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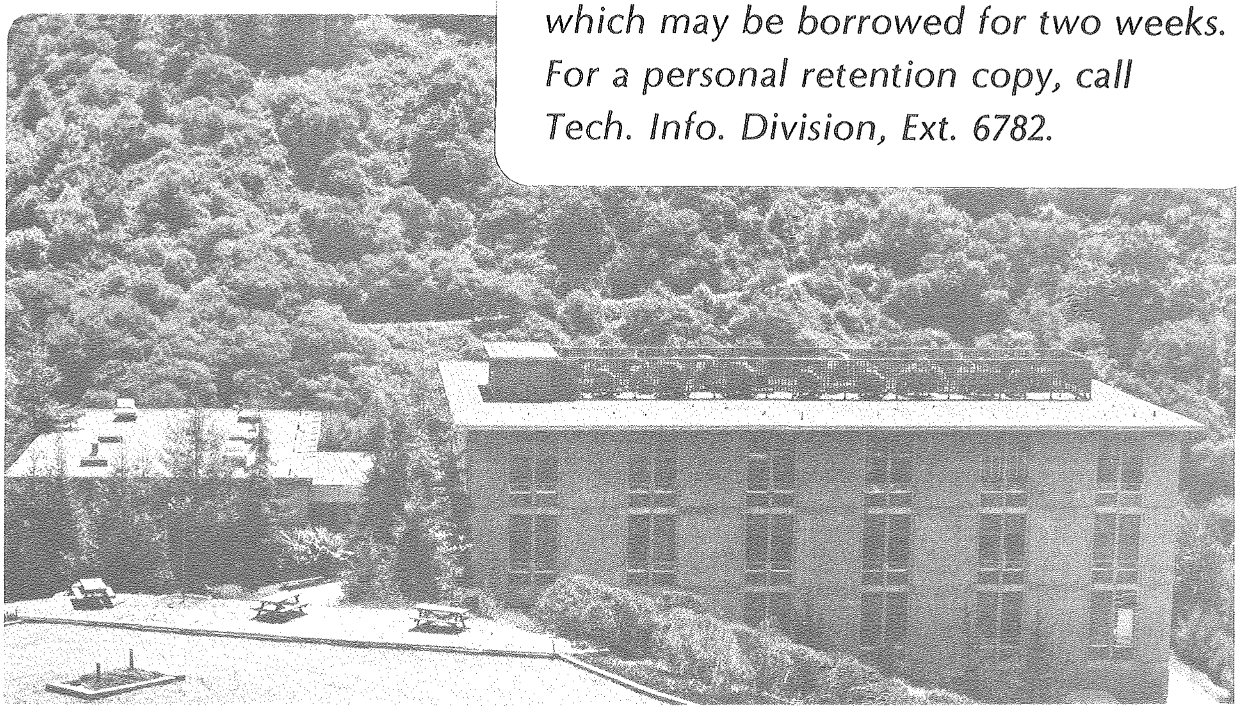

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Specific Sequestering Agents for the Actinides. 6. Synthetic and Structural Chemistry of Tetrakis(dialkylhydroxamate)-thorium(IV) Complexes[1]

By

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Abstract

Hydroxamate complexes of the actinides have been investigated as structural achetypes in the design of actinide-specific sequestering agents. The complexes $Th[(CH_3)_2CHC(O)N(O)R]_4$ have been prepared, from aqueous solutions of Th(IV) and the corresponding hydroxamic acid, for $R = C(CH_3)_3$ or $CH_2C(CH_3)_3$ (compounds 1 and 2, respectively). Both complexes 1 and 2 are hydrocarbon soluble and remarkably volatile, subliming near 100° at 10^{-3} Torr. They are fluxional and rapidly exchange hydroxamate ligands in $CHCl_3$ solution. The uranium(IV) analogue of 1 was also prepared, but the uranium(IV) hydroxamates undergo an internal redox reaction that involves oxygen atom transfer from the ligand to the metal to give a bis(hydroxamate)uranyl complex and the amide of one hydroxamate ligand. The physical properties of the thorium hydroxamate complexes seem to be due to their hydrocarbon substituents, and the different steric constraints imposed by the C-substituent tert-butyl and neopentyl groups of 1 and 2, respectively, give rise to dramatically different coordinate geometries. The t-butyl groups of 1 dominate the stereochemistry of the complex by assuming a tetrahedral disposition around the metal. The coordination polyhedron of 1, which has $\bar{4}$ (S_4) crystallographic symmetry, is nearly cubic. The localization of charge on the nitrogen oxygen of the hydroxamate group makes this ligand unsymmetrical and this gives rise to a 0.14 Å difference in $R(Th-O_N)$ [2.357(3) Å] and $R(Th-O_C)$ [2.492(3) Å]. The sterically less constrained neopentyl derivative, 2, shows a more typical eight-coordinate geometry — the D_{2d} trigonal-faced (mmmm) dodecahedron. Although there is no crystallographically imposed symmetry for 2, the polyhedron is close to

