Hg]_n$ chain in which each Hg atom lies in an irregular 4-coordinate environment[26] (v).



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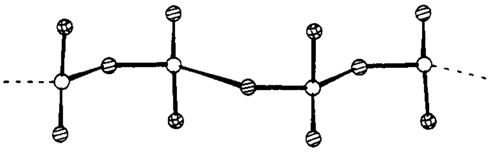
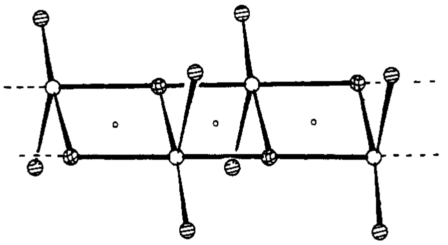


v

In addition to these halogen-bridged structures, in the compound (dehydrodithizone)$HgCl_2$ the donor atom becomes the bridge atom and a sulfur-bridged polymer results[28] (vi).



vi

With the data currently available, it has been possible for the chloro compounds to rationalize observed structure in terms of steric and electronic properties of donor ligands.[18] Preliminary single-crystal X-ray photographic studies indicate that often the equivalent bromo compounds behave similarly.[17,18,25,29] Little definitive data, however, is available for the iodo analogues apart from the incomplete structure of $(AsEt_3)HgI_2$[2] and the preliminary single-crystal photographic study of $(PPh_3)HgI_2$;[17] these studies infer dimeric structures.

To bolster present information on the iodo compounds, in this paper we report the structure of $(TePh_2)HgI_2$. As far as we are aware, this is the first report of a 1:1 $(L)HgX_2$ structure in which Te is the donor atom. The ^{125}Te Mössbauer and the Raman spectra of this compound and a series of other $(TeR_2)HgX_2$ complexes have previously been reported.[14] It should be noted that, on resynthesis of $(TePh_2)HgI_2$, two compounds of different stoichiometry, namely $(TePh_2)HgI_2$ and $(TePh_2)_2HgI_2$, could be isolated. Re-examination of the Raman spectrum of the 1:1 complex indicates that the previously reported spectrum was in fact due to a mixture of the 2:1 and 1:1 compounds. Raman data (400–50 cm^{-1}) has been recollected for the complete $(TePh_2)HgX_2$ (X = Cl, Br, or I) series, and in addition, the far-IR study has been repeated at low temperature (ca. 100 K) over an extended wavenumber range (down to 70 cm^{-1}). Interpretation of these spectra are made in light of the $(TePh_2)HgI_2$ crystal structure.

Table I. Crystal Data

compd	(diphenyltelluro)diiodomercury(II)
fw	736.21
formula	$C_{12}H_{10}HgI_2Te$
space group	$P2_1/c$
a, Å	14.827 (2)
b, Å	13.438 (3)
c, Å	15.245 (2)
β, deg	90.32 (1)
V, Å^3	3037.5
Z	8
d_{obsd}, g cm^{-3}	3.19
d_{calcd}, g cm^{-3}	3.220
cryst dimens, mm	0.06 × 0.13 × 0.10
μ, cm^{-1}	160.24

Experimental Section

X-ray Structure Determination and Refinement. The crystal data may be found in Table I. A crystal suitable for data collection was mounted in a Lindemann glass capillary tube. Weissenberg and precession photographs were used to obtain approximate cell dimensions and to uniquely define the space group as $P2_1/c$ ($h0l$ present for $l = 2n$; $0k0$ present for $k = 2n$). Accurate cell dimensions were determined by least-squares refinement of 38 accurately centered reflections ($2\theta = 24.9–29.9°$; λ(Mo Kα) = 0.709 26 Å). Data were collected by using an automatic Picker FACS-I four-circle diffractometer with a graphite monochromator and a scintillation counter with pulse height discrimination. The takeoff angle was 3°, and a symmetrical θ–2θ scan (2°/min) of $(1.5 + 0.692 \tan \theta)°$ was used. Stationary-crystal, stationary-counter background counts of 10% of the scan time were taken at each side of the scan. The peak profile of each reflection was analyzed and used to derive its intensity and associated error.[32] Intensity measurement of two standards every 70 reflections showed no evidence of crystal deterioration nor unstability of the detection chain.

