As expected, the effect in the IR of adding a Lewis acid to the sulfur of $Cp_2Fe_2(CO)_3(CS)$ is to increase all of the $\nu(CO)$ frequencies (Table I). The effect on the $\nu(CS)$ absorption is to shift it to lower frequency and to substantially decrease its relative intensity.

The electron-withdrawing effect of the Lewis acids may also be seen in the downfield shift of the Cp protons in the ^1H NMR spectra of the adducts as compared to that of the free dimer (Table I). The nonlinear C=S—A bond should make the two Cp rings inequivalent in the ^1H NMR spectra of the adducts, as observed in several *S*-alkyl derivatives.[3,6,18] However, in none of the adducts are the Cp rings inequivalent. In the $HgCl_2$ adduct, it is possible that dissociation and association of $HgCl_2$ occur sufficiently rapidly to make the Cp rings equivalent on the NMR time scale. However, for the other complexes, it seems unlikely that dissociation would be so rapid. In these cases, the Cp groups could be fortuitously equivalent or they could become equivalent on the NMR time scale by rapid rotation around the C=S bond or inversion at the sulfur atom. The reason for their equivalence is not clear from the data currently available.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $Cp_2Fe_2(CO)_3CS{\cdot}HgCl_2$, 80422-41-9; $Cp_2Fe_2(CO)_3CS{\cdot}HgBr_2$, 80422-42-0; $Cp_2Fe_2(CO)_3CS{\cdot}HgI_2$, 80422-43-1; $[Cp_2Fe_2(CO)_3CS\text{–}HgMe]PF_6$, 80422-37-3; $Cp_2Fe_2(CO)_3CS{\cdot}Cr(CO)_5$, 80422-40-8; $Cp_2Fe_2(CO)_3CS{\cdot}W(CO)_5$, 80434-41-9; $[Cp_2Fe_2(CO)_3CS{\cdot}CpFe(CO)_2]BF_4$, 80422-39-5; $Cp_2Fe_2(CO)_3(CS)$, cis isomer, 71154-94-4; $Et_4N[Cr(CO)_5I]$, 14780-98-4; $Et_4N[W(CO)_5I]$, 14781-01-2; $[CpFe(CO)_2(THF)]BF_4$, 63313-71-3; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0; MeHgCl, 115-09-3; $[Cp_2Fe_2(CO)_3(CS\text{–}Me)]PF_6$, 76189-80-5; $Cp_2Fe_2(CO)_3(CS)$, trans isomer, 80446-94-2.

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Specific Sequestering Agents for the Actinides. 8. Synthesis and Structural Chemistry of Tetrakis(thiohydroxamato)hafnium(IV) in $Hf(CH_3C_6H_4(S)N(O)CH_3)_4{\cdot}C_2H_5OH$[1]

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A continuing project in this laboratory has been the design and synthesis of specific sequestering agents for the actinide(IV) ions. The degree of success so far achieved in this goal has been reviewed recently.[1-4] The approach used relies on the similar coordination chemistry of high-spin Fe^{3+} and Pu^{4+} [2,3,5] and the molecular architecture of the siderophores (ferric ion specific chelating agents of microbial origin). While hydroxamate and catecholate chelating groups are the primary functional groups in siderophores, the thiohydroxamate chelating unit also occurs in at least one compound of natural origin.[6]

Table I. Summary of Crystal Data for $Hf(C_9H_{10}NOS)_4{\cdot}C_2H_5OH$

formula weight	945.5
space group	$P\bar{1}$
cell constants[a]	
a	10.501 (1) Å
b	10.958 (1) Å
c	18.684 (2) Å
α	97.388 (8)°
β	93.136 (8)°
γ	98.205 (9)°
cell volume	2014.4 (4) $Å^3$
formula units/cell, *Z*	2
calcd density	1.49 g cm^{-3}
obsd density	1.50 (1) g cm^{-3}
cryst dimens	0.35 × 0.30 × 0.18 mm
abs coeff, μ(Mo Kα)	28.5 cm^{-1}

[a] Conditions: ambient temperature 23 °C; Mo $K\alpha_1$ radiation; $\lambda = 0.709\,26$ Å.

