Table III. Structural Trans Influence in Pt(II) and Pd(II) Complexes

$$\mathrm{L'{-}\overset{|}{\underset{|}{M}}{-}L}$$

Compound	L′	L	M–L, Å	Δ(M–L),[a] Å	Ref
$PtCl_4^{2-}$	Cl	Cl	2.308 (2)		*b*
$PdCl_4^{2-}$	Cl	Cl	2.313 (2)		*b*
trans-$Pt(P(C_2H_5)_3)\{C(NC_6H_5CH_2)_2\}Cl_2$	Cl	Cl	2.31 (1)		*c*
trans-$Pt(P(C_6H_5)_2(C_2H_5))_2HCl$	H	Cl	2.422 (9)	0.11	*d*
cis-$Pt(P(CH_3)_3)_2Cl_2$	P	Cl	2.376 (8)	0.07	*e*
cis-$Pt(P(C_2H_5)_3)\{C(NHC_6H_5)(OC_2H_5)\}Cl_2$	P	Cl	2.368 (7)	0.06	*f*
cis-$Pt(CNC_2H_5)[P(C_2H_5)_2(C_6H_5)]Cl_2$	P	Cl	2.390 (8)	0.08	*g*
	CNR	Cl	2.314 (10)	0.00	*g*
cis-$Pt(CNC_6H_5)_2Cl_2$	CNR	Cl	2.309 (5)	0.00	*g*
cis-$Pt(P(C_2H_5)_3)\{C(NHC_6H_5)(OC_2H_5)\}Cl_2$	$C(sp^2)$	Cl	2.365 (5)	0.06	*f*
$Pd(C_2N_4H_4(CH_3)_2)Cl_2$	$C(sp^2)$	Cl	2.387 (1)	0.08	*h*
cis-$Pt(P(CH_3)_3)_2Cl_2$	Cl	P	2.247 (7)		*e*
cis-$Pt(CNC_2H_5)[P(C_2H_5)_2(C_6H_5)]Cl_2$	Cl	P	2.244 (8)		*g*
trans-$Pt(P(C_2H_5)_3)_2Br_2$	P	P	2.315 (4)	0.07	*i*
$Pd(C_2N_4H_4(CH_3)_2)Cl_2$	Cl	$C(sp^2)$	1.948 (5)		*h*
cis-$Pt(P(C_2H_5)_3)\{C(NHC_6H_5)(OC_2H_5)\}Cl_2$	Cl	$C(sp^2)$	1.98 (2)		*f*
$Pt(CNCH_3)_2(C_5H_{11}N_4)^+$	$CNCH_3$	$C(sp^2)$	1.95 (2), 2.06 (3)	?	*j*
trans-$Pt(CNCH_3)_2\{C(NHCH_3)(SC_2H_5)\}_2^{2+}$	$C(sp^2)$	$C(sp^2)$	2.058 (7)	~0.10	*k*
trans-$Pt(P(C_2H_5)_3)\{C(NC_6H_5CH_2)_2\}Cl_2$	P	$C(sp^2)$	2.00 (3)	?	*c*

[a] The structural trans effect of Cl is arbitrarily defined as zero; Δ(M–L) is the difference between the M–L distance with L′ trans to L and the distance with Cl trans to L. [b] R. H. B. Mais, P. G. Owston, and A. M. Wood, *Acta Crystallogr., Sect. B*, 28, 393 (1972). [c] See ref 10. [d] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965). [e] G. G. Messmer, E. L. Amma, and J. A. Ibers, *ibid.*, 6, 725 (1967). [f] See ref 3. [g] See ref 23. [h] See ref 4. [i] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 5, 1775 (1966). [j] See ref 8. [k] This work.

with a trans influence similar to phosphines. The bottom section of Table III considers the susceptibility of M–$C(sp^2)$ distances to the trans influence of other ligands. Here the results are less definitive because the errors on the Pt–C distances are rather large for three of the examples, but the two compounds whose M–C distances are well defined, $Pd(C_2N_4H_4(CH_3)_2)Cl_2$ (1) and *trans*-$[Pt(CNCH_3)_2\{C(NHCH_3)(SC_2H_5)_2\}_2]^{2+}$, do give Δ(M–L) ≈ 0.10 Å (14σ). Some caution is required in ascribing this difference solely to the susceptibility of M–$C(sp^2)$ distances to trans influence because the carbene ligands in these two complexes are not identical. It has been shown that in the series of compounds $(CO)_5Cr\{CR(R')\}$ (where R = OMe, R′ = Ph; R = NHMe, R′ = Me; R = NEt_2, R′ = Me)[24] the metal-carbene bond length ranges from 2.04 to 2.16 Å.

Registry No. $[Pt(CH_3NC)_2\{C(NHCH_3)(SCH_2\text{-}CH_3)\}_2]\cdot(PF_6)_2$, 37668-70-5.