Intensities were measured for 3987 independent reflections ($2\theta \leq 45°$), of which 2734 were classed as observed [$I \geq 2.3\sigma(I)$]. Lorentz and polarization corrections have been made. An absorption correction[34], based upon the method of Gaussian quadrature,[37] has also been applied; transmission coefficients varied from 0.040 to 0.168.

The heavy atoms were located by using MULTAN. All carbon atoms were located in successive difference Fourier syntheses. The hydrogen atoms of the phenyl rings were included in refinement as fixed contributions in their calculated positions with isotropic temperature factors related to those of their parent carbon atoms.

Block-diagonal least-squares refinement, with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for hydrogen atoms, gave final agreement factors of $R = 0.043$ ($R = \sum||F_o| - |F_c||/\sum|F_o|$) and $R_w = 0.055$ [$R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$] for 289 variables.

Analysis of the data as a function of $(\sin \theta)/\lambda$ and Miller indices indicated that a weighting scheme of the form $w = 1/\sigma^2(F_o) + (kF_o)^2$ (where $k = 0.03$) should be applied.

Atomic scattering factors, including anomalous dispersion, were taken from ref 33. The computer programs used here were from ref 34. Final positional parameters are given in Table II. Thermal parameters and structure factor tables have been deposited as supplementary material.

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(32) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1977**, *11*, 114.

(33) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(34) Gabe, E. J.; Larson, A. C.; Lee, F. L.; Wong, Y. "The NRC pdp-8e Crystal Structure System"; Chemistry Division, NRC: Ottawa, Canada, 1979.

(35) Kessler, K. Ph.D. Thesis, University of Bristol, 1977.

(36) Bell, N. A.; Goldstein, M.; Jones, T.; Nowell, I. W., unpublished results.

(37) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180.

Table II. Final Positional Parameters for $(TePh_2)HgI_2$[a]

	x	y	z	B_{iso}[b]
Hg(1)	0.12599 (4)	0.00889 (5)	0.05020 (5)	4.43 (3)
Hg(2)	0.31744 (4)	0.26080 (5)	0.14038 (5)	4.09 (3)
I(1)	−0.02292 (7)	−0.12344 (8)	0.07911 (8)	3.63 (5)
I(2)	0.15860 (6)	0.11882 (8)	0.19805 (7)	3.59 (5)
I(3)	0.32086 (8)	0.38050 (9)	0.28172 (9)	4.89 (6)
I(4)	0.44823 (7)	0.13424 (10)	0.09035 (9)	4.68 (6)
Te(1)	0.27862 (6)	−0.06990 (8)	−0.02488 (7)	3.47 (5)
Te(2)	0.22764 (6)	0.32844 (8)	−0.01173 (7)	3.72 (5)
C(1)	0.3137 (8)	−0.1742 (12)	0.0769 (10)	3.2 (7)
C(2)	0.3971 (10)	−0.1651 (13)	0.1162 (11)	4.2 (9)
C(3)	0.4237 (10)	−0.2396 (13)	0.1736 (12)	4.6 (9)
C(4)	0.3667 (11)	−0.3117 (14)	0.1943 (12)	4.7 (9)
C(5)	0.2792 (10)	−0.3204 (13)	0.1555 (10)	4.1 (8)
C(6)	0.2545 (9)	−0.2478 (11)	0.0984 (10)	3.3 (7)
C(7)	0.2141 (10)	−0.1821 (11)	−0.1057 (10)	3.3 (7)
C(8)	0.2665 (10)	−0.2597 (11)	−0.1252 (12)	3.7 (8)
C(9)	0.2298 (11)	−0.3381 (14)	−0.1777 (11)	4.4 (8)
C(10)	0.1417 (10)	−0.3247 (14)	−0.2089 (11)	4.7 (9)
C(11)	0.0924 (10)	−0.2435 (12)	−0.1883 (11)	3.9 (8)
C(12)	0.1280 (10)	−0.1729 (23)	−0.1381 (10)	3.7 (8)
C(13)	0.1461 (8)	0.4410 (11)	0.0462 (10)	3.1 (7)
C(14)	0.1120 (10)	0.4289 (12)	0.1297 (11)	3.6 (8)
C(15)	0.0577 (10)	0.5064 (13)	0.1630 (11)	4.3 (8)
C(16)	0.0383 (9)	0.5886 (12)	0.1161 (10)	3.3 (7)
C(17)	0.0716 (9)	0.5967 (11)	0.0338 (11)	3.6 (7)
C(18)	0.1245 (8)	0.5227 (11)	−0.0030 (11)	3.6 (7)
C(19)	0.3321 (8)	0.4298 (10)	−0.0545 (9)	2.6 (6)
C(20)	0.3549 (9)	0.5081 (11)	0.0019 (11)	3.4 (7)
C(21)	0.4156 (9)	0.5767 (11)	−0.0275 (11)	3.6 (8)
C(22)	0.4519 (10)	0.5629 (13)	−0.1114 (12)	4.6 (9)
C(23)	0.4305 (11)	0.4866 (14)	−0.1672 (12)	4.7 (9)
C(24)	0.3666 (10)	0.4155 (12)	−0.1350 (11)	3.8 (8)