the ideal dodecahedron. The average R(Th-O_N) [2.36(1) Å] is again shorter than R(Th-O_C) [2.46(2) Å]. There is apparently no sorting of sites by ligand charge, since the O_N and O_C atoms are equally distributed between the A and B sites of the dodecahedron. Detailed analysis of the geometries of 1 and 2 are carried out in terms of their shape parameters, and explicitly compared to related eight-coordinate complexes. Both compounds 1 and 2 are colorless. Crystals of 1 conform to space group $I4_1/a$ with a = 17.338(4) and c = 12.706(4) Å. For 4 formula units per cell the calculated density, d_{calc} is 1.50 and d_{obs} is 1.50(1) g cm^{-3}. Crystals of 2 conform to space group $P\bar{1}$ with a = 9.777(2), b = 14.633(2), c = 18.515(1) Å, α = 74.061(8), β = 88.41(1), γ = 74.71(2)°. For 2 formula units per cell d_{calc} = 1.30, d_{obs} = 1.19 g cm^{-3}. Full matrix least squares refinement of both structures using all averaged, independent data with $F^2 > 3\sigma(F^2)$ gave: for 1 with 1798 data and 117 variables, R = 0.027 and R_w = 0.032; for 2 with 6978 data and 467 variables, R = 0.034, R_w = 0.042.

Introduction

A biomimetic approach to the design of tetravalent actinide specific sequestering agents modeled after bacterial iron transport agents has suggested the incorporation of catechol or hydroxamic acid ligating groups in an octadentate macrochelate.[1,2] The complexes formed by actinide(IV) ions and these ligands, in which the steric constraints of a macrochelate are absent, serve as structural archetypes for designing the optimum actinide(IV) macrochelate. The actinide(IV) catecholates have been observed[3] to have coordination polyhedra very close to the idealized trigonal-faced dodecahedron in which the m edges are spanned by the ligands. While hydroxamic acids have been used in quantitative analysis and solvent extraction of actinides,[4] the complexes formed have not been structurally characterized. In order to characterize fully the formulation and coordination geometry of these compounds, the structures of tetrakis(N-isopropyl-3,3-dimethylbutano- and -2,2-dimethylpropanohydroxamato)thorium(IV) (Figure 1) have been determined by single crystal X-ray diffraction.

Experimental

The hydroxamic acids were synthesized as described elsewhere.[5] Anhydrous UCl_4 was purchased from ROC/RIC and $ThCl_4 \cdot 8H_2O$ was obtained from City Chemical Company. Reactions using U(IV) were performed under dry argon on a vacuum line using degassed solvents. Solutions of U(IV) were manipulated using Schlenk techniques and solids were handled in a Dri-Lab HE-43 glove box under dry argon.

Infrared spectra were obtained on a Perkin-Elmer 283 spectrophotometer as KBr pellets. ^{1}H NMR spectra were recorded on a Varian A-60 spectrophotometer. Melting points were taken in open capillaries on a Büchi apparatus and are uncorrected. Microanalyses were performed by Analytical Services, Chemistry Department, University of California, Berkeley.