The tetrakis(catecholato)metalate(IV) complexes of Th(IV), U(IV), and Hf(IV) have all been prepared and structurally characterized.[7,8] They are isostructural, with the D_{2d} coordination symmetry of the trigonal-faced dodecahedron. Both the hydroxamate complexes tetrakis(*N*-isopropyl-3,3-dimethylbutanehydroxamato)thorium(IV)[2] and tetrakis(*N*-phenylbenzohydroxamato)hafnium(IV)[9] have this same D_{2d} geometry. In contrast, the more sterically hindered complex, tetrakis(*N*-isopropyl-2,3-dimethylpropanehydroxamato)thorium(IV), is distorted substantially toward a cubic coordination polyhedron.[2] No tetrakis(thiohydroxamate) complexes have been structurally characterized to date.

Determination of the coordination geometry of the unconstrained tetrakis(bidentate)metalate(IV) complexes are a fundamental component in the design of an octadentate chelating agent that incorporates four such functionalities to form an optimum metal coordination environment. While we have prepared thiohydroxamate complexes of Th(IV), no crystals suitable for structure analysis have been obtained. Instead, we report the synthesis and structural characterization of the hafnium complex, the title compound.

Experimental Section

Synthesis of Compounds. Tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV)–Ethanol. An aqueous solution of hafnium tetrachloride (1.0 g, 3.12 mmol) in 10 mL of water was added to a stirred aqueous solution of sodium *N*-methyl-*p*-thiotolylhydroxamate (2.53 g, 12.5 mmol); the mixture was stirred for 5 min, and the white precipitate was filtered, washed with water, and dried in vacuum over P_2O_5. The compound was recrystallized from acetone–ethanol solution by slow evaporation. The crystals lose solvent easily in air. A sample for analysis was dried under high vacuum. The complexes are very hygroscopic and were partially hydrated just prior to analysis. Anal. Calcd for $Hf(C_9H_{10}NOS)_4$: C, 48.13; H, 4.49; N, 6.23; S, 14.27. Calcd for $Hf(C_9H_{10}NOS)_4{\cdot}H_2O$: C, 47.13; H, 4.61; N, 6.10; S, 14.00. Found: C, 47.43; H, 4.74; N, 6.12; S, 13.05.

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(1) Previous paper in this series: Weitl, F. L.; Raymond, K. N. *J. Org. Chem.* **1981**, *46*, 5234–37. A preliminary account of this work appeared at the 180th National Meeting of the American Chemical Society, Las Vegas, Aug 1980 (see Abstract INOR 300).

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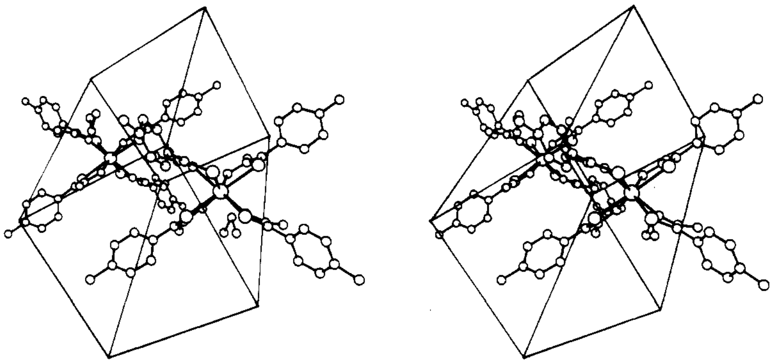

Figure 1. Packing diagram for tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV)–ethanol.

Thorium complexes with *N*-methylthiobenzohydroxamate and *N*-methyl-*p*-thiotolylhydroxamate were prepared by similar methods and were recrystallized from chloroform–isopropyl alcohol by slow evaporation. Again, the dried compounds are very hygroscopic. Anal. Calcd for tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)thorium(IV) [$Th(C_9H_{10}NOS)_4 \cdot H_2O$): C, 44.53; H, 4.36; N, 5.77. Found: C, 44.25; H, 4.26; N, 5.66.