[a] Esd's refer to the last digit printed. [b] $B_{iso} = 8\pi^2(U_{11}^2 + U_{22}^2 + U_{33}^2)^{1/2}$; units Å^2.

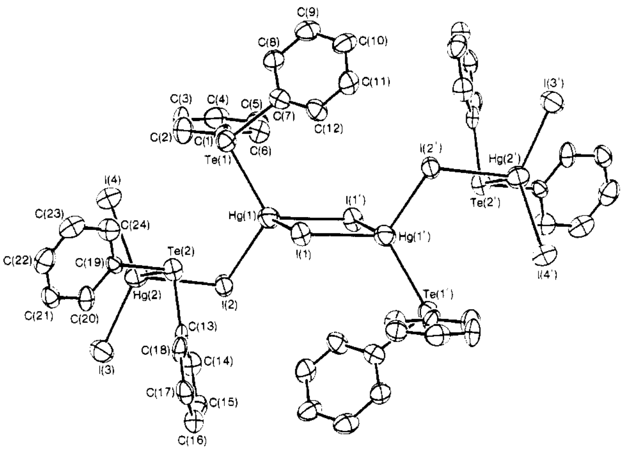

Figure 1. Molecular structure and labeling scheme for $(TePh_2)HgI_2$ (ORTEP diagram; 50% probability contours for all atoms).

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $(TePh_2)HgI_2$[a]

	Distances		
Hg(1)–I(1)	2.871 (1)	Hg(2)–I(2)	3.159 (1)
Hg(1)–I(1′)	2.925 (1)	Hg(2)–I(3)	2.689 (1)
Hg(1)–I(2)	2.736 (1)	Hg(2)–I(4)	2.693 (1)
Hg(1)–Te(1)	2.753 (1)	Hg(2)–Te(2)	2.818 (1)
Te(1)–C(1)	2.15 (2)	Te(2)–C(13)	2.13 (2)
Te(1)–C(7)	2.17 (1)	Te(2)–C(19)	2.17 (1)
	Angles		
I(1)–Hg(1)–I(1′)	91.72 (3)	I(2)–Hg(2)–I(3)	98.57 (4)
I(1)–Hg(1)–I(2)	109.91 (4)	I(2)–Hg(2)–I(4)	103.68 (4)
I(1)–Hg(1)–Te(1)	117.40 (4)	I(2)–Hg(2)–Te(2)	94.26 (4)
I(1′)–Hg(1)–I(2)	111.12 (4)	I(3)–Hg(2)–I(4)	126.46 (5)
I(1′)–Hg(1)–Te(1)	110.47 (4)	I(3)–Hg(2)–Te(2)	118.24 (4)
I(2)–Hg(1)–Te(1)	114.09 (4)	I(4)–Hg(2)–Te(2)	107.96 (4)
Hg(1)–I(1)–Hg(1′)	88.28 (4)	Hg(1)–I(2)–Hg(2)	103.03 (4)
C(1)–Te(1)–C(7)	93.5 (6)	C(13)–Te(2)–C(19)	95.0 (5)
Hg(1)–Te(1)–C(1)	98.4 (4)	Hg(2)–Te(2)–C(13)	98.9 (4)
Hg(1)–Te(1)–C(7)	98.2 (4)	Hg(2)–Te(2)–C(19)	96.6 (4)

[a] Detailed bond parameters for the phenyl rings have been deposited as supplementary data [C–C(phenyl) distances range from 1.32 (1)–1.43 (2) Å; C–C–C(phenyl) angles range from 116 (1) to 125 (2)°].