Tetrakis(N-hydroxy-N-isopropyl-2,2-dimethylpropanamido)thorium(IV), 1. A solution of 1.04 g (2 mmol) of $ThCl_4 \cdot 8H_2O$ in 10 ml of 0.01 M HCl was added slowly to a stirred solution of 1.59 g (10 mmol) of N-hydroxy-N-isopropyl-2,2-dimethylpropanamide in 10 ml of 1 M NaOH. After washing with water, the precipitate was dissolved in 10 ml of methanol. The solvent was removed and the residue was dissolved in ether. The ether was removed on a rotovap to leave a white powder which was very soluble in most organic solvents, but only slightly soluble in hexane. This material was purified by sublimation ($\sim$ 95°C at 10^{-3} Torr) to yield 1.0 g (60% of theory) of 1, mp 126.5–7.5°C.
Anal. Calcd. for $C_{32}H_{64}N_4O_8Th$: C, 44.44%; H, 7.46%; N, 6.48%.
Found: C, 44.46%; H, 7.29%; N, 6.41%.
^{1}H NMR ($CDCl_3$-Me_4Si) δ 1.23 [s, 36 H, $-C(CH_3)_3$], 1.27 [d, J = 6 Hz, 24 H, $>C(CH_3)_2$], 4.25 ppm (septet, J = 6 Hz, 4 H, $\gt$CH).

Tetrakis(N-hydroxy-N-isopropyl-3,3-dimethylbutanamido)thorium(IV), 2. Using N-hydroxy-N-isopropyl-3,3-dimethylbutanamide and the above procedure, 2 was prepared in 78% yield. Compound 2 is soluble in hexane, mp 116–7°C, sublimes $\sim$ 100°C at 10^{-3} Torr.
Anal. Calcd. for $C_{36}H_{72}N_4O_8Th$: C, 46.95%; H, 7.88%; N, 6.08%.
Found: C, 46.95%; H, 7.78%; N, 6.06%.

^1H NMR ($CDCl_3$-Me_4Si) δ 1.05 [s, 36 H, $-C(CH_3)_3$], 1.22 [d, J = 7 Hz, 24 H, $>C(CH_3)_2$], 2.05 (s, 8 H, $-CH_2-$), 4.1 ppm (septet, 4 H, $\rightarrow$CH).

Tetrakis(N-hydroxy-N-isopropyl-2,2-dimethylpropanamido)uranium(IV). The above method was used to synthesize the green uranium complex U[*i*-PrN(O)C(O)-*t*-Bu]$_4$ from UCl_4 and N-hydroxy-N-isopropyl-2,2-dimethylpropanamide. In contrast to the thorium complex, on exposure to air solutions of U[*i*-PrN(O)C(O)-*t*-Bu]$_4$ quickly turn red in the formation of an uranyl complex; the solid is more air stable. This compound decomposed near 80°C during an attempted sublimation to give a red, uranyl compound. Red crystals of an uranyl complex also formed slowly on the walls of a Schlenk tube that contained a deareated hexane solution of U[*i*-PrN(O)C(O)-*t*-Bu]$_4$ under an argon atmosphere, such that all of the U(IV) was converted to UO_2^{2+} in about two weeks. After filtration, the hexane was removed and a mixture of unreacted hydroxamic acid and N-isopropylpivaloylamide was sublimed from the residue. The infrared spectra of the isolated amide and of a synthesized sample[5] were identical.

X-ray Diffraction Studies

Compound 1

Colorless crystals of Th[*i*-PrN(O)C(O)-*t*-Bu]$_4$, which in ideal form were shaped as bicapped square prisms, were obtained by slow evaporation of an ether-hexane solution. An irregularly shaped crystal with non-identifiable faces which approximated a sphere of 0.11 mm radius was sealed in a thin-walled glass capillary. Precession photographs and diffraction data showed tetragonal symmetry in the Laue group 4/m and systematic absences: $hk\ell$, $h + k + \ell \neq 2n$; $hk0$, $h \neq 2n$ ($k \neq 2n$); 00ℓ,

$\ell \neq 4n$; consistent with the space group $I4_1/a$. In addition, reflections $hk\ell$, $2h + \ell \neq 2n + 1$ or $4n$ ($2k + \ell \neq 2n + 1$ or $4n$) were absent or weak which implied that the Th atom occupies the special position (0, 1/4, 1/8) with $\bar{4}$ site symmetry. Since the other atoms are located on general positions, the asymmetric unit is comprised of 1/4 Th atom and one ligand molecule. Graphite monochromatized MoKα radiation ($\lambda_{MoK\alpha_1} = 0.70930$ Å) was used for the precise measurement of the cell constants and for data collection on a Nonius CAD-4 automated four-circle diffractometer.[6] Cell parameters, obtained by a least-squares fit to the measured coordinates of 22 reflections ranging in 2θ from 37.5 to 48.8° at 24°C, are listed in Table I.