Structure Determination. The crystal diffraction symmetry and lack of systematic absences imply the triclinic space groups $P1$ or $P\bar{1}$. The latter is confirmed by the final structure. The crystal density was determined by the flotation technique in bromoform–heptane solution. Crystal and unit cell data are given in Table I. Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer controlled by a PDP-8/E computer, using monochromatic Mo Kα radiation.[10,11] The data were collected so as to minimize absorption for each data point. Since the empirical range of absorption variation was less than 10%, no absorption correction was applied. The 8231 data were reduced to F^2 and $\sigma(F^2)$ as previously described[11-13] and averaged to give 7507 reflections with $F^2 > 3\sigma(F^2)$.

The structure was solved by direct phasing (MULTAN) and Fourier and least-squares techniques. The positions of the phenyl hydrogen atoms were calculated and found to match those found in the difference Fourier. The phenyl and most methyl and some ethanol hydrogen atoms were introduced as fixed atoms in the final refinement. Full-matrix least-squares refinement with 470 variables and using the 7507 reflections with $F^2 > 3\sigma(F^2)$ led to convergence with R = 2.8% and R_w = 4.4%.[14] Final positional parameters are given in Table IIa.

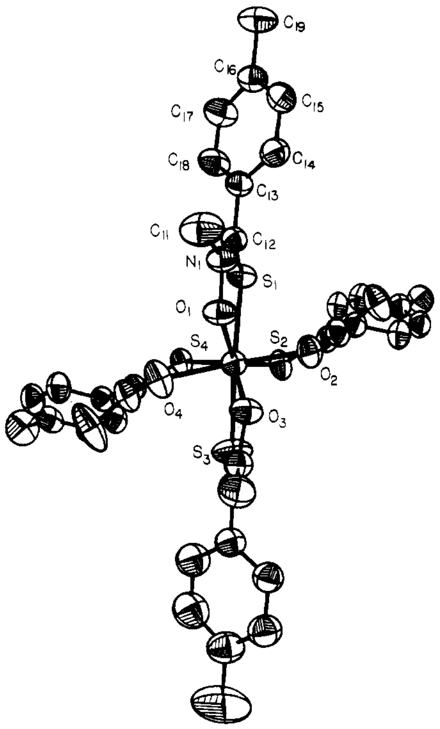

Figure 2. Perspective view and atom numbering scheme for tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV).

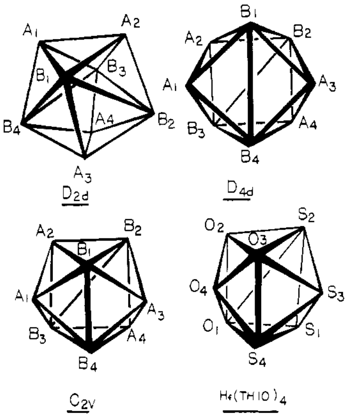

Figure 3. Coordination polyhedron of tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV) compared to the ideal dodecahedron, bicapped trigonal prism, and square antiprism.

Description of the Structure and Discussion

While thorium(IV) complexes with *N*-unsubstituted thiohydroxamic acids have been obtained, they are unstable toward hydrolysis. Green tetrakis(thiohydroxamato)uranium(IV) complexes have also been obtained under oxygen-free conditions [the metal undergoes oxidation to uranium(VI) in the presence of oxygen]. In contrast, the colorless hafnium complex reported here is quite stable and its structure consists of tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV) and ethanol molecules of crystallization (Figure 1). The structure of the complex and the atom numbering scheme used within it is shown in Figure 2. Relevant bond lengths and angles of the thiohydroxamato molecules are given in Table V. The thiohydroxamato rings are planar and bend away from the hafnium atom such that the Hf-to-plane distances are 0.62,

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(10) The Enraf-Nonius Fortran IV system, which operates the CAD-4 diffractometer, and locally written or modified programs for the CDC-7600 have been described in ref 12 and 13.

(11) The intensities of a unique set of reflections $(+h,\pm k,\pm l)$ with $2° < 2\theta < 53°$ were measured, with a θ–2θ scan technique [the duplicates were measured for $(0,\pm k,\pm l)$ as a check]. The instrument parameters used in data collection were those described in ref 13. A p factor of 0.03 was used in data reduction.

