merization of **7** to **5** via $PhNH_2$ elimination seems unlikely since this reaction in independent experiments was found to be very slow and does not yield **5** cleanly.

The observed phosphazane products and the product formation order are consistent with those expected in a series that requires successively decreasing $PhNH_2$:PCl_3 ratios. Reactant ratios for formation of **8** and **9** are 6:1 (eq 8) and 5.5:1 (eq 9), respectively.

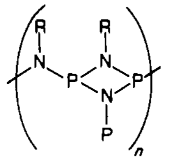
$$6PhNH_2 + PCl_3 \rightarrow 3PhNH_3Cl + (PhNH)_3P \quad (8)$$

$$11PhNH_2 + 2PCl_3 \rightarrow 6PhNH_3Cl + [(PhNH)_2P]_2NPh \quad (9)$$

The ideal reactant ratio for oligomers **6** and **7** is 5.0:1.0 (eq 3 and 4), and that for the final product **5** is 4.75:1.0 (eq 2).

Having observed the complexity of the PCl_3–$PhNH_2$ reaction product mixture, how sensitive the product distribution is to reaction conditions, and that the final reaction products **6** (or **7**) and **5** have closely similar elemental analytical compositions, we were not surprised that products previously characterized as $[(PhNH)PNPh]_2$ had widely different properties, especially melting points. On the basis of our data, we conclude that material reported to melt at 145–153 °C was mainly $[(PhNH)PNPh]_2$ (**7**),[18-20] that melting at 249–251 °C was $[(PhNH)P_2(NPh)_2]_2NPh$ (**5**),[17,21] and materials with intermediate melting ranges were mixtures of varying amounts of **5**, **6**, or **7**. Only in one case were ^{31}P NMR data reported.[23] Interestingly, a two-resonance pattern like that observed by us for **5** was described; however, the pattern was attributed to a mixture of isomers of **5**.

The 1,3,2,4-diazadiphosphetidines **5**, **6**, and **7** are phosphazanes whose relationships to each other and other phosphazanes is of interest to note: (i) Compound **5** represents the longest oligomeric extension so far of systems based on linked P_2N_2 rings. **5** and **7** can be regarded as the $n = 1$ and $n = 2$ members of diazadiphosphetidine-based series $[(RN)_3P_2]_n$ (**11**), in which the end groups are H and PhNH. The known $(RN)_6P_4$ cages[14,15] are also members of this class; however, they can be regarded as nonlinear cluster phosphazanes. The ubiquitous formation of diazadiphosphetidines rings in the higher order condensation products **5** and **6** suggests that perhaps other series of similar P_2N_2-based oligomer/polymers can be obtained. (ii) Compounds **6** and **7** are two members of a limited oligomeric series of type $[(PhNH)PNPh]_n$. Monomer ($n = 1$) and tetramer ($n = 4$; **12**) members have not been observed; however, their existence in concentrations too low to detect or as intermediates in interconversion processes cannot be excluded. (iii) Compound **6** is a triphosphazane of formula analogous to that of the previously reported six-membered-ring compound $(PClNMe)_3$ (**2**; X = Cl, R = Me, Et).[7,11] It is not clear from the studies done so far whether or not **2** is in fact thermodynamically preferred; however, from our studies there seems to be no question that for the Ph-substituted system the P_2N_2 isomer form is thermodynamically preferred.



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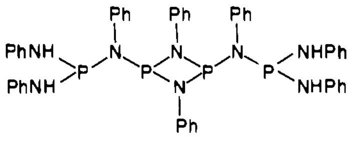

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Acknowledgment. Support of this work by National Science Foundation Grants CHE-7909497 and CHE-8312856 is gratefully acknowledged.

Supplementary Material Available: Tables of anisotropic thermal parameters, rigid-group derived parameters, least-squares planes, equations, and deviations from planes (10 pages); listings of structure factors (17 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structures of $Hg_3(NbF_5)_2SO_4$, $Hg_3(TaF_5)_2SO_4$, and $Hg_4(Ta_2F_{11})_2$