The intensities of two equivalent forms, h, k, ±ℓ, of all reflections with $2\theta \leq 55°$ were measured and processed as previously described.[7] A maximum of 60 s was used to scan a reflection through a variable scan angle of 0.5 + 0.35 tanθ using an aperture with a variable width of (2.0 + tanθ) mm. The orientation was checked every 250 reflections. The intensity of three standards measured every 7200 s showed an anisotropic decrease of 11% along a and a correction was applied. A spherical absorption correction was included during data processing.[8] Equivalent forms were averaged and, to avoid overweighting the strong reflections, the p factor was chosen as 0.04 as previously described.[4]

Compound 2

Colorless rhombic needles of the more hydrocarbon-soluble Th[i-PrN(O)C(O)neopentyl]$_4$ were obtained by slow evaporation from hexane. Precession photographs showed triclinic symmetry and the subsequent structure determination established the space group as $P\bar{1}$ with the presence of 1/2 molecule of hexane per thorium atom. A piece of crystal of dimensions 0.11 x 0.23 x 0.42 mm, cleaved from a long needle with a scalpel, was sealed in a capillary. Cell constant and intensity data collection and processing were done in a manner similar to that for <u>1</u>. All unique reflections, h, ±k, ±ℓ, with $2° < 2 \leq 50°$ were measured with a maximum of 90 s and a variable scan angle of $0.75 + 0.35 \tan\theta$. The setting angles were calculated to minimize absorption by choosing the orientation around the diffraction vector that came closest to bisecting the incoming and diffracted X-ray beams with the plate face (001 direction). The data were corrected for an isotropic 10% decay in intensity of three standards measured every 2 hr. An analytical absorption correction,[9] which ranged from 1.49 to 2.79, was applied to the data and its validity was checked by several azimuthal scans. Equivalent forms were averaged. To avoid overweighting the strong reflections, the p factor was chosen as 0.04.[4]

<u>Structure Determination and Refinement</u>. For both compounds, the positions of the thorium and the hydroxamate atoms were found in Patterson maps. The remaining atoms were located by standard difference Fourier and least-squares refinement techniques.[10] In both cases, hydrogen atoms found in a difference Fourier agreed well with calculated positions. Methyl hydrogens were treated as rigid groups (C-H = 1.0 Å, H-C-H = 109.5°) which were allowed to rotate about the C-C vector. In <u>1</u> each group of methyl hydrogens was refined with its own isotropic temperature factor, while in <u>2</u> the isotropic temperature factors were constrained to be equal.

The position of the methylidine hydrogen in 1 was refined with an isotropic temperature factor. The methylene and methylidine hydrogen atoms of 2 were held fixed to their calculated positions and a single combined isotropic temperature factor was refined.

After refinement of the Th[i-PrN(O)C(O)neopentyl]$_4$ molecule (2), a diffuse mass of electron density, with an integrated density of ∿ 20 eÅ^{-3}, was found in a large channel near the inversion center at (1/2, 0, 0). This is consistent with a hexane molecule (1/2 hexane = 25 eÅ^{-3}) rotationally disordered about the long axis of the planar zig-zag conformation, in which the long axis lies parallel to the channel and is centered at (1/2, 0, 0). A rigid group comprised of the carbon atoms of the 1/2 hexane molecule and the carbon atoms generated by rotations of 90, 180 and 270° about the long axis was used to approximate the disorder. Each atom was given 1/4 occupancy and a single combined isotropic group temperature factor was used. The group was calculated using C-C bond lengths of 1.537 Å and angles of 109.47°.[11] Inclusion of the hexane molecule decreased the average value of E, the error in an observation of unit weight,[12] from 45.1 to 13.3 for reflections with $\sin\theta/\lambda <$ 0.2; and from 4.2 to 2.5 for all data.

Final full-matrix, least-squares refinement for compound 1 on 1798 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 117 variables, including a correction for secondary extinction,[13] led to convergence with R = 0.027, R_w = 0.032 and E = 1.25.[12] Final refinement of 2 on 6978 reflections with $F_o^2 >$ $3\sigma(F_o^2)$ and 467 variables led to convergence with R = 0.034, R_w = 0.042 and E = 1.64. The function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, was minimized in all refinements. Except for the group and the hydrogen atoms discussed above, all atoms were refined with anisotropic temperature factors. Atomic scattering factors were for neutral atoms and those for thorium were corrected for anomalous dispersion.[14] A final difference Fourier for 1 showed maximum residual peaks of 1.71 and -2.38 e$Å^{-3}$; for peaks more than 2 Å from the Th the largest was 0.5 e$Å^{-3}$. Maximum residual peaks of 1.44 and -0.86 e$Å^{-3}$ were found in the final difference Fourier for compound 2. The final positional and thermal parameters are in Tables II-V. Information regarding supplementary materials can be found in the last paragraph of this paper.

