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 $1,4\text{-}S_6N_2H_2$ 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.

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

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

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

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

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

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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Table I. Infrared and Raman Spectra (cm^{-1}) of S_2NAsF_6 and S_2NSbCl_6

S_2NAsF_6[a]		S_2NSbCl_6[c]			$CsAsF_6$[d]	
IR, Nujol mull	Raman,[b] solid	IR, solid	Raman, solid	assignts[c,d]	IR	Raman
1494 (m)		1498 (m)		ν_3 (S_2N^+)		
1088 (w)				$\nu_1 + \nu_2$ (S_2N^+)		
818 (w)				AsF_6^-		
	798 (18, br)		766 (17)	$2\nu_2$ (S_2N^+)		
	779 (3, ?)		747 (2)	$2\nu_2$ ($^{32}S^{34}SN^+$)		
	696 (100)		688 (44)	ν_1 (S_2N^+)		
			680 (8)	ν_1 ($^{32}S^{34}SN^+$)		
		374 (m)		ν_2 (S_2N^+)		
	682 (30)		333 (100)	ν_1 ((A_{1g}) AsF_6^-, $SbCl_6^-$)		685 (10)
697 (vs)		320 (s)		ν_3 ((T_{1u}) AsF_6^-, $SbCl_6^-$)	699 (s)	
391 (s)				ν_4 ((T_{1u}) AsF_6^-)	392 (m)	
	573 (8)		293 (12)	ν_2 ((E_g) AsF_6^-, $SbCl_6^-$)		576 (2.3)
			283 (8)			
			180 (26)	ν_5 ((T_{2g}) AsF_6^-, $SbCl_6^-$)		
	368 (10)		175 (48)			372 (2.6)
			167 (4)			
			78 (100)	lattice modes		
			62 (76)			

[a] This work. [b] 5145-Å exciting line; intensities in parentheses. [c] Reference 2. [d] Reference 14.

acterized from the reaction of S_4N_4 with AsF_5 in CCl_4.[7] This adduct has also been isolated from the reactions of S_4N_4 with $Se_8(AsF_6)_2$ in CH_2Cl_2 and with $Te_4(AsF_6)_2$ in SO_2 and its structure determined.[8]

Experimental Section

General Considerations. Except where stated, apparatus and chemicals have been described.[9-11] The vessel used in preparation 2 was larger (~150 cm^{-3}) in order to accommodate evolved nitrogen. The $S_8(AsF_6)_2$ and S_4N_4 were prepared according to ref 12 and 13, respectively. Sodium azide (BDH) was vacuum-dried before use.

Preparation of S_2NAsF_6. (1) In a typical reaction an excess of AsF_5 relative to eq 3 (3.04 g, 17.9 mmol) and a trace of bromine (0.04 g, 0.22 mmol) were condensed onto frozen SO_2 (5.45 g, 85.1 mmol) over a mixture of S_8 (0.37 g, 1.44 mmol) and S_4N_4 (0.53 g, 2.88 mmol) in one side of a two-bulb glass vessel equipped with a Teflon-stemmed J. Young valve and a sintered-glass frit. After 20 h of stirring at room temperature, the product was a dark red-green solution over a crystalline yellow solid. The volatiles (SO_2, AsF_3, and AsF_5) were removed and replaced by 5.14 g (80.3 mmol) of SO_2 as the salt is less soluble in SO_2 than in the AsF_3/SO_2 mixture. The SO_2 was slowly transferred across the frit, by placing the initially empty bulb in a cold water bath, until a small volume of solvent remained over the yellow crystalline product. This solution was filtered, and the crystals were washed several more times with small quantities of SO_2 to remove the more soluble impurity. The solvent was then removed by evacuation. The yellow crystalline product (1.65 g, 6.18 mmol, 54% yield based on S_4N_4 and eq 3) was identified as S_2NAsF_6 by its IR and Raman spectra (Table I). The more soluble crude yellow-green product (1.33 g) contained largely S_2NAsF_6 (IR). Sulfur dioxide (5.18 g, 80.8 mmol) was condensed onto a sample of this crude mixture (1.21 g) and additional S_8 (0.10 g, 0.39 mmol) in a similar vessel. The added S_8 reacted with the impurities to form a more soluble product possibly including $S_x(AsF_6)_2$ ($x \geq 16$).[15,16] The soluble material was then quantitatively transferred across the frit in a series of washings, leaving behind insoluble unreacted S_8. Crystalline S_2NAsF_6 (0.70 g, 2.62 mmol) was then obtained by washing with SO_2, as described above. The more soluble dark red-brown impure product contained S_2NAsF_6 and a mixture of unidentified species (IR). The overall yield of purified S_2NAsF_6 (2.35 g) was 77%. Anal. Calcd for S_2NAsF_6: S, 24.01; N, 5.25. Found: S, 24.00; N, 5.21.

(2) In a typical reaction, SO_2 (33.3 g, 520.0 mmol) was condensed onto a mixture of NaN_3 (1.36 g, 20.9 mmol) and $S_8(AsF_6)_2$ (10.61 g, 16.7 mmol). When the mixture warmed to room temperature, a green solution formed and nitrogen was evolved. After 20 h of stirring, the solution became dark red-brown. The solution was then filtered, and the cream-colored insoluble materials (S_8 and $NaAsF_6$, Raman spectrum) were washed several times. On several days of standing, more S_8 precipitated from solution, and the solution was filtered into a third bulb. The SO_2 and N_2 (0.86 g, 30.7 mmol) were removed, yielding 4.46 g of soluble and 6.65 g of insoluble product. The soluble product was recrystallized from SO_2 solution, giving yellow crystals of S_2NAsF_6 (0.89 g, 3.33 mmol, 20% yield based on $S_8(AsF_6)_2$ and eq 1) and a more soluble dark brown impurity.

Discussion

The S_2N^+ cation is likely to be a useful building block in sulfur–nitrogen chemistry and a precursor to a variety of new compounds. It is readily synthesized according to eq 3 in good yield (77%). Further oxidation of S_2NAsF_6 did not occur with a greater than twofold excess of arsenic pentafluoride. In the absence of bromine the reaction was much slower, and the recovered yield was less (ca. 30%). The compound S_2NAsF_6 was also prepared in low yield according to eq 1, presumably via S_xN^+ (S_7N^+ and S_3N^+ are electronically similar to S_8^{2+}[17] and S_4^{2+}[3,12]), which may slowly eliminate sulfur leading to S_2N^+. The other soluble product had the characteristics (color, solubility, etc.) of $S_x(AsF_6)_2$ ($x \geq 16$),[10,15,16] formed by the reaction of $S_8(AsF_6)_2$ starting material with precipitated sulfur.

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Registry No. S_2NAsF_6, 80485-40-1; AsF_5, 7784-36-3; S_4N_4, 28950-34-7; S_8, 10544-50-0; $S_8(AsF_6)_2$, 33248-05-4; NaN_3, 26628-22-8.

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