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$Hg_3(NbF_5)_2SO_4$ (I) and the isostructural $Hg_3(TaF_5)_2SO_4$ (II) were produced as minor products during the reactions of Hg with SO_2 solutions of $Hg(MF_6)_2$ (M = Nb, Ta). Similarly $Hg_4(Ta_2F_{11})_2$ (III) was prepared by the reaction of an SO_2 solution of $Hg(Ta_2F_{11})_2$ with Hg. Crystal data for these compounds are as follows: I [corresponding values for II in brackets], orthorhombic, space group *Fdd*2 with $a = 18.048$ (2) Å [18.078 (7) Å], $b = 15.699$ (2) Å [15.705 (4) Å], $c = 9.166$ (2) Å [9.153 (2) Å], $V = 2597$ (1) $Å^3$ [2599 (2) $Å^3$], $Z = 8$, $D_{exptl} = 5.485$ (4) g cm^{-3} [6.387 (4) g cm^{-3}], $\mu = 37.3$ mm^{-1} [54 mm^{-1}], $F(000) = 3680$ [4192], $R = 0.048$ [0.109] for 1515 unique [1433] reflections; III, monoclinic, space group *I*2/*c*, $a = 18.556$ (8) Å, $b = 7.528$ (3) Å, $c = 14.714$ (8) Å, $\beta = 91.72$ (4)°, $V = 2054$ (2) $Å^3$, $Z = 4$, $D_{exptl} = 6.285$ (5) g cm^{-3}, $\mu = 52.9$ mm^{-1}, $F(000) = 3240$, $R = 0.056$ for 1248 unique reflections. Compounds I and II contain nearly linear Hg_3^{2+} ions (Hg–Hg = 2.559 (2) Å (×2); Hg–Hg–Hg = 166.6 (1)°) linked through Hg···O interactions (2.28 (1) Å) involving the two terminal oxygen atoms of the $(MF_5)_2SO_4^{2-}$ (M = Nb, Ta) anions. The structure of III consists of $Ta_2F_{11}^-$ anions and almost linear Hg_4^{2+} cations linked into infinite zigzag chains by a weak interaction (Hg···Hg = 3.033 (2) Å) between the terminal Hg atoms of symmetry-related cations. Hg–Hg bond lengths in the cation are 2.593 (2) and 2.630 (2) Å.

Introduction

In recent years there has been a considerable increase in our knowledge of the lower oxidation states of Hg. The structure of Hg_3^{2+} was first reported in $Hg_3(AlCl_4)_2$ by Ellison, Levy, and Fung,[1] and a second example in $Hg_3(AsF_6)_2$ was reported by Cutforth, Davies, Dean, Gillespie, Ireland, and Ummat.[2] The existence of the Hg_4^{2+} ion was first reported by Cutforth, Gillespie, and Ireland,[3] and the crystal structure of $Hg_4(AsF_6)_2$ was later described by Cutforth, Gillespie, Ireland, Sawyer, and Ummat.[4]

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(1) Ellison, R. D.; Levy, H. A.; Fung, K. W. *Inorg. Chem.* **1972**, *11*, 833.
(2) Cutforth, B. D.; Davies, C. G.; Dean, P. A. W.; Gillespie, R. J.; Ireland, P. R.; Ummat, P. K. *Inorg. Chem.* **1973**, *12*, 1343.
(3) Cutforth, B. D.; Gillespie, R. J.; Ireland, P. R. *J. Chem. Soc., Chem. Commun.* **1973**, 723.

0020-1669/87/1326-0689$01.50/0

Table I. Summary of the Structure Determinations

	Ia	Ib	II	III
General Information				
diffractometer	Nicolet P3	Enraf-Nonius CAD4	Nicolet $P2_1$	Nicolet P3
radiation	graphite-monochromated Mo $K\bar{\alpha}$ ($\lambda = 0.71069$ Å)			
syst	orthorhombic	orthorhombic	orthorhombic	monoclinic
Cell Constants				
a, Å	18.068 (6)	18.048 (2)	18.078 (7)	18.556 (8)
b, Å	15.734 (5)	15.699 (3)	15.705 (4)	7.528 (3)
c, Å	9.176 (4)	9.166 (2)	9.153 (2)	14.714 (8)
β, deg				91.72 (4)
reflecns used in cell determination	15	25	15	15
2θ range, deg	$18 < 2\theta < 47$	$16 < 2\theta < 30$	$19 < 2\theta < 32$	$24 < 2\theta < 30$
mode	$\theta-2\theta$			
scan speeds, deg min^{-1}	4–29.3	*a*	5–29.3	2–20.0
max 2θ, deg	55			
octants	$0 \le h \le 23, -20 \le k \le 20, -11 \le l \le 11$	*b*	$-4 \le h \le 23, -7 \le k \le 20, -11 \le l \le 11$	$0 \le h \le 25, -10 \le k \le 10, 0 \le l \le 20$
standards	10,0,2; 0,10,2	206; 0,10,$\bar{2}$; $9\bar{1}\bar{5}$	202; $13\bar{1}$	$0\bar{4}0$; 408
esd of std reflecns, %	1.3, 1.2	≤3	2.1, 2.7	2.1, 1.5
no. of std measmts	63	25	56	62
no. of reflecns measd	2974	2260	2302	2394
no. of unique reflecns	1515	939	1433	1248
Absorption Correction				
linear abs coeff used, μ, mm^{-1}	37.9	37.3	54	52.9
program	DIFABS[c,10]	ABSCOR (SDP)[d,5]	PSI SCAN[c,10]	DIFABS[c,10]
μR for spherical Born abs cor	4.3		9.4	6.9
no. of reflecns to define cor	2676		14	1743
max cor	1.496[e]	0.1387	0.0392	0.934[e]
min cor	0.702[e]	0.0712	0.0009	0.481[e]
internal agreement after cor	0.036	0.028	0.125	0.043
Structure Refinement				
programs	SHELX76[8]	SDP package[5]	SHELX76[8]	SHELX76[8]
scattering factors used	*f*	*f*	*f*	*f*
final *R*	0.048	0.033[g]	0.109	0.056
final R_w	0.045	0.040[g]	0.111	0.049
no. of reflecns used	1508	847 ($I > 3\sigma(I)$)	1019 ($I > 3\sigma(I)$)	1217
function refined	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ for all structures			
Weights				
$w = k[\sigma(\text{counting}) + gF_o^2]^{-1}$	$g = 0.00035$, $k = 0.9077$		$g = 0.0115$, $k = 1.3698$	$g = 0.0004$, $k = 0.779$
$w = 4F^2[\sigma^2(I) + (gF_o^2)^2]^{-1}$		$g = 0.065$		
max Δ/σ final cycle	0.071	0.008	0.332	0.089
av Δ/σ final cycle	0.014		0.015	0.022
secondary extinction cor[6] *g*	$3\ (1) \times 10^{-5}$	$2.1\ (2) \times 10^{-7}$	2×10^{-5}	$3\ (1) \times 10^{-5}$
no. of params refined	92	57	57	137
max residual electron density, e Å^{-3}	3.6 (near Hg(2))	2.5	25.5[h] (near Hg)	1.20
min residual electron density, e Å^{-3}	−6.1 (near Hg(1))		−10.4[h] (near Ta)	−1.40

