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Kamal Abu-Dari and Kenneth N. Raymond

July 1981

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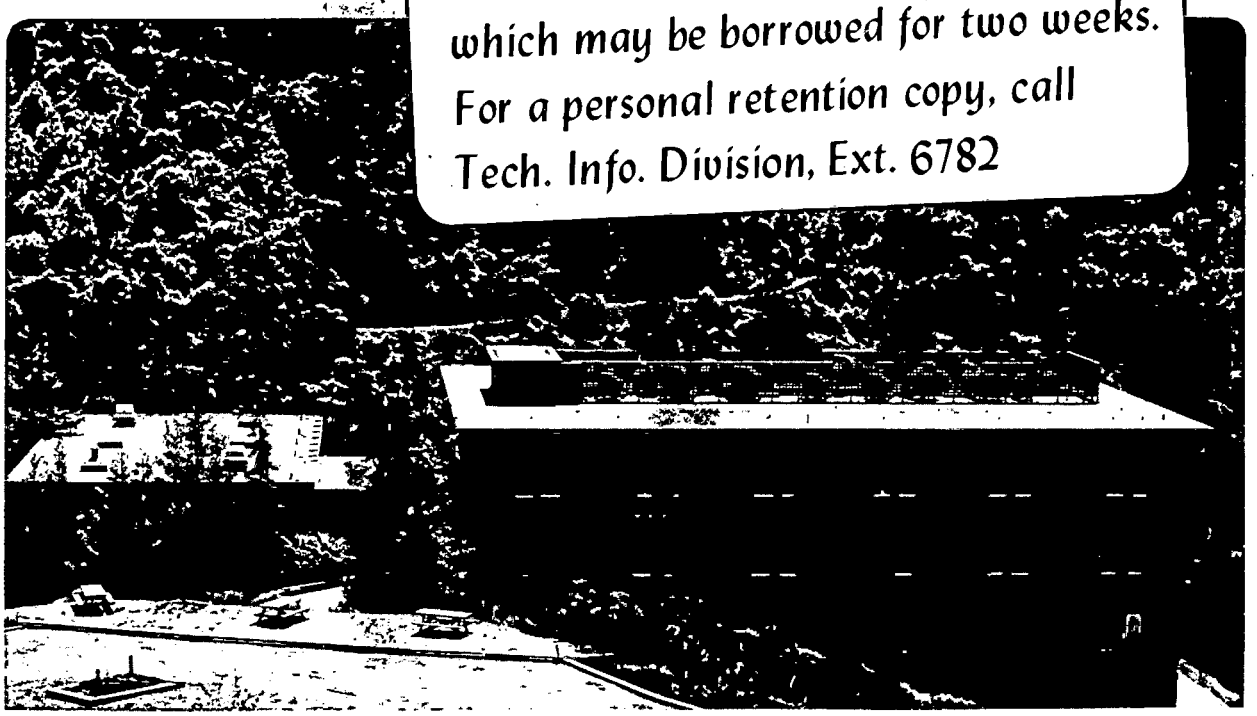

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Specific Sequestering Agents for the Actinides. 7. Synthesis and Structural Chemistry of Tetrakis(thiohydroxamato)hafnium(IV) in $Hf(CH_3C_6H_4(S)N(O)CH_3)_4 \cdot C_2H_5OH$[1]

By

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Introduction

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]

The tetrakis(catecholato)metallate(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-dimethylbutanohydroxamato)thorium(IV)[1] 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-dimethylpropanahydroxamato)thorium(IV), is distorted substantially toward a cubic coordination polyhedron.[1] No tetrakis(thiohydroxamate) complexes have been structurally characterized to date.

Determination of the coordination geometry of the unconstrained tetrakis(bidentate)metallate(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

Synthesis of Compounds

Tetrakis(N-methyl-p-thiotolylhydroxamato)hafnium(IV). Ethanol. An aqeuous solution of hafnium tetrachloride (1.0 g, 3.12 mmol) in 10 mL 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 five minutes 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. Calc. for $Hf(C_9H_{10}NOS)_4$: C, 48.13; H, 4.49; N, 6.23; S, 14.27.
Calc. 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%.