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Contribution from the Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, 41001 Zagreb, Yugoslavia

Crystal Structure of Mercury(II) Hydroxide Fluoride

D. GRDENIC* and M. SIKIRICA

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Mercury(II) hydroxide fluoride, Hg(OH)F, crystallizes in the orthorhombic system, space group $P2_12_12_1$, with four formula units per unit cell. The unit cell dimensions are $a = 4.963 \pm 0.005$ Å, $b = 5.920 \pm 0.005$ Å, and $c = 6.857 \pm 0.005$ Å; the measured and calculated densities are 7.77 and 7.80 g/cm³, respectively. The structure was solved from Patterson and electron density maps and refined by least-squares methods to a conventional R index of 0.091 for 222 independent, nonzero reflections collected by the use of equiinclination Weissenberg photographs. The mercury atom is surrounded by three fluorine and three oxygen atoms in an irregular octahedral coordination. By sharing two opposite edges the octahedra form infinite columns along the c axis. These columns are linked by shared corners and by O–H· · ·F hydrogen bonds of length 2.76 ± 0.10 Å. The closest Hg–O distances of 2.06 ± 0.06 and 2.11 ± 0.06 Å occur within a column in the planar zigzag –O–Hg–O–Hg– chain. The compound may be conveniently described as polymeric mercurioxonium fluoride, $[Hg(OH)]_n^{n+},nF^-$.

Introduction

Mercury(II) hydroxide fluoride, Hg(OH)F, described for the first time by Djordjevic,[1] is the only known basic fluoride of this metal. At the same time all other basic mercury(II) halides are oxide halides defined by the general formula $Hg_nX_2O_{n-1}$, with n = 1.5, 3, 4, and 5, but with oxygen functioning differently in the various structures.[2,3] In

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[1] C. Djordjevic, *Ark. Kemi*, 27, 137 (1955); *Chem. Abstr.*, 50, 6237*f* (1956).

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Table I. Atomic Coordinates and Thermal Parameters with Their Estimated Standard Deviations in the Last Figure (in Parentheses)

Atom	x	y	z	B, Å^2
Hg	0.2611 (10)	0.5094 (5)	0.6136 (3)	
O	0.547 (11)	0.104 (3)	0.139 (11)	4.43 (1.01)
F	0.418 (14)	0.151 (10)	0.637 (16)	7.72 (1.57)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg[a]	0.0141 (7)	0.0101 (4)	0.0123 (4)	0.0055 (15)	−0.0027 (14)	0.0024 (8)

[a] Anisotropic temperature factors expressed as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

the structure of basic mercury(II) chlorate and bromate, $Hg(OH)ClO_3$ and $Hg(OH)BrO_3$, a polymeric oxonium ion in the form of an endless planar zigzag chain -(OH)-Hg-(OH)-Hg- was found[4] and recently confirmed by an elaborate crystal structure analysis of the bromate.[5] By an incomplete structure analysis it was shown[6] that such a polymeric oxonium ion also occurs in the crystal structure of mercury(II) hydroxide fluoride. The complete crystal analysis based on three-dimensional X-ray diffraction data is reported only now.

Experimental Section

Crystals of mercury(II) hydroxide fluoride were obtained from a solution of mercury(II) oxide in hydrofluoric acid according to Dotzer and Meuwsen.[7] The pale yellow prism-shaped crystals are quite stable in dry air.

The crystals belong to the orthorhombic system. The unit cell constants were determined from oscillation and Weissenberg photographs at room temperature using nickel-filtered Cu Kα radiation, and standard deviations were estimated from several film measurements.

The cell constants are $a = 4.963 \pm 0.005$ Å, $b = 5.920 \pm 0.005$ Å, and $c = 6.857 \pm 0.005$ Å. The density obtained picnometrically in decalin is 7.77 g/cm^3 while the calculated density, assuming 4 formula units per unit cell, is 7.80 g/cm^3.

The systematic absence of reflections $h00$ for h odd, $0k0$ for k odd and $00l$ for l odd uniquely determined the space group $P2_12_12_1$.

It follows that the previously reported[1] density value (and herewith the number of formula units per unit cell) as well as the space group was incorrect. The correct density value but not the space group was reported recently.[8]

Three-dimensional intensity data $0kl \ldots 2kl$, $h0l \ldots h3l$, $hk0 \ldots hk3$ were recorded on equiinclination Weissenberg photographs with Ni-filtered Cu Kα radiation (λ 1.5418 Å). Multiple films were used, and the reflections were integrated with a Nonius-Delft camera; the intensities were measured photometrically. Two crystal specimens obtained by grinding were used: (i) a cylinder of length 0.03 cm and diameter 0.02 cm and (ii) a sphere of 0.02-cm diameter. The absorption correction (μ 1480 cm^{-1}) was applied using Bond's tables.[9] In this way in total of 408 reflections was measured and the intensities of 222 independent nonzero reflections were determined. The usual Lorentz and polarization corrections were applied.