Preparative Methods. The compounds $(TePh_2)HgX_2$ (X = Cl, Br, or I) were prepared by mixing equimolar quantities of HgX_2 and $TePh_2$ solutions in ethanol. For HgI_2, however, $(TePh_2)_2HgI_2$ is obtained if $TePh_2$ is present in excess. Anal. Calcd for X = Cl: C, 26.05; H, 1.82. Found: C, 25.77; H, 1.69. Calcd for X = Br: C, 22.44; H, 1.57. Found: C, 22.19; H, 1.55. Calcd for X = I: C, 19.58; H, 1.37. Found: C, 18.89; H, 1.09.

Spectroscopic Procedures. Raman spectra were measured with the Spex Ramalog 5 spectrometer (University of British Columbia), equipped with an argon ion laser (514.5 nm). All samples were powders.

Far-infrared data were collected on the Nicolet 7199 interferometer (University of Bristol). Powdered samples were studied as pressed disks in polyethylene. Low temperature (ca. 100 K) were achieved with use of a liquid-nitrogen cell.

Description and Discussion of Structure

The molecular structure and numbering scheme is shown in Figure 1, while important bond parameters are given in Table III. The geometries of the $TePh_2$ ligands appear normal, and bond information has been deposited as supplementary material.

The molecule is a centrosymmetric tetramer that contains two symmetry-independent, but geometrically similar, $(TePh_2)HgI_2$ units per molecule (Figure 1). The atom Hg(1) is situated in a roughly tetrahedral coordination environment [91.72 (3)–117.40 (4)°], bonding to three bridging I atoms at distances of 2.736 (1), 2.871 (1), and 2.925 (1) Å and a terminal Te atom at 2.753 (1) Å. The coordination environment aroung Hg(2) appears to be intermediate between tetrahedral and trigonal pyramidal. There are three terminal bonds viz. Hg(2)–I(3) at 2.689 (1) Å, Hg(2)–I(4) at 2.693 (1) Å, and Hg(2)–Te(2) at 2.818 (1) Å, and a relatively long bridge bond between Hg(2) and I(2) at 3.159 (1) Å. The "tetrahedral" angles vary from 94.26 (4)° for I(2)–Hg(2)–Te(2) to 126.46 (5)° for I(3)–Hg(2)–I(4), while the sum of the angles constituting the "trigonal" plane range from 107.96 (4)° for I(4)–Hg(2)–Te(2) to 126.46 (5)° for I(3)–Hg(2)–I(4) [Hg(2) in fact lies 0.427 Å out of the plane made by I(3), I(4), and Te(2)].

The mode and extent of Hg–I bridging in this molecule is, as far as we know, unique, although another quite different tetrameric arrangement has been reported for α-(P-*n*-Bu_3)-$HgCl_2$[16,17] (iv). There are two types of bridging I atoms: (a) I(1) and the centrosymmetrically related I(1′), which both link the same two Hg atoms enclosed in a four-membered ring and (b) I(2) and I(2′) both of which bridge two Hg atoms in an open arrangement. The Hg–I–Hg angles for the two configurations are 88.28 (4) and 103.03 (4)°, respectively.

The central moiety of the molecule (vii), involving I(1) and I(1′), resembles the dimeric iodine-bridged species $[S_3C_2N_2Et_4]^{2+}[Hg_2I_6]^{2-}$[30] and (cyclopentadienylide)HgI_2,[22] whereas the open I-bridged arrangement involving I(2) at the periphery of the molecule is reminiscent of the bridging found in the "polymeric" structures $[NMe_4][HgBr_3]$[31] and (guanosine-N^7)$HgCl_2$.[26] It is interesting to speculate as to why the

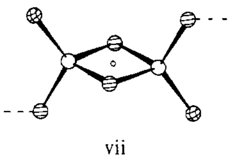

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Table IV. Low-Temperature (ca. 100 K) Far-Infrared and Raman Spectral Data (cm^{-1}) for $(TePh_2)HgX_2$ (X = Cl, Br, or I)