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. Analysis for tetrakis(N-methyl-p-thiotolylhydroxamato)thorium(IV) is:

Anal. Calc. for $Th(C_9H_{10}NOS)_4 \cdot H_2O$: 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 date were collected on an Enraf-Nonius CAD-4 automated diffractometer controlled by a PDP-8/E computer, using monochromatic MoK_α radiation.[10,11] The 8231 data were reduced to F^2 and $\sigma(F^2)$ as previously described[11-13] and averaged to give 7507 reflections with $F^2 > 3\sigma(F^2)$.

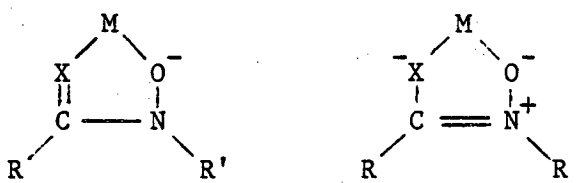
The structure was solved by direct phasing (MULTAN), Fourier and least-squares techniques. The positions of the phenyl hydrogen atoms were calculated and found to match those found in the difference Fourier. The phenyl, and most methyl and some ethanol, hydrogen atoms were introduced as fixed atoms in 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]

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, 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-thiotolylhydroxamato)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.[13,15-17]



Ia Ib

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.

Acknowledgment

We thank the U.S.A.I.D. (K.A.D.) and N.I.H. for support. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

Supplementary Material

Table II, III and IV and a listing of structure factor amplitudes. Ordering information is given on current masthead page.

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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 Refs. 12 and 13.

11. The intensities of a unique set of reflections (+h, ±k, ±ℓ) with $2° < 2\theta < 53°$ were measured, using a θ-2θ scan technique [the duplicates were measured for (0, ±k, ±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: $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, 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 final error in an observation of unit weight is 1.63. The largest peaks in the final difference Fourier were < 0.35 $e^-/Å^3$. Table II gives the positions and thermal parameters of the non-hydrogen atoms. Table III lists the rms 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.

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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)
Formula units/cell, Z	2
Calculated density	1.49 g cm^{-3}
Observed density	1.50(1) g cm^{-3}
Crystal dimensions	0.35 x 0.30 x 0.18 mm
Absorption coefficient, μ MoK_α	28.5 cm^{-1}

[a] Ambient temperature of 23°C; MoK_{α_1} radiation, λ = 0.70926 Å.

Table V

Bond distances and angles for Hf(N-methyl-p-thiotolylhydroxamato)hafnium(IV)[a]

	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)

[a]Bond (Å) or angle (deg).

Table VI

Shape parameters for Hf(N-methyl-p-thiotolylhydroxamate)$_4$

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

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[a] See Figure 3.

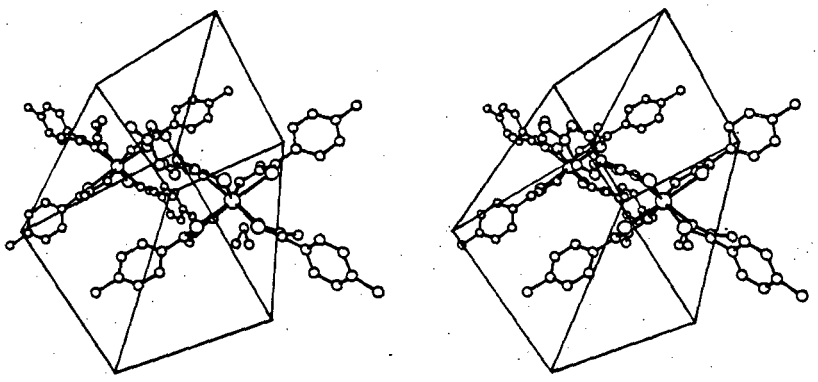
[b] In defining the dihedral angle, atoms in parenthesis represent the edge, the other two atoms form the two intersecting triangles with the edge.

Figure Captions

Figure 1. Packing diagram for tetrakis(N-methyl-p-thiotolylhydroxamato)-hafnium(IV)·C_2H_5OH.