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(14) Definitions of the indicators are $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. The error in an observation of unit weight is $[(\Sigma w(|F_o| - |F_c|)^2)/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v is the number of variables. The largest peaks in the final difference Fourier were <0.35 e/Å^3. Table IIb gives the thermal parameters of the nonhydrogen atoms. Table III lists the root-mean-square amplitudes of vibration of these atoms. Table IV gives the positional and thermal parameters assigned to the hydrogen atoms. These tables are all available as supplementary material; see the paragraph at the end of the paper.

Table IIa. Positional Parameters (×10^4) for the Nonhydrogen Atoms of Tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV)

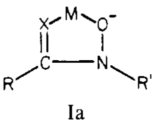
	x	y	z
Hf	.59275(1)	.93610(1)	.287501(8)
S(1)	.68875(9)	1.05840(9)	.18181(5)
S(2)	.5405(1)	.76404(9)	.17059(5)
S(3)	.3998(1)	1.0026(1)	.20681(7)
S(4)	.5882(2)	1.1722(1)	.33954(6)
O(1)	.8000(3)	.9912(3)	.3094(2)
O(2)	.6636(3)	.7711(2)	.3112(1)
O(3)	.4108(3)	.8440(3)	.3140(2)
O(4)	.6133(3)	.9522(2)	.4031(1)
N(1)	.8727(3)	1.0865(4)	.2830(2)
N(2)	.6538(3)	.6599(3)	.2690(2)
N(3)	.3040(3)	.8150(3)	.2682(2)
N(4)	.6397(3)	1.0595(3)	.4499(2)
C(11)	.9793(6)	1.1428(7)	.3333(3)
C(12)	.8363(4)	1.1227(4)	.2235(2)
C(13)	.9207(4)	1.2176(4)	.1907(2)
C(14)	1.0483(4)	1.2048(5)	.1801(3)
C(15)	1.1250(4)	1.2961(5)	.1493(3)
C(16)	1.0752(5)	1.3977(5)	.1274(3)
C(17)	.9492(5)	1.4072(5)	.1371(3)
C(18)	.8734(4)	1.3186(4)	.1690(3)
C(19)	1.1655(7)	1.4912(7)	.0918(4)
C(21)	.7279(5)	.5748(5)	.3013(3)
C(22)	.5962(3)	.6433(3)	.2037(2)
C(23)	.5786(4)	.5190(3)	.1590(2)
C(24)	.6183(5)	.5058(4)	.0896(2)
C(25)	.5965(5)	.3912(4)	.0471(2)
C(26)	.5354(4)	.2878(3)	.0721(2)
C(27)	.4930(4)	.3015(4)	.1402(2)
C(28)	.5138(4)	.4163(4)	.1839(2)
C(29)	.1578(5)	.1586(4)	.0261(3)
C(31)	.2259(5)	.6991(5)	.2803(3)
C(32)	.2834(4)	.8829(4)	.2177(2)
C(33)	.1621(4)	.8607(4)	.1710(2)
C(34)	.0411(4)	.8485(4)	.1987(3)
C(35)	-.0693(4)	.8393(5)	.1539(3)
C(36)	-.0647(4)	.8413(4)	.0797(3)
C(37)	.0545(5)	.8526(5)	.0521(3)
C(38)	.1670(4)	.8635(5)	.0964(3)
C(39)	-.1873(5)	.8370(6)	.0321(3)
C(41)	.6809(5)	1.0362(4)	.5220(2)
C(42)	.6272(4)	1.1672(4)	.4282(2)
C(43)	.6421(4)	1.2826(4)	.4804(2)
C(44)	.5690(4)	1.2959(4)	.5385(2)
C(45)	.5820(5)	1.4081(5)	.5829(3)
C(46)	.6652(6)	1.5095(5)	.5720(3)
C(47)	.7344(7)	1.4989(5)	.5103(4)
C(48)	.7235(6)	1.3869(5)	.4647(3)
C(49)	.683(1)	1.6278(6)	.6226(5)
O(EtOH)	.9605(6)	.8397(7)	.3751(4)
C1(EtOH)	.919(1)	.8167(9)	.4428(5)
C2(EtOH)	1.007(1)	.714(1)	.4557(6)