[a] Scan speeds chosen to give $I/\sigma(I) \ge 25$ within the maximum scan time of 80 s over scan ranges $(0.85 + 0.35 \tan\theta)°$ with use of data collected in prescans at 20 min^{-1}. [b] Data collected on monoclinic cell (2070 reflections in octants $h,k,\pm l$ (exclusive of C-centered reflections) and 190 symmetry-related reflections with negative *h* and *k* indices) and transformed ((010), (102), (100)) into the orthorhombic cell. [c] Samples were approximate spheres without well-defined faces. [d] The crystal was a needle with the following faces (distance from origin in mm): (110), 0.04; $(1\bar{2}\bar{2})$, 0.062; $(\bar{1}22)$, 0.062; (101), 0.062; $(\bar{1}0\bar{1})$, 0.062. An 8 × 10 × 10 grid was used in the calculation. [e] Contribution from DIFABS only. [f] Scattering factors: neutral Nb, Ta, and Hg atoms from ref 9; International Tables for X-ray crystallography (1974)[9]. F, S, and O atoms stored in the SHELX program[8] and the SDP package.[5] [g] Goodness of fit 0.93 e. The alternative "hand" with signs for $\Delta f''$ reversed gave $R_1 = 0.053$, $R_w = 0.082$. [h] Only poor-quality crystals were available, hence the large residual electron densities.

In this paper we describe the preparation and crystal structures of three other compounds in this series, $Hg_3(NbF_5)_2SO_4$ (I), $Hg_3(TaF_5)_2SO_4$ (II), and $Hg_4(Ta_2F_{11})_2$ (III).

Experimental Section

Preparations. (a) $Hg_3(NbF_5)_2SO_4$ (I). Niobium pentafluoride (Ozark-Mahoning) was purified by repeated extractions with dry SO_2. Niobium pentafluoride (0.314 g, 1.67 mmol) was allowed to react with the stoichiometric amount of HgF_2 (0.21 g, 0.88 mmol) in dry SO_2 to give a solution of $Hg(NbF_6)_2$ together with some solid. The solution was filtered onto mercury (0.840 g, 4.19 mmol) at room temperature (293 (2) K). Almost at once golden crystals of $Hg_{3-\delta}NbF_6$ were observed to form on the surface of the mercury. The reaction was left undisturbed for 2 months, during which time a crystalline white solid gradually precipitated and the golden crystals transformed to silver crystals of Hg_3NbF_6 together with unreacted mercury and a few orange-purple crystals. The latter were hand-picked in a drybox and were mounted in sealed capillaries for X-ray studies.

(b) $Hg_3(TaF_5)_2SO_4$ (II). This compound was prepared and the purple crystals were isolated in exactly the same manner as for I.

(c) $Hg_4(Ta_2F_{11})_2$ (III). Tantalum pentafluoride (3.620 g, 13.118 mmol of TaF_5) was allowed to react with the stoichiometric amount of HgF_2 (0.78 g, 3.269 mmol, Ozark-Mahoning) in dry SO_2 at 293 (2) K to give a solution of $Hg(Ta_2F_{11})_2$ together with some solid. The solution was filtered onto mercury (1.970 g, 9.821 mmol of Hg) at 293 (2) K. When the mixture was stirred for 3 days, an orange solution together with silver crystals of Hg_3TaF_6, a white solid, and unreacted mercury were obtained. The orange solution was filtered, and on slow evaporation crystals were obtained from a deep red solution. They consisted of shiny black needles together with an unidentified gray material. The black needles were hand-picked in a drybox and were mounted in sealed capillaries for X-ray studies.