Description of the Structure of Th[*i*-PrN(O)C(O)-*t*-Bu]$_4$

The thorium atom in this complex sits on a crystallographic $\bar{4}$ axis, as shown in the packing diagram of Figure 2. This limits the possible eight-coordinate polyhedra to the dodecahedron and the cube (tetragonal prism). In order to minimize steric interactions, the bulky *tert*-butyl groups migrate to the corners of a tetrahedron, resulting in the distorted cubic geometry of the complex shown in Figures 3-5. This steric strain also manifests itself in a C(=O)-C(*t*-Bu) bond length [1.547(5) Å] which is significantly longer than the length normally found for an sp^2-sp^3 C-C bond [1.506(5) Å].[15] As seen in Table VI, the other ligand bonding parameters are close to their expected values. The chelate ring of the hydroxamic acid is planar, with an average deviation of 0.007 Å from the calculated least-squares plane, The substituent carbon atoms, C2 and C6, are displaced -0.099 and 0.174 Å from this plane.

Because the hydroxamate anion is an unsymmetrical ligand with more of the charge localized on the nitrogen oxygen, the Th-O_N bond [2.357(3) Å] is 0.14 Å shorter than the Th-O_c bond [2.492(3) Å]. The average Th-O bond (2.425 Å) is very close to the average Th-O bond found in

$[Th(catechol)_4]^{4-}$ (2.420 Å).[3] The O_N-M-O_C (or bite) angle observed in 1 [62.32(9)°] is smaller than that calculated using a hard-sphere model to successfully span an edge of a cube (70.53°). The disparity in Th-O bond lengths and observed bite angle cause a distortion toward the gggg-isomer of a trigonal faced dodecahedron accompanied by a 10.3° twist in the dodecahedral BAAB trapezoid (see Figure 5 for these definitions). As predicted from an electrostatic model,[16,17] the more negatively charged nitrogen oxygens are located at the B sites of the dodecahedron, but this could also be a steric effect of the tert-butyl groups.

The relationship of the cube and the dodecahedron to the coordination polyhedtron of 1 is shown in Figure 5 and a detailed shape parameter analysis is presented in Table VII. The similarity of this complex to a cube is shown by the equal edge lengths of those not spanned by the ligands, the m and g' edges, and the dihedral angles, δ, which are close to 90° about the m and g edges. The a and b edges are face diagonals in the cube and the dihedral angles about these edges measure the distortion toward the dodecahedron. Although calculations based on electronic repulsions in eight-coordinate complexes favor the dodecahedron, large steric repulsions are expected to predominate, when present.[16,17] Thus, the bulky alkyl substituents direct the geometry of complex 1 toward a cube. Although somewhat rare, cubic coordination has been observed in $U(2,2'\text{-bipyridyl})_4$[19] and in $[La(2,2'\text{-bipyridine-}1,1'\text{-dioxide})_4]^{3+}$.[20] Both these complexes involve ligands that are bulky near the coordination sites. In contrast, the cubic coordination in $(Et_4N)_4[U(NCS)_8]$[21] is attributed to crystal packing forces, since this geometry is not retained in solution, and the geometry of $[U(NCS)_8]^{4-}$ in the cesium salt is close to an ideal square antiprism.[22]

Because the ligands span alternate edges of two parallel square faces, the complex Th[i-PrN(O)C(O)-t-Bu]$_4$ (1) is best designated as the ssss isomer of a cube (after the designations for a square-antiprism made by Hoard and Silverton[16]) with an actual point group symmetry of S_4.