Table V. Bond Distances (Å) and Angles (Deg) for Tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV)

	ring 1	ring 2	ring 3	ring 4
Hf-S	2.688 (1)	2.673 (1)	2.699 (1)	2.653 (1)
Hf-O	2.175 (3)	2.139 (3)	2.144 (3)	2.141 (3)
C-S	1.709 (4)	1.694 (4)	1.701 (4)	1.695 (4)
N-O	1.365 (4)	1.352 (4)	1.347 (5)	1.357 (4)
C-N	1.284 (5)	1.310 (5)	1.301 (5)	1.317 (5)
C-C(Ph)	1.484 (5)	1.485 (5)	1.476 (6)	1.478 (6)
CH_3-N	1.434 (6)	1.465 (5)	1.461 (5)	1.459 (5)
O-Hf-S	70.11	71.67 (7)	70.28 (8)	72.35 (7)
S-C-N	118.8 (3)	119.7 (3)	118.5 (3)	119.3 (3)
S-C-C(Ph)	120.2 (3)	120.0 (3)	119.3 (3)	119.6 (3)
N-C-C(Ph)	121.1 (3)	120.3 (3)	122.2 (3)	121.1 (4)
O-N-C(CH_3)	111.1 (4)	112.0 (3)	111.8 (3)	111.3 (3)
O-N-C	120.7 (3)	120.4 (3)	120.8 (3)	120.8 (3)

0.11, 0.77, and 0.34 Å for chelate rings 1, 2, 3, and 4, respectively.

Bond distances in the thiohydroxamato ring compare well with the corresponding bond distances in other thiohydroxamato complexes.[15] The N-O and N-C bond distances, 1.355 (4) and 1.303 (7) Å, in tetrakis(*N*-methyl-*p*-thiotolyhydroxamato)hafnium(IV) are slightly shorter than the corresponding bond distances, 1.37 (2) and 1.32 (2) Å, found in the tetrakis(*N*-phenylbenzohydroxamato)hafnium(IV) structure.[9] This reflects the increase in contribution of structure Ib to the bonding in thiohydroxamato complexes.



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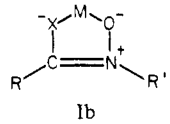

Ib

[13,15-17] Note also that all the sulfur atoms lie on two adjacent trigonal faces (Figures 2 and 3). This maximizes the polarity of the complex. In the same fashion, the cis (C_3 symmetry) isomer of the Fe(III) octahedral complexes of the hydroxa-

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Table VI. Shape Parameters for Tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV)

1. Dihedral angles, δ (degrees)

Edge[b]	Porai-Koshits/Aslanov notation for C_{2v}	Observed angle	Calculated angle for ideal		
			D_{2d}	D_{4d}	C_{2v}
$S_2(S_1S_3)S_4$	P_1	58.3	51.3	52.4	60.8
$O_1(O_2O_4)O_3$	P_1	58.7	51.3	52.4	60.8
$S_1(S_2S_3)O_3$	P_1	62.6	62.5	52.4	60.8
$O_2(O_1O_4)S_4$	P_1	45.6	62.5	52.4	60.8
$S_2(O_3S_3)S_4$	P_2	66.7	51.3	76.2	60.8
$O_1(O_4S_4)O_3$	P_2	75.7	51.3	76.2	60.8
$O_3(S_3S_4)S_1$	P_2	71.0	62.5	76.2	60.8
$O_2(O_3O_4)S_4$	P_2	62.6	62.5	76.2	60.8
$O_1(O_2S_2)O_3$	t_1	82.1	51.3	76.2	90.0
$S_2(O_1S_1)S_4$	t_1	74.5	51.3	76.2	90.0
$O_2(O_3S_2)S_3$	t_2	47.5	29.5	52.4	48.2
$O_4(O_1S_4)S_1$	t_2	45.3	29.5	52.4	48.2
$O_4(O_2O_3)S_2$	t_2	39.5	62.5	52.4	48.2
$O_1(S_1S_4)S_3$	t_2	58.2	62.5	52.4	48.2
$O_1(S_1S_2)S_3$	h_1	71.4	62.5	76.2	70.9
$O_4(O_1O_2)S_2$	h_1	65.4	62.5	76.2	70.9
$O_4(O_3S_4)S_3$	h_2	21.1	29.5	0.0	21.8
$O_2(O_1S_2)S_1$		9.8	29.5	0.0	0.0