Solution of the Structure. It followed from preliminary mercury atom parameters, obtained from the Patterson $0kl$ and $hk0$ projections by means of von Eller's Photosommateur,[10] that the contribution of the mercury atom to many reflections was very small so that the heavy-atom method could not be applied. Therefore, preliminary light-atom parameters were obtained from the Patterson projections calculated only with the intensities of those reflections for which the mercury atom contribution was negligible. An improved set of atomic parameters was then obtained from Fourier projections. At this stage of the analysis the main features of the structure were evident.[6] The structure was then refined by five cycles of full-matrix least-squares calculations,[11] with isotropic thermal parameters, to the reliability index $R = 0.120$. Seven cycles of refinement were then computed using anisotropic thermal parameters for the mercury atom only. The weighting scheme adopted was $w = 1$ for all reflections whose intensities were determined by means of an optical densitometer and $w = 0.25$ for reflections slightly above the film background, which had been estimated visually. The final reliability index R for the observed reflections was $R = 0.091$. Table I gives the final atomic coordinates together with thermal parameters.[12] The values of the atomic scattering factors for mercury, oxygen, and fluorine were taken from ref 13 with corrections for anomalous scattering of the mercury, $\Delta f' = 4.990$ e and $\Delta f'' = 7.686$ e.[14] The structure factor and least-squares refinement calculations were carried out on the CAE 90.40 computer of the Institute of Mathematics, University of Zagreb.

Description of the Structure and Discussion

The interatomic distances and bond angles are given in Table II. The clinographic projection of the unit cell with a part of the neighboring cells is shown in Figure 1. The mercury atom is surrounded by three oxygen atoms (*viz.*, O(1), O(2), O(3)) and three fluorine atoms (*viz.*, F, F(1), F(4)) in a distorted octahedron. By sharing two opposite edges these octahedra form columns arranged parallel along the [001] direction. The columns are interconnected in such a way that the fluorine or oxygen atom, which belongs to the common octahedral edge within one column, belongs also separately to the octahedral corner of the adjacent column. The shortest distances within the octahedron are the two mercury-oxygen bonds Hg-O(1) and Hg-O(2), which do not differ practically, being 2.06 and 2.11 Å, and which are nearly collinear, the angles O(1)-Hg-O(2) and Hg-O(1)-Hg(3) being 175.9 and 110.8°, respectively. These bonds form an endless zigzag chain, which is planar, the mercury atom being only 0.02 Å out of the plane defined by the oxygen atoms within one column. Since each oxygen atom in the structure belongs to the hydroxo group, the mercury-oxygen chain is a polymeric cation $[Hg(OH)]_n{}^{n+}$, and basic mercury fluoride is a mercurioxonium fluoride, [Hg(OH)]F, rather than hydroxide fluoride. This is supported by the perfect analogy with such a mercury-oxygen chain found in the structure of basic mercury(II) bromate[5] in which coplanar mercury-oxygen bonds of 2.07 Å form angles of 175.2° (at mercury) and 123.1° (at oxygen). The length

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(12) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-544.

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Table II. Interatomic Distances (Å) and Bond Angles[a] (deg) with Their Estimated Standard Deviations in the Last Figure (in Parentheses)

Hg-O(1)	2.11 (6)	O(1)-O(3)	3.36 (9)
Hg-O(2)	2.06 (6)	O(2)-O(3)	3.57 (9)
Hg-O(3)	2.75 (6)	O(2)-F	3.29 (10)
Hg-F	2.26 (8)	O(2)-F(4)	3.51 (10)
Hg-F(1)	2.60 (8)	O(3)-F(1)	3.75 (10)
Hg-F(4)	2.48 (8)	O(3)-F(4)	3.76 (10)
O(1)-(F)	2.80 (10)	F-F(1)	3.33 (11)
O(1)-F(1)	3.48 (10)	F-F(4)	3.43 (11)
O(1)-F(4) O(2)-F(1)	3.06 (10)	O(2)· · ·F(5) O(5)· · ·F(4)	2.76 (10)
O(1)-Hg-O(2)	175.9 (24)	F-Hg-O(2)	99.0 (26)
F(1)-Hg-F(4)	177.7 (26)	O(3)-Hg-O(1)	86.2 (21)
F-Hg-O(3)	164.4 (23)	Hg-O(1)-Hg(3)	110.8 (28)
F(1)-Hg-O(1)	94.9 (25)	Hg-F(4)-Hg(3)	84.9 (25)
F(4)-Hg-O(1)	81.1 (25)	Hg-O(2)-F(5)	103.6 (28)
F(4)-Hg-O(2)	100.9 (25)	Hg-F(4)-O(5)	110.4 (31)
F(1)-Hg-O(2)	81.1 (25)	Hg(5)-F(5)-O(2)	103.1 (31)
		Hg(6)-O(5)-F(4)	89.5 (24)