Cl		Br		I		
IR	Ra	IR	Ra	IR	Ra	assgnt[b]
284 s	285 m	194 s	192 s	155 s	159 mw	$\nu(HgX)_t$
276 s						
227 s[a]	230 m[a]	152 m	158 sh	133 s	131 s	$\nu(HgX)_b$
223 s[a]		140 m				
		137 sh				
				126 s		
152 m	134 s	129 m	127 vs	103 s	111 vs	
		124 m				
		115 m		99 s		
		112 m				
133 sh	100 s	107 m	58 s		58 sh	bending and lattice modes
126 m	60 s	99 sh				
119 sh		90 w				
115 sh		85 w				
112 vs		80 w				
108 s		74 m				
102 vs						
96 s						
269 s	276 sh	272 m	273 w	267 s	269 w	internal modes of $TePh_2$
264 sh	259 m	260 s	260 m	257 s	259 w, sh	
259 s						
241 m	240 sh	244 w			240 w	
227 s	221 sh	230 w	225 w, br	226 m	224 w	
223 s						
214 m		219 w		213 w		
189 w	189 sh			206 w		
179 w	180 w			183 m		

[a] These bands probably contain some contribution from internal ligand modes. [b] Assignment of terminal and bridge modes applies strictly to $(TePh_2)HgI_2$; see text for further detail concerning chloro and bromo compounds.

$(TePh_2)HgI_2$ molecule exhibits the open-bridged arrangement at the periphery of the molecule, as it does, and also why it does not associate beyond the tetramer stage.

In examples of $(L)HgX_2$ compounds where association beyond the dimer stage occurs, there are two factors that appear to be common, i.e., relatively large $L-Hg-X_s$ angles[18b] (where $Hg-X_s$ is the shortest Hg–X bond) and relatively small ligands. For example, the $P-Hg-Cl_s$ angles for $(PMe_3)HgCl_2$[18] and $(PEt_3)HgCl_2$[18] for which the donor ligands are also quite small, are 162.1 (1) and 145.4 (3)°, respectively, giving rise to a continuous structure containing triply bridging Cl atoms in the case of the former (iii) and a polymeric chain involving doubly bridged Cl atoms in the case of the latter (ii). In α-(P-*n*-Bu_3)$HgCl_2$,[17] where $P-Hg-Cl_s$ values are 147.8 (7) and 150.6 (7)° and the ligand is potentially flexible but fairly bulky, a "tetramer" is formed between two weakly held dimers (iv). When $L-Hg-Cl_s$ is relatively small (e.g., 127–136°) and the ligand is quite bulky (as when L = PPh_3,[17] 1,2,5-triphenylphosphole,[17] $SePPh_3$,[20] or methylpyrrolidine-1-carbodithioate[21]), dimeric structures result.

Consideration of the central region of $(TePh_2)HgI_2$ (vii) indicates that the Te(1)–Hg(1)–I(2) angle of 114.09 (4)° is relatively small. This value when considered together with the bulk of the $TePh_2$ ligand is certainly not conducive to the associated structures formed by $(PR_3)HgCl_2$ (where R = Me, Et, or *n*-Bu_3). On the other hand, the combination of Te(1)–Hg(1)–I(2) angle and ligand size is not such that association is limited to a dimer, instead I(2) and I(2′) behave as bridges in an open arrangement extending the molecule by a monomer at each end. Further association beyond the tetramer stage is apparently hindered by the orientation of the $TePh_2$ ligand, which one assumes is required for steric reasons by the central region of the molecule.

The shortest Hg–I distances observed in the molecule, not surprisingly, are those between Hg(2) and the unbridged atoms I(3) and I(4) at 2.689 (1) and 2.693 (1) Å, respectively. The longer Hg(2)–Te(2) distance of 2.818 (1) Å compared with 2.753 (1) Å for Hg(1)–Te(1) probably originates from these stronger Hg–I interactions.