Description of the Structure of Th[i-PrN(O)C(O)neopentyl]$_4$

The influence of the alkyl substituent in determining structure is greatly reduced by the introduction of a methylene group between the carbonyl carbon and the tert-butyl group. A packing diagram of 2 is shown in Figure 6. The structure shown in Figures 7-9 is close to the mmmm-dodecahedron found in the majority of other eight-coordinate actinide complexes with bidentate ligands.[1] The bending of the ligands seen in Figure 7 is due to steric interactions of molecular packing. The hydroxamate groups are all planar with average deviations from their least-square planes of 0.001, 0.013, 0.003, and 0.002 Å. In each case the methylene and methylidine carbon atoms are displaced slightly (-0.21 to +0.09 Å) from the hydroxamate plane. The hydroxamate chelate rings nearly coincide with the dodecahedral mirror planes containing the m-edges (see Figure 8). Because of thermal motion, the isopropyl C-C bond lengths are artifactually shortened. Using a riding model,[23] an average corrected C-C bond length of 1.530(6) Å is obtained. The bond parameters between other ligand atoms, which are presented in Table VIII, are close to the expected values.

While the lack of crystallographic symmetry in 2 would allow structures such as the square antiprism or the bicapped trigonal prisms, the smallest dihedral angle is 35.5° and this precludes the presence of any square faces in the coordination polyhedron (for which $\delta = 0$). The resemblance of the coordination polyhedron to the dodecahedron is shown in Figure 10, but as seen in Table VII the complex is distorted from the ideal geometry. The bite angle of the ligands [av = 63.0(1)°], which governs the length of the m edges, is smaller than that of an ideal dodecahedron (73.7°, hard-sphere model). This results in the flattening of the B tetrahedron as evidenced by the increased angle between the Th-O_B vector and the pseudo $\bar{4}$ axis, θ_B, and by the lengthened g edges. As before, the Th-O_N bond [av = 2.36(1) Å], is shorter than the Th-O_C bond [av = 2.46(2) Å]. There is apparently no site preference for the charged oxygen since the O_N and O_C atoms are equally distributed over the A and B sites of the dodecahedron. This results in a ~~mmmm~~-dodecahedron with C_1 symmetry.

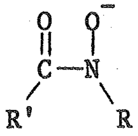
Results and Discussion

In addition to the compounds reported here, thorium complexes of arylhydroxamic acids have been isolated from aqueous solution but with relatively little characterization.[24-26] In the case of compounds 1 and 2, upon complexation the ligand C=O infrared stretching frequency increases in relative intensity and shifts from 1583 to 1538 cm^{-1} in 1 and from 1598 to 1570 cm^{-1} in 2. Similarly, the N-O stretch shifts from 940 to 927 cm^{-1} in 1 and from 938 to 910 cm^{-1} in 2. The hydroxyl peak is absent in the IR spectra of both complexes. A few other bands had frequency shifts or intensity variations between free and complexed ligands; these changes are more pronounced in the spectrum of 1, which also showed the emergence of a strong band at 977 cm^{-1} upon complexation.

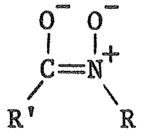
In the room-temperature ^{1}H NMR spectra of these complexes in chloroform solution, only one set of signals was observed, which were slightly shifted upfield from the uncomplexed ligands, and establish the presence of a single isomer or a fluxional molecule. In the presence of excess ligand an average signal was observed, which indicates rapid ligand exchange.

Analogous complexes of uranium(IV) were prepared and handled under anhydrous, anaerobic conditions. Uranium(IV) has been found to rapidly undergo a redox reaction with N-phenylbenzohydroxamic acid,[4] which probably proceeds through a radical anion intermediate that is stabilized by the aryl substituent on the nitrogen. Alkyl substituents would not be expected to stabilize such a free-radical intermediate. However, on standing or heating the uranium(IV) complexes of N-alkylhydroxamic acids form uranyl ion and amide in an analogous manner, but at a much slower rate than the N-arylhydroxamates.

As shown by the bond distances in Table IX,[27-42] the N-hydroxy group little effects the C=O and C-N bond lengths of hydroxamic acids as compared to the amide precursor [amide C=O = 1.235(5) Å, amide C-N = 1.333(5) Å].[15] Corresponding distance comparisons are made for the thiohydroxamate derivatives in Table X.[43-48] The bonding in hydroxamic acids appears to be



Ia

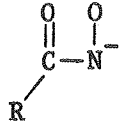


IIa

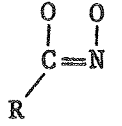
dominated by resonance structure Ia, with structure IIa accounting for the partial double bond character of the C-N bond and the planarity of the hydroxamic acid group. The slightly longer C=O bond and the shorter C-N and N-O bonds indicate increased participation of form IIa in the complexes. With the exception of the chromic complex, which favors pure octahedral symmetry due to a crystal field effect,[7] the $M-O_N$ bond in the hydroxamic acid complexes is much shorter than the $M-O_C$ bond. This large inequivalence in M-O bond lengths is explained by a higher charge density on the nitrogen oxygen, which requires a major contribution from structure Ia.