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

Figure 3. The coordination polyhedron of Hf(N-methyl-p-thiotolyl-hydroxamate)$_4$ compared to the ideal dodecahedron, bicapped trigonal prism and square antiprism.



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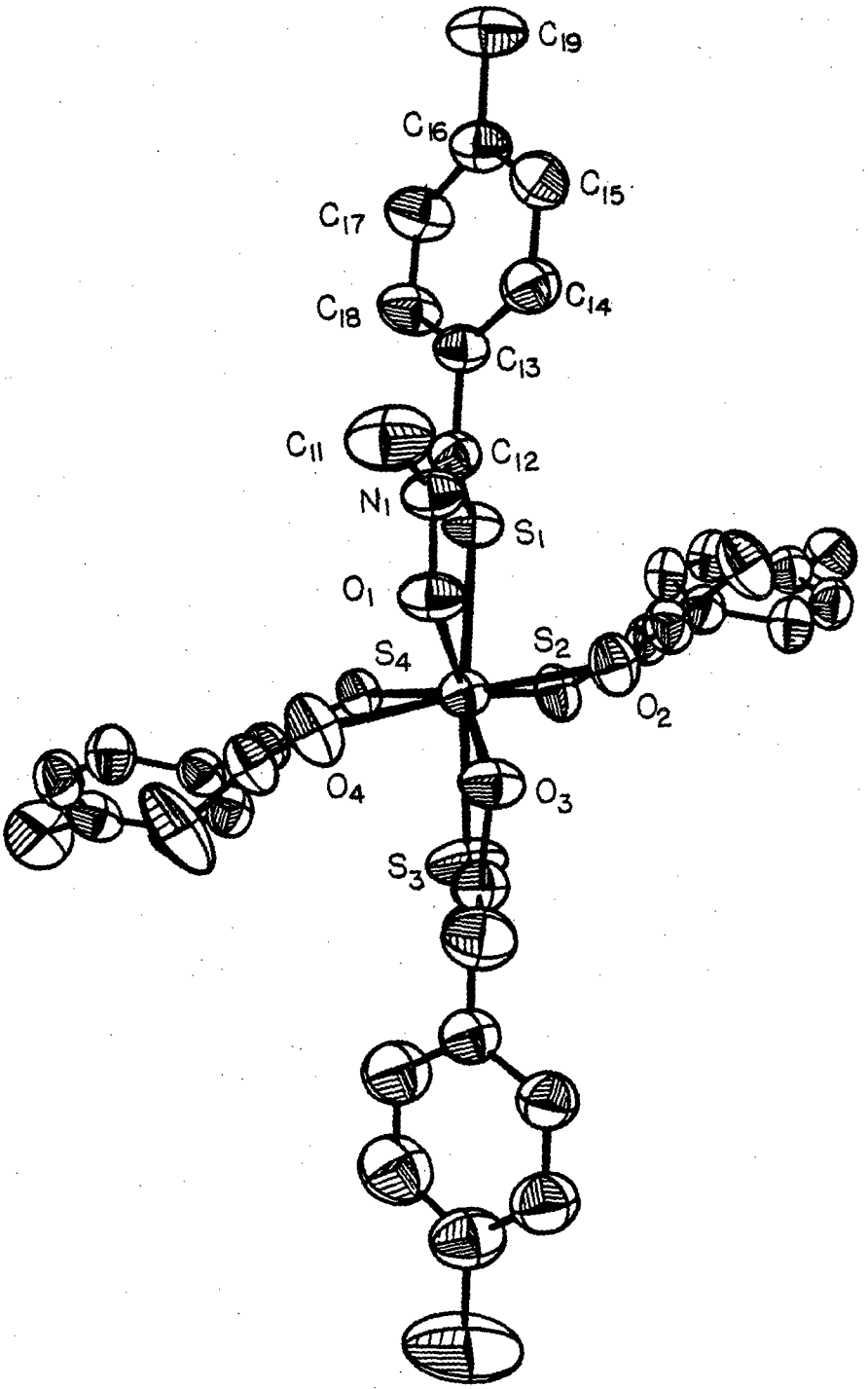