Structure Determination and Refinement. All X-ray measurements were performed at 293 (2) K. Precession photographs were used to

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(4) Cutforth, B. D.; Gillespie, R. J.; Ireland, P.; Sawyer, J. F.; Ummat, P. K. *Inorg. Chem.* **1983**, *22*, 1344.

identify the space group of all three compounds. The symmetry of the diffraction pattern and systematic absences are consistent with the space group *Fdd*2 for I and II and *I*2/*c* or *Ic* for III. The nonstandard body-centered setting of the last compound was chosen in order that $\beta \approx 90°$. Two independent determinations of structure I were made and are reported separately; that labelled Ia was performed at McMaster University and that labelled Ib at the University of Toronto. Details of the single-crystal X-ray structure determination are summarized in Table I. Lorentz and polarization corrections were applied to all intensities measured. Absorption corrections were applied at a later stage of the refinements with the programs ABSCOR and DIFABS (see below). The structure of I was found by using Patterson and difference synthesis techniques. The formula was initially assumed to be $Hg_3(NbF_6)_2$, but refinement with these atoms showed that the anions were connected by a group of three atoms that could only be identified as SO_2. It was then necessary to assume that the atom linking S and Nb was O rather than F (see Discussion of the $(MF_5)_2SO_4^{2-}$ Ions). One refinement (Ib) was initially performed in space group *Cc* (a subgroup of *Fdd*2), but this led to the same structure. The structure of II was assumed to be the same as that of I. The structure of III was solved by direct methods (SHELX)[8] and difference electron density maps.

A ψ-scan absorption correction (PSI[7]) was applied at this stage to II, and an empirical absorption correction (DIFABS[10]) was applied to the structure factors in determinations of Ia and III as follows. The original (unaveraged) measured F_o's were first corrected for isotropic absorption effects. A least-squares refinement with isotropic temperature factors from these structure factors gave $R_{iso} = 0.139$ for Ia and 0.109 for III. The program DIFABS[10] was then used in order to remove the macroscopic anisotropy in the F_o's by finding the anisotropic absorption correction that gives the best fit between the observed and calculated structure factors. The corrected structure factors were averaged and the standard deviations, σ_A, between equivalent reflections calculated. Since usually only two equivalent reflections were included in the averaging, the values of σ_A showed a large scatter, but their variation with F_o was accurate enough to give a reasonable estimate of the proportionality parameter *g* in the expression $\sigma_T^2 = \sigma^2(\text{counting}) + gF_o^2$ on the assumption that σ_T is a reasonable representation of the standard error of which σ_A is an estimate. Weights for Ia and III were set equal to σ_T^{-2}.

The weighted refinements proceeded with anisotropic temperature factors on all atoms (heavy atoms only in the case of Ib and II). Further details of the structure determination are given in Table I, and the atomic coordinates are given in Table II.

Further details of the determinations of Ia and III are given by Tun.[11]

Comparison of the Two Determinations of I. Although both unit cells were measured at 293 K, that measured in Ia is 0.1–0.2% larger than that in Ib, a systematic difference that is 3 or 4 times larger than the estimated standard errors. The values measured in Ib are given in the abstract. The normal probability plot of the differences in the atomic positions shows a slope of 1.0, indicating that there is no significant discrepancy between the two refinements even though the largest difference (y(F4)) of 3σ leads to differences in bond distances on the order of 0.03 (1.5σ) Å. The rms atomic displacement parameters (temperature factors) determined in Ia are significantly larger (40%) than those in Ib, a difference that can probably be attributed to the difficulty in making an adequate absorption correction. These differences do not, however, have an appreciable effect on the molecular geometry.

Discussion of the $(MF_5)_2SO_4^{2-}$ Ions. The appearance of the $(NbF_5)_2SO_4^{2-}$ and $(TaF_5)_2SO_4^{2-}$ ions in the reactions that produced compounds I and II is unexpected, and consequently its inclusion in these structure determinations needs justification. The first refinement, in which the structure was modeled as $Hg_3(NbF_6)_2$, gave an *R* factor of 0.13 (with two of the F atoms omitted). In addition to the missing F atoms the difference map showed two additional peaks, one on a twofold axis corresponding to about 20 electrons and the second about 1.5 Å away corresponding to about 10 electrons.

The larger peak can only reasonably be an S atom. The light atoms could be either F or O, but if the sulfur is S^{VI} as indicated by its tetrahedral geometry, charge balancing requires all its ligands to be O.

Table II. Atomic Positional Coordinates ($\times 10^4$)

(a) $Hg_3(NbF_5)_2SO_4$ (I) and $Hg_3(TaF_5)_2SO_4$ (II)[a]