Low-Wavenumber Vibrational Spectra

The vibrational data presented here for $(TePh_2)HgX_2$ (X = Cl, Br, or I) have been improved over those previously reported[14] by extending the wavenumber range for far-IR spectra from 200 down to 70 cm^{-1}. Furthermore, the IR data in this work were recorded at low temperature (ca. 100 K) with the result that peak widths are narrower, thus revealing considerably more spectral detail than obtained at room temperature. The room-temperature Raman spectra of the chloro and bromo compounds are as previously reported,[14] but as already mentioned, the spectra of $(TePh_2)HgI_2$ were previously in error. Table IV contains new assignments based upon the now known structure of $(TePh_2)HgI_2$ and some of the more recent spectroscopic studies of $(L)HgX_2$ compounds.[5,8,9,19,35,36] The internal modes of the $TePh_2$ ligand are extremely prevalent in the region 280–180 cm^{-1} in both IR and Raman spectra and interfere with $\nu(HgX)$ assignment, especially for the case where X = Cl. Nonetheless, we are reasonably confident that these modes have been correctly assigned. Consider first $(TePh_2)HgI_2$, a tetrameric molecule belonging to the C_i point group. Point-group analysis predicts the following $\nu(HgTe)$ and $\nu(HgI)$ modes (assuming $TePh_2$ to be a point mass):

$$\Gamma(\nu(HgTe)) = 2\ A_g\ (Ra) + 2\ A_u\ (IR)$$

$$\Gamma(\nu(HgI)_t) = 2\ A_g\ (Ra) + 2\ A_u\ (IR)$$

$$\Gamma(\nu(HgI)_b) = 4\ A_g\ (Ra) + 4\ A_u\ (IR)$$

As Table IV shows, assignment of all these modes was impossible; the Raman spectrum in particular shows only three definite bands compared with the eight predicted. Accidental coincidences of this type do not seem unreasonable when one considers that all the "TeHgI" skeletal modes are expected to be compressed between 160 and 70 cm^{-1}. Low-temperature

Raman spectra could possibly alleviate this problem. Regardless, the bands at 159 (Ra) and 155 cm^{-1} (IR) are assigned to one of the two $\nu(\mathrm{HgI})_t$ modes associated with vibration of the two terminal, and also shortest, Hg–I bonds; the second IR- and Ra-active $\nu(\mathrm{HgI})_t$ modes are possibly accidentally coincident with the first pair. The bands at 131 and 111 cm^{-1} in the Raman spectrum and 133, 126, 103, and 99 cm^{-1} in the IR spectrum are assigned to $\nu(\mathrm{HgI})_b$ modes.[5,8,9,19,35,36] The wavenumber positions of all these modes lie in ranges consistent with more recent $\nu(\mathrm{HgI})_t$ and $\nu(\mathrm{HgI})_b$ assignments. It is worthwhile noting that these spectra, particularly at room temperature, could quite reasonably have been interpreted as those of a discrete dimeric molecule, therefore serving as a warning against the use of such data for structural prediction without first some very careful consideration.

Examination of the gross features of the $(\mathrm{TePh_2})\mathrm{HgBr_2}$ spectra suggested a different structure to that of the iodo compound. The IR spectrum is particularly curious in the region 152–99 cm^{-1}, where a large number of bands can be assigned $\nu(\mathrm{HgBr})_b$, whereas the Raman spectrum in contrast is very simple with $\nu(\mathrm{HgBr})_b$ modes assigned at 158 and 127 cm^{-1}. The bands at 192 (Ra) and 194 cm^{-1} (IR) can confidently be assigned to $\nu(\mathrm{HgBr})$ modes associated with relatively short Hg–Br bond(s). No firm structural proposal can be made other than to tentatively predict a complicated bridging system.

Although hindered by the presence of internal modes of the $\mathrm{TePh_2}$ ligand, $\nu(\mathrm{HgCl})$ modes have been assigned. The bands at 284 (IR) and 276 cm^{-1} (IR) almost certainly arise from $\nu(\mathrm{HgCl})$ modes associated with relatively short Hg–Cl bonds; the Ra band at 285 cm^{-1} no doubt has similar origins. Bands associated with $\nu(\mathrm{HgCl})_b$ are assigned at 230 and 134 cm^{-1} in the Raman spectrum and 227, 223, and 152 cm^{-1} in the IR spectrum. Unfortunately no firm structural proposal can be made.