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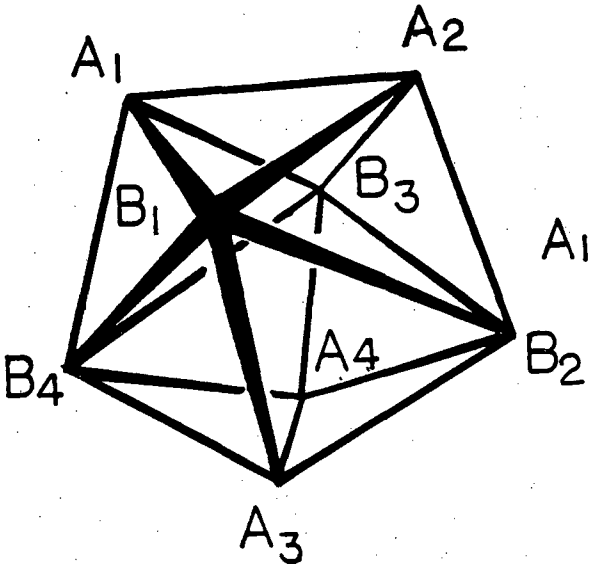
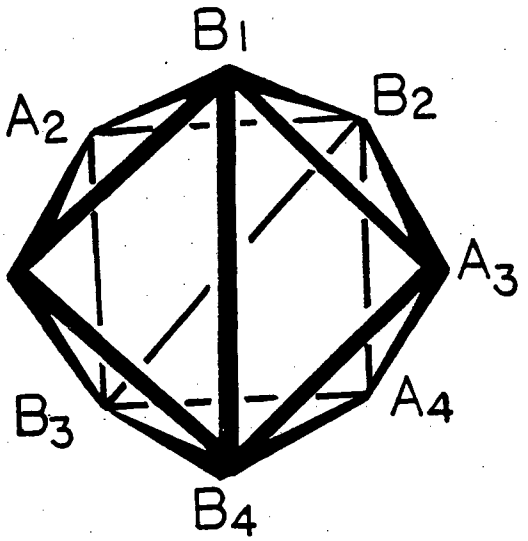
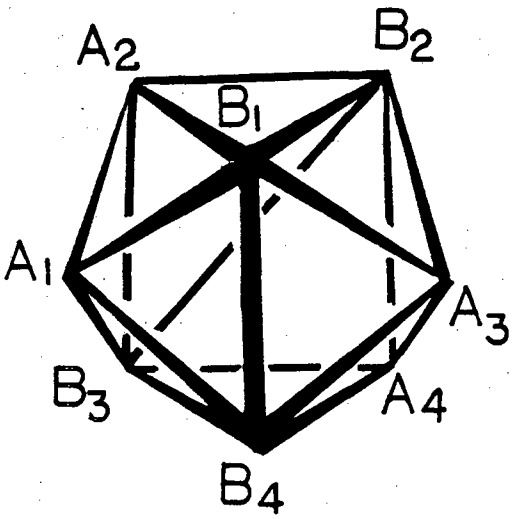


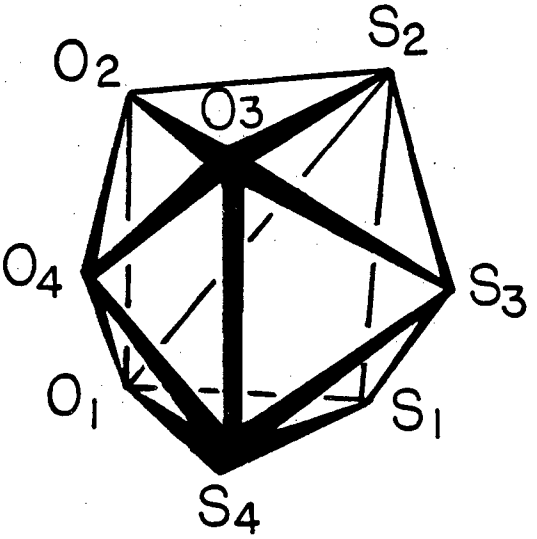
D_{2d}



D_{4d}



C_{2V}



$Hf(TH10)_4$

XBL 808-11271

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