	x	*y*	*z*	U_{eq}/U_{iso}
Hg(1)	0	0	0	33 24 20
Hg(2)	994 (1) 992.8 (4) 988 (2)	1146 (1) 1146.0 (4) 1146 (2)	9672 (1) 9674 (1) 9664 (6)	35 25 19
Nb	1927 (1) 1927.5 (8)	4409 (1) 4407.8 (9)	7436 (2) 7437 (2)	28 19
Ta	1932 (2)	4402 (2)	7419 (7)	13
S	$^1/_4$	$^1/_4$	8536 (7) 8535 (7) 8508 (31)	28 19 18
F(1)	1809 (7) 1807 (6) 1781 (22)	5570 (7) 5580 (7) 5571 (28)	7277 (18) 7271 (13) 7368 (59)	28 39 (3) 19 (8)
F(2)	1959 (8) 1961 (6) 1944 (28)	4263 (10) 4280 (8) 4228 (33)	5428 (15) 5448 (13) 5347 (53)	49 39 (3) 24 (10)
F(3)	1885 (8) 1877 (6) 1878 (33)	4379 (9) 4382 (7) 4390 (35)	9482 (16) 9485 (13) 9527 (63)	54 36 (3) 36 (13)
F(4)	911 (6) 899 (6) 868 (25)	4250 (9) 4215 (8) 4298 (32)	7352 (17) 7376 (14) 7316 (60)	50 40 (3) 25 (9)
F(5)	2961 (6) 2967 (6) 2962 (24)	4567 (8) 4582 (7) 4548 (26)	7532 (18) 7541 (12) 7448 (56)	49 33 (3) 19 (9)
O(1)	2139 (8) 2131 (6) 2130 (39)	3118 (8) 3119 (8) 3136 (44)	7551 (18) 7539 (14) 7612 (73)	37 26 (3) 36 (16)
O(2)	1954 (7) 1956 (6) 1938 (33)	2073 (9) 2080 (7) 2076 (40)	9441 (15) 9453 (13) 9386 (63)	33 23 (3) 23 (12)

(b) $Hg_3(Ta_2F_{11})_2$ (III)[b]

	x	*y*	*z*	U_{eq}
Hg(1)	664 (1)	2669 (2)	2799 (1)	64
Hg(2)	2031 (1)	2625 (2)	3324 (1)	65
Ta(1)	3510 (1)	7290 (1)	3673 (1)	44
Ta(2)	3947 (1)	3057 (1)	5224 (1)	44
F(1)	398 (1)	522 (2)	438 (1)	56
F(2)	303 (1)	906 (2)	302 (1)	55
F(3)	268 (1)	591 (2)	378 (2)	72
F(4)	440 (1)	835 (3)	358 (2)	100
F(5)	337 (1)	816 (3)	486 (1)	67
F(6)	374 (2)	593 (2)	266 (2)	69
F(7)	451 (1)	449 (2)	601 (1)	53
F(8)	393 (1)	114 (2)	601 (2)	72
F(9)	472 (1)	225 (2)	461 (1)	59
F(10)	332 (1)	214 (2)	426 (2)	71
F(11)	315 (1)	425 (2)	566 (2)	84

[a] For each group of values, the top line is from the refinement for Ia, the middle line from that for Ib, and the bottom line from that for II. Atomic displacement factors (*U*) are U_{iso} for F in Ib and II; otherwise, they are $U_{eq} = {}^1/_3 \text{ Tr } U$ ($\times 10^3$ Å^2). [b] Definitions are as in part a of this table.

The final agreement indices (*R* factors) were 0.04 for both structure determinations of I using the coordinates listed in Table IIa, and no significant features remained in the electron density. Refinement in space group *Cc* led to the same structure with no significant differences. The rms atomic displacement parameters on all atoms were normal, and a bond valence analysis of the model (Table III) indicates that the bond lengths and angles are consistent with the atom assignments. None of these factors conclusively rule out the possibility of other interpretations, but there is nothing in the structure or its analysis to suggest that the refined model is not correct.

The formation of such an anion in an SO_2 solution is surprising. However, we found, after having completed the crystal structure determinations, that the HgF_2 used in the preparations contained a small

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(5) "Enraf-Nonius Structure Determination Package"; B. A. Frenz and Associates: College Station, TX, 1981.

(6) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(7) PSI, a local adaptation of the Nicolet R3 ψ-scan program.

(8) Sheldrick, G. M. "SHELX76, a Program for Crystal Structure Determination"; University of Cambridge, Cambridge, England, 1976.

(9) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72, 99, 149.

(10) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(11) Tun, Z. Ph.D. Thesis, McMaster University, 1985.

Table III. Bond Valences in $Hg_3(NbF_5)_2SO_4$[a]

	Hg(1)	Hg(2)	Nb	S	valence sum
F(1)	0.02	0.05 0.02	1.00		1.09
F(2)		0.02	0.97		0.99
F(3)		0.07	0.91		0.98
F(4)	0.04		0.98		1.02
F(5)		0.06 0.04	0.89		0.99
O(1)			0.64	1.50 (1.43[b])	2.14 (2.05[b])
O(2)	0.04	0.36		1.62 (1.58[b])	2.02 (1.99[b])
anions in cation environ	X2	X1	X1	X2	
valence sum	0.20	0.62	5.39	6.24 (6.00[b])	

[a] Bond valences are calculated as $\exp((R_0 - R)/0.35)$, where R = bond length taken from Ia and R_0 has the following values: Hg–O, 1.916; Hg–F, 1.866; Nb–O, 1.916; Nb–F, 1.846; S–O, 1.622. [b] Calculated from angles at S (see Appendix). In this case the valence sum at S is constrained to be 6.00.