Assignment of $\nu(\mathrm{HgTe})_t$ modes is difficult in view of their nonexistence in the literature and the absence of any obvious halogen-mass independent bands in the $(\mathrm{TePh_2})\mathrm{HgX_2}$ spectra. Considering the effective mass of Te, when attached to two phenyl groups, and the position of $\nu(\mathrm{HgP})_t$ modes in $(\mathrm{PAr_3})\mathrm{HgX_2}$ (X = Cl, Br, or I; Ar = $\mathrm{C_6H_6}$[36] or o-$\mathrm{CH_3C_6H_5}$[9]), which have been tentatively assigned in the 140-cm^{-1} region, one may speculate that the present $\nu(\mathrm{HgTe})_t$ modes lie below this value. Unfortunately, this is an especially complicated region in our spectra.

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Registry No. $(\mathrm{TePh_2})\mathrm{HgI_2}$, 87509-57-7; $[(\mathrm{TePh_2})\mathrm{HgI_2}]_4$, 87509-60-2; $(\mathrm{TePh_2})\mathrm{HgCl_2}$, 87509-58-8; $(\mathrm{TePh_2})\mathrm{HgBr_2}$, 87509-59-9.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom positions and temperature factors, bond distances and angles, and observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Structure, Magnetism, and Mössbauer Spectrum of the Five-Coordinate Complex Chlorobis(*N*-methylbenzothiohydroxamato)iron(III)

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A detailed study of the structural, magnetic, ESR, and Mössbauer spectroscopic properties of a five-coordinate iron(III) thiohydroxamate complex has been made. The complex, chlorobis(*N*-methylbenzothiohydroxamato)iron(III), contains two trans bidentate {SO} donor groups and one Cl atom in each mononuclear unit and has bond distances Fe–Cl = 2.221 (2) Å, Fe–S = 2.389 (2) Å (average), and Fe–O = 1.946 (3) Å. This high-spin d^5 molecule has an overall ligand field strength provided by the $\{\mathrm{S_2O_2Cl}\}$ donor set similar to that in related β-diketonate $\{\mathrm{O_4Cl}\}$ complexes but weaker than that in intermediate-spin dithiocarbamate $\{\mathrm{S_4Cl}\}$ species. Magnetic moment measurements between 4.2 and 300 K are generally consistent with the presence of large zero-field splitting effects although the decrease in μ_{Fe} at low temperatures is unusually rapid. In line with the low molecular symmetry and observation of $g = 4.3$ and 9.9 ESR spectral lines, a spin-Hamiltonian analysis, which includes rhombic and axial components, was carried out. The best-fit parameters were $D = 10 \pm 0.5$ cm^{-1} and $E = 3 \pm 0.5$ cm^{-1}. Weak antiferromagnetic coupling ($J = -0.1 \pm 0.05$ cm^{-1}) was also evident in the low-temperature susceptibility data and possibly occurs via a {Fe–Cl···Cl–Fe} superexchange pathway. Exchange coupling of this kind is common among other chloro–iron(III) chelate complexes containing a variety of oxygen, nitrogen, or sulfur donor groups. Zero-field Mössbauer spectra measured between 4.2 and 300 K on the present complex support the $S = {}^5/_2$ spin-state assignment and show unusual temperature-dependent area and peak height asymmetry. Applied magnetic field spectra at 4.2 K confirm the large and positive zero-field splitting of the $^6A_1$ ground state.

Introduction

Our recent studies of thiohydroxamate complexes of iron(III) afforded both bis- and tris-chelated species.[2,3] The properties of the tris chelate have been described in detail, and it is the purpose of this paper to report the results of a structural and electronic investigation on a representative bis chelate, chlorobis(*N*-methylbenzothiohydroxamato)iron(III) (labeled I). The compound has the formula $[\mathrm{Fe(PhCSNMeO)_2Cl}]$.

This five-coordinate complex is an example of a class of iron(III) compounds of general formulas [Fe(bidentate)$_2$X] and [Fe(tetradentate)X]. It is the first of such species containing the donor atoms {SO} within the chelate ligand although the tris complex $[\mathrm{Fe(PhCSNMeO)_3}]$ is well-known. Other donor sets that are known include {SS} in dithiocarbamates,[4] {OO} in β-diketonates,[5] {ON} in 8-hydroxy-

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[2] Mitchell, A. J.; Murray, K. S.; Newman, P. J.; Clark, P. E. *Aust. J. Chem.* **1977**, *30*, 2439.

[3] Murray, K. S.; Newman, P. J.; Gatehouse, B. M.; Taylor, D. *Aust. J. Chem.* **1978**, *31*, 983.

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