[a] The positions without a label are given by x, y, z as in Table I; labels are as follows: (1) $-{}^1/_2 + x, {}^1/_2 - y, 1 - z$; (2) $1 - x, {}^1/_2 + y, {}^1/_2 - z$; (3) ${}^1/_2 - x, 1 - y, {}^1/_2 + z$; (4) $1 - x, {}^1/_2 + y, {}^3/_2 - z$; (5) ${}^1/_2 + x, {}^1/_2 - y, 1 - z$; (6) $1 - x, -{}^1/_2 + y, {}^3/_2 - z$.

of these bonds differs only slightly from the sum of the corresponding covalent radii of mercury and oxygen.[2,3,15]

The other mercury-oxygen and mercury-fluorine distances within the coordination octahedron are greater than the sum of covalent radii but smaller than the sum of van der Waals radii as observed so far in the majority of the crystal structures containing mercury.[2,15] Even the shortest mercury-fluorine distance of 2.26 Å is greater than the sum of the covalent radii and also greater than the Hg-F distance of 2.24 Å found in the structure of $RbHgF_3$.[16] The contact of mercury to the nearest oxygen atom (*viz.*, Hg-O(3)) from the next zigzag chain of 2.75 Å is also equal to the usually observed value for the analogous contacts in other mercury structures containing oxygen.[2,3]

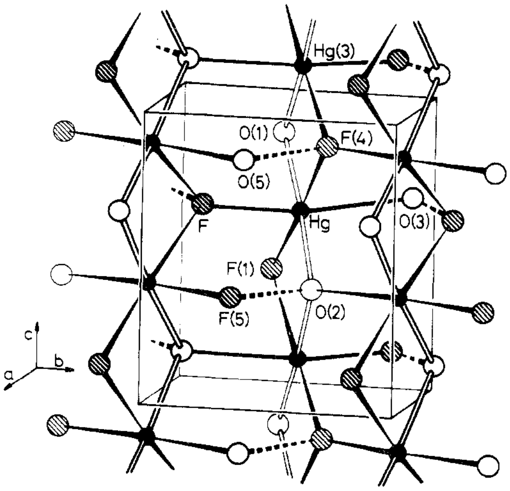

Figure 1. Clinographic projection of the crystal structure of Hg(OH)F.

It would not be possible to determine the hydrogen atom position from the present intensity data. But, from geometrical and chemical considerations, it follows undoubtedly that the oxygen-to-fluorine atom contacts of 2.76 Å belong to hydrogen bonds of the O-H· · ·F type. These contacts, shown in Figure 1 as O(2)· · ·F(5) and O(5)· · ·F(4) related by the screw symmetry operation, are located in channels formed by columns alternating along the [001] direction. The bond angle at the oxygen atom, Hg-O(2)-F(5), as well as that at the fluorine atom, Hg-F(4)-O(5), with values of 103.6 and 110.4°, respectively, is also favorable for the O-H· · ·F bond formation. There is no previous example of the O-H· · ·F bond observed in the crystal structure known to the authors. It is equivalent to an O-H· · ·O bond[17] with the length of 2.83 Å which is the most frequently observed value.

Registry No. Hg(OH)F, 37164-31-1.

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Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Crystal Structure of Tetramethylammonium Tetradecahydrodecaborate. Structure of the $B_{10}H_{14}^{2-}$ Ion

DOUGLAS S. KENDALL and WILLIAM N. LIPSCOMB*

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The $B_{10}H_{14}^{2-}$ ion has two BH_2 groups and two bridging hydrogen atoms, in a 2632 topology of three-center bond theory. The isolated ion has C_{2v} symmetry. Unit cell parameters of tetramethylammonium tetradecahydrodecaborate, $(N(CH_3)_4)_2B_{10}H_{14}$, are $a = 9.60$ (1) Å, $b = 16.29$ (1) Å, $c = 12.27$ (1) Å, $\beta = 91.63$ (1)°, and $z = 4$, and the crystal symmetry is $P2_1/c$. Full-matrix least-squares refinement of the structure yields a value of $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ of 0.085 for 2058 X-ray diffraction maxima measured on a four-circle diffractometer. The relationships of the structure of $B_{10}H_{14}^{2-}$ to its bonding and probable reactivity are discussed briefly.

The two-electron reduction of $B_{10}H_{14}$ to $B_{10}H_{14}^{2-}$ was predicted from three-center valence theory,[1] and the ion was subsequently synthesized[2] by reduction of $B_{10}H_{14}$ by sodi-

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