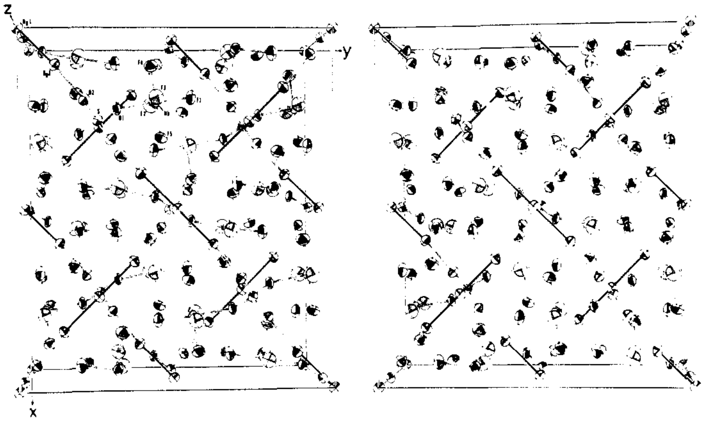

Figure 1. Stereographic view of $Hg_3(NbF_5)_2SO_4$ down the *c* axis.

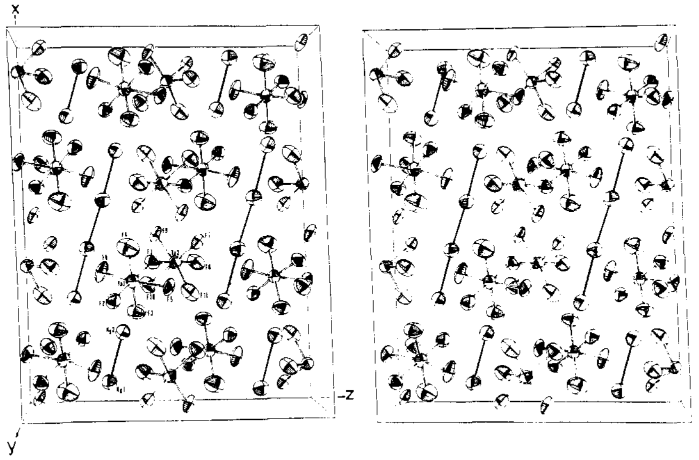

Figure 2. Stereographic view of $Hg_4(Ta_2F_{11})_2$ down the *b* axis.

Table IV. Bond Lengths (Å) in $Hg_3(NbF_5)_2SO_4$ (I) and $Hg_3(TaF_5)SO_4$ (II)

	Ia	Ib	II
Nb/Ta–F(1)	1.845 (11)	1.860 (13)	1.86 (4)
–F(2)	1.858 (14)	1.835 (13)	1.92 (5)
–F(3)	1.880 (15)	1.880 (13)	1.93 (4)
–F(4)	1.854 (11)	1.881 (13)	1.93 (4)
–F(5)	1.887 (11)	1.899 (12)	1.88 (4)
–O(1)	2.070 (13)	2.059 (13)	2.03 (7)
S–O(1) (×2)	1.479 (15)	1.490 (13)	1.45 (7)
–O(2) (×2)	1.454 (14)	1.451 (13)	1.46 (6)
Hg(2)–O(2)	2.276 (13)	2.283 (12)	2.27 (6)
–F(1)	2.950 (15)	2.935 (13)	3.00 (5)
	3.286 (13)	3.278 (12)	3.33 (4)
–F(2)	3.247 (14)	3.266 (13)	3.15 (5)
–F(3)	2.809 (15)	2.802 (13)	2.76 (6)
–F(5)	2.964 (14)	2.942 (12)	2.98 (5)
	2.990 (13)	2.958 (12)	3.00 (4)
Hg(1)–O(2) (×2)	3.050 (14)	3.033 (13)	3.10 (6)
–F(1)	3.290 (11)	3.270 (13)	3.30 (4)
–F(4)	2.960 (14)	2.983 (14)	2.86 (5)
Hg(1)–Hg(2)	2.562 (1)	2.557 (1)	2.554 (3)

Table V. Bond Lengths (Å) and Angles (deg) for $Hg_4(Ta_2F_{11})_2$ (III)[a]

Hg(2)–Hg(1)	2.630 (2) [2.620 (2)]		
Hg(1)–Hg(1)	2.593 (2) [2.588 (2)]		
Hg(2)···Hg(2)	3.033 (2) [2.985 (3)]		
Ta(1)–F(1)	2.05 (2)	Ta(2)–F(1)	2.05 (2)
Ta(1)–F(2)	1.86 (2)	Ta(2)–F(7)	1.88 (2)
Ta(1)–F(3)	1.88 (2)	Ta(2)–F(8)	1.86 (2)
Ta(1)–F(4)	1.84 (3)	Ta(2)–F(9)	1.83 (2)
Ta(1)–F(5)	1.89 (2)	Ta(2)–F(10)	1.94 (2)
Ta(1)–F(6)	1.86 (2)	Ta(2)–F(11)	1.86 (2)
Hg(2)–F(10)	2.74 (2)	Hg(1)–F(7)	2.99 (2)
Hg(2)–F(11)	2.97 (2)	Hg(1)–F(9)	3.23 (2)
Hg(2)–F(5)	2.82 (2)	Hg(1)–F(6)	3.01 (2)
Hg(2)–F(2)	3.18 (2)	Hg(1)–F(8)	3.22 (2)
Hg(2)–F(3)	2.82 (2)		
Hg(2)–Hg(1)–Hg(1)	177.2 (1) [177.3 (1)]		
Hg(1)–Hg(2)···Hg(2)	109.7 (1) [124.2 (1)]		
Ta(1)–F(1)–Ta(2)	153 (1)		
		Hg(1)–Hg(2)–F(10)	165.1 (5)
Hg(1)–Hg(2)–F(11)	92.1 (5)	Hg(1)–Hg(2)–F(5)	90.0 (5)
Hg(1)–Hg(2)–F(2)	78.0 (4)	Hg(1)–Hg(2)–F(3)	117.3 (4)