2. Twist angle in the BAAB trapezoid, ϕ

Observed	Calculated for		
	D_{2d}	D_{4d}	C_{2v}
15	0.0	24.5	14.1

[a] See Figure 3. [b] In defining the dihedral angle, atoms in parentheses represent the edge; the other two atoms form the two intersecting triangles with the edge.

mates and thiohydroxamates seem to be slightly more stable in aqueous solution than the less polar trans.[6]

Detailed analyses of eight-coordinate polyhedra have been carried out by several workers.[18-21] The general conclusion is that the trigonal-faced dodecahedron (D_{2d}) and the square antiprism (D_{4d}) lie very close in energy, with the bicapped trigonal prism (C_{2v}) at slightly higher energy[21] (Figure 3). Both the bicapped trigonal prism and the square antiprism can be generated from the intermediate dodecahedron by changing the length of one or two b edges.[21] A set of shape parameters have been proposed to describe eight-coordinate geometries, where δ is the dihedral angle between faces of the polyhedron defined by the ligand atoms; and ϕ measures the nonplanarity of the trapezoidal-type atoms BABA in the dodecahedron (Figure 3). The ϕ and the δ values for the compound tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV) are given in Table VI, along with the corresponding calculated values for the ideal dodecahedron, square antiprism and bicapped trigonal prism. The average value for ϕ (15°) is very close to that for C_{2v} geometry (14.1°). The δ values also support the conclusion that the solid-state (thiohydroxamato)hafnium complex has a geometry close to a bicapped trigonal prism. The largest deviations from C_{2v} geometry are for t_1 edges and for the diagonal edges of the tetragonal face. These deviations are ascribed to the difference in the size of the sulfur and oxygen atoms.

In conclusion, the thorium and hafnium complexes of thiohydroxamic acids have been prepared and characterized. The structure of the compound tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV) displays a bicapped trigonal prismatic coordination polyhedron, a polyhedron not observed for the catecholato and hydroxamato complexes studied to date.

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Registry No. $Hf(C_9H_{10}NOS)_4 \cdot C_2H_5OH$, 80531-99-3.

Supplementary Material Available: Table IIb (thermal parameters of nonhydrogen atoms), Table III (root-mean-square amplitudes of vibration of nonhydrogen atoms), Table IV (positional and thermal parameters of hydrogen atoms), and a listing of structure factor amplitudes (54 pages). Ordering information is given on current masthead page.

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A Convenient Synthesis of Dithionitronium Hexafluoroarsenate(V), S_2NAsF_6

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A salt containing the S_2N^+ cation, S_2NSbCl_6, was first reported by Faggiani et al.,[2] prepared in unspecified yield by the reaction of S_7NH, S_7NBCl_2, or 1,4-$S_6N_2H_2$ with $SbCl_5$ in liquid SO_2. Concurrently, we were investigating the reactions of azides with $S_8(AsF_6)_2$, which yielded S_2NAsF_6 (in low yield according to eq 1) rather than the sought-after S_xNAsF_6 (x = 7 or 8) species.

$$S_8(AsF_6)_2 + NaN_3 \xrightarrow{SO_2} S_2NAsF_6 + NaAsF_6 + N_2 + {}^3/_4S_8 \tag{1}$$

Sulfur and excess arsenic pentafluoride in sulfur dioxide react to give $S_8(AsF_6)_2$. In the presence of traces of bromine[3] further oxidation takes place and the reaction proceeds essentially quantitatively according to eq 2. We wish to report

$$^1/_2S_8 + 3AsF_5 \xrightarrow[Br_2]{SO_2} S_4(AsF_6)_2 + AsF_3 \tag{2}$$

that traces of elemental bromine also facilitate the formation of S_2NAsF_6 in good yield according to eq 3.

$$^1/_2S_8 + S_4N_4 + 6AsF_5 \xrightarrow[Br_2]{SO_2} 4S_2NAsF_6 + 2AsF_3 \tag{3}$$

Gillespie et al.[4] have reported that S_4N_4 and AsF_5 in a 3:1 ratio or greater give $S_4N_4^{2+}$, and with small amounts of sulfur,[4-6] $S_6N_4^{2+}$. The $S_4N_4 \cdot AsF_5$ adduct has also been char-

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