[a] Values given in brackets are the corresponding values observed in $Hg_4(AsF_6)_2$.[4]

impurity of HgO. Thus it seems probable that the anions $(NbF_5)_2SO_4^{2-}$ and $(TaF_5)_2SO_4^{2-}$ were formed during the preparation of $Hg(TaF_6)_2$ and $Hg(TaF_6)_2$ perhaps in a step in which Hg(II) was reduced to Hg(I); e.g.

$$2HgO + 2TaF_5 + SO_2 \rightarrow Hg_2^{2+}TaF_5SO_4TaF_5^{2-}$$

That the formation of this anion is associated with a small amount of HgO impurity in the HgF_2 is consistent with the fact that only very small amounts of I and II were obtained. Also it should be noted that Kubas[12] has shown that SO_2 weakly bonded through S to a B type (soft) metal (Hg in this case) can be oxidized to SO_4^{2-} under suitable circumstances. Since I and II were produced only in small yield over a long period of time, it is reasonable to assume that only a small amount of oxidant need be present. If this is the case, it is possible that the molecular species $(MF_5)O–S–O(MF_5)$ (M = Nb, Ta) coordinated through S to Hg is first produced and that it is subsequently oxidized to I and II.

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Table VI. Hg Compounds with Polyatomic Cations

material	oxidn state of Hg	Hg–Hg dist, Å	arrangement of Hg atoms	ref
Hg_2F_2	+1	2.507 (1)	isolated ions	13
$Hg_3(AsF_6)_2$	$+^2/_3$	2.552 (5)	isolated ions	2
$Hg_3(AlCl_4)_2$		2.551 (1), 2.562 (1)		1
$Hg_3(NbF_5)_2SO_4$		2.562 (1)		present work (Ia)
		2.557 (1)		present work (Ib)
$Hg_3(TaF_5)_2SO_4$		2.554 (3)		present work (II)
$Hg_4(AsF_6)_2$	$+^1/_2$	2.620 (2), 2.588 (2), 2.985 (3)	nonuniform zigzag chains[a]	4
$Hg_4(TaF_{11})_2$		2.630 (2), 2.593 (2), 3.033 (2)		present work (III)
$Hg_{3-\delta}MF_6$ (M = As, Sb, Nb, Ta)	$\sim+^1/_3$	2.671 (1)	uniform straight chains with metallic bonds	14–16

[a] The Hg–Hg–Hg angles in these two compounds are given in Table IV.

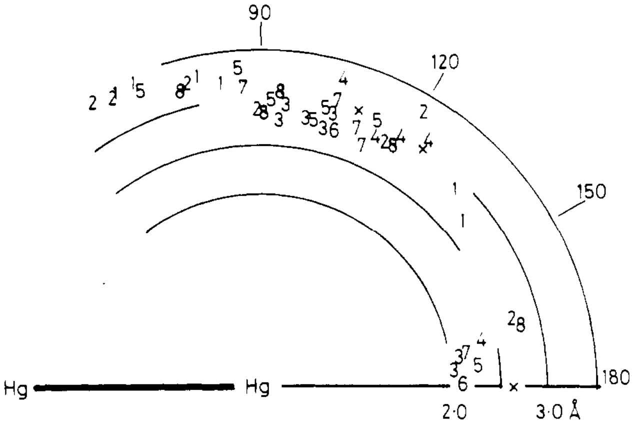

Figure 3. Correlation between Hg–X bond length (X = O, F, Cl) and Hg–Hg–X angle: (1) $Hg_4(AsF_6)_2$;[4] (2) $Hg_4(Ta_2F_{11})_2$ (III); (3) $Hg_3(AlCl_4)_2$;[1] (4) $Hg_3(AsF_6)_2$;[2] (5) $Hg_3(NbF_5)_2SO_4$ (I); (6) Hg_2F_2;[10] (7) $Hg_2SiF_6{\cdot}2H_2O$;[10] (8) $Hg_3(TaF_5)_2SO_4$ (II); (X) Hg–Hg bonds. The Hg–Cl distances have been reduced by 0.45 Å, the difference between the ionic radii of Cl and F. For comparison the short interionic Hg···Hg distances seen in the Hg_4^{2+} compounds are also shown.

Discussion

Stereoscopic projections of I and III are shown in Figures 1 and 2, and selected bond distances and angles are given in Tables IV and V. Compound II is isostructural with I. In compound I the Hg_3^{2+} cation and the $(NbF_5)_2SO_4^{2-}$ anion both lie on crystallographic twofold axes. They are linked into infinite chains running along the [110] and [$1\bar{1}0$] directions with the terminal O atoms situated at a distance 2.28 (1) Å from the terminal Hg along the axis of the cation (Hg–Hg···O = 174.8 (3)°, S–O···Hg = 149.2 (8)°). In this respect the environment of the Hg_3^{2+} ion is similar to that found in II, $Hg_3(AlCl_4)_2$, and $Hg_3(AsF_6)_2$ (see Table VI). In both compounds the Hg_3^{2+} ion shows the same tendency to form strong axial bonds to the anions. The Hg–Hg distances in the Hg_3^{2+} cation (2.559 (1) Å) are the same in all four compounds, though there are significant differences in the Hg–Hg–Hg angles (166.58 (6)° (I), 166.2 (2)° (II), 174.42 (4)° ($Hg_3(AlCl_4)_2$),[1] 180° ($Hg_3(AsF_6)_2$[2])). The bond distances within the anion and between the anion and cation are normal as indicated by the sums of the bond valences being close to the oxidation numbers (see Table III). The bond angles at Nb lie between 86 and 96°, and those at S are close to 109°, that subtended by O(1)–O(1) being noticeably smaller (105°) as expected for the longer bond length (see Appendix). The Nb–O–S angle is 138.4 (9)°. The results for II are not significantly different.

The Hg_4^{2+} ion in $Hg_4(Ta_2F_{11})_2$ (III) is almost linear and is intersected by the twofold axis (see Table V). As in $Hg_4(AsF_6)_2$ the central Hg–Hg bond is slightly shorter than the two terminal bonds.[4] The interionic Hg···Hg distance between terminal Hg atoms is only 3.033 (2) Å (Hg–Hg···Hg = 109.7 (1)°), which is comparable to the shortest distance found in α-Hg (2.99 Å).[17] It links the Hg_4^{2+} ions into zigzag chains running the entire length of the crystal in the *a* direction. Very similar zigzag chains were observed[4] in $Hg_4(AsF_6)_2$, where the Hg···Hg distance of 2.985 (3) Å makes an angle of 124.2 (1)° with the terminal Hg–Hg bond of the cation. The $Ta_2F_{11}^{2-}$ ion is normal with Ta–F–Ta = 153°.

In none of the known compounds containing Hg_2^{2+} and Hg_3^{2+} do these ions show any tendency to link together in the solid state, but in both Hg_4^{2+} compounds the Hg_4^{2+} ions are weakly linked to form zigzag chains. The limiting case is found in the infinite-Hg-chain compounds ($Hg_{3-\delta}MF_6$, $\delta \approx 0.1$, M = As, Sb, Nb, Ta), in which the oxidation state of Hg is close to $+^1/_3$ and the chains become essentially straight and uniform.[14-16] Table VI shows that the tendency for the ions to link into chains is associated with a lower formal oxidation state, the chains appearing when the Hg atoms have a charge less than $\sim+^1/_2$.

In Figure 3 the environment of the terminal Hg atoms in various compounds is plotted as a polar diagram showing Hg···X distance vs. Hg–Hg···X angle, where X = F, O, Cl, Hg. The shortest Hg···X distance corresponds to the largest Hg–Hg···X angle in every compound. As one would expect, the Hg···Cl bonds are significantly longer than the Hg···F bonds of similar angle but are of comparable strength if the difference in ionic radii between Cl and F is taken into account. The Hg atoms of the Hg_4^{2+} compounds are also shown in the plot, and it should be noted that the Hg···Hg distances are very similar to the Hg···F distances that occur at the same angle.

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Appendix

In a previous paper,[18] one of us has shown that the angle (θ_{ij}) between two bonds (i and j) in a tetrahedron can be calculated by using the relation

$$\theta_{ij} = 109.5 + 180(\langle S\rangle_{ij}/V - 1/4) - 652(\langle S\rangle_{ij}/V - 1/4)^2$$

where $\langle S\rangle_{ij}$ is the average valence of the bonds i and j and V is the oxidation state of the central atom.

This equation can be rewritten as

$$\langle S\rangle_{ij} = V(0.388 - 0.0302(121.9 - \theta_{ij})^{1/2})$$

Since each bond, i, is involved in three angles θ_{ij}, there are three estimates of each of the bond valences S_i of the form

$$S_i = \langle S\rangle_{ij} + \langle S\rangle_{ik} - \langle S\rangle_{jk}$$

From these three values one can calculate a mean and a standard deviation, which measures the internal agreement between the three estimates. With use of the angles O(1)–S–O(1) = 105°, O(1)–S–O(2) = 110.6°, and O(2)–S–O(2) = 110° found in the $(NbF_5)_2SO_4^{2-}$ ion the valences calculated are 1.43 ± 0.11 (S–O(1)) and 1.58 ± 0.11 (S–O(2)) (see Table III).

Supplementary Material Available: A table of anisotropic atomic displacement factors (1 page); tables of structure factor amplitudes for Ib and II (14 pages). Ordering information is given on any current masthead page. Structure factors for Ia and III are given in ref 11.

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