The relative contributions of structures Ia and IIa to the bonding in hydroxamic acids may be estimated from the calculated bond orders of the C(O)-N and C=O bonds. An empirical relationship between bond order and length of carbon-carbon bonds was reported by Pauling.[48] Using a carbon-oxygen single bond distance of 1.426 Å, 1.213 Å is calculated for a carbon-oxygen double bond, which agrees closely with 1.215(5) Å, the length of the average reported C=O bond found in ketones and aldehydes.[15] The calculated bond orders in Table XI show that while resonance structure Ia dominates, the contribution of structure IIa is slightly greater in hydroxamic acids than in amides. The contribution of IIa further increases in the hydroxamate complexes such that the C-O and C(O)-N bond orders are equal.

In a similar manner, resonance structures Ib and IIb may be used to explain the bonding in hydroximic acids and their complexes.



Ib



IIb

Structure IIb dominates in the hydroximic acids and their complexes, but the contribution of Ib is significant in the complexes. Both the increased effective size of the sp^3 nitrogen and the charge repulsion which result from a significant contribution of Ib cause an 0.057 Å increase in the N-O bond between hydroxamate and hydroximate complexes.

The replacement of the carbonyl oxygen with sulfur gives the corresponding thiohydroxamic acids and thiohydroximic acids. The increased importance of IIa in thiohydroxamate complexes is shown by the 0.02 Å decrease in the N-O bond length compared to hydroxamate complexes. As shown by the bond orders of the C-S and C(S)-N bonds, the bonding in thiohydroxamate complexes is analogous to that of hydrox*i*mate complexes. This is because any form involving a C=S double bond will be strongly destabilized by the poor π overlap. Similarly, the importance of IIb is more important in thiohydroximate complexes than in hydroximate complexes. Thus the importance of resonance structure II increases in the order; amides $\sim$ hydroxamic acids < hydroxamate complexes < hydroximate complexes $\sim$ thiohydroxamate complexes < hydroximic acids $\sim$ thiohydroximate complexes, such that structures I and II contribute equally to the bonding of hydroxamate complexes.

Summary

The remarkable volatility and hydrocarbon solubility of complexes 1 and 2 are due to their bulky alkyl substituents. The dominance of steric interactions between these substituents is evident in the structure of 1, in which the *tert*-butyl groups occupy the corners of a tetrahedron and force the complex into a distorted cubic geometry with

S_4 point symmetry. Insertion of a methylene group between the carbonyl carbon and the *tert*-butyl group relaxes the steric requirements, and **2** assumes the dodecahedral geometry found in the actinide (IV) catecholates.[3] Such a dodecahedral arrangement of ligating sites is predicted to give maximum stability to an optimized macrochelate designed specifically for the tetravalent actinides. The corresponding uranium(IV) complexes undergo an oxygen transfer from the ligand to the metal to give a uranyl bis(hydroxamate) complex and the amide of the ligand.

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Supplementary Material

A listing of structure factor amplitudes. Ordering information is given on current masthead page.

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12. Definitions of indicators are: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2}$ and E, the error in an observation of unit weight, $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v is the number of refined variables.

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Table I. Crystal Data for Th[*i*-PrN(O)C(O)R]$_4$.

R	*tert*-Butyl	Neopentyl
Molecular Formula	$ThC_{32}H_{64}N_4O_8$	$ThC_{39}H_{79}N_4O_8$
Molecular Weight	864.92 g mol^{-1}	964.12 g mol^{-1}
Space Group	$I4_1/a$ (C_{4h}^6)	$P\bar{1}$ (C_i^1)
Cell Constants		
a	17.338(4) Å	9.777(2) Å
b		14.633(2) Å
c	12.706(4) Å	18.515(1) Å
α		74.061(8)°
β		88.41(1)°
γ		75.71(2)°
Volume	3819(2) Å^3	2466.0(7) Å^3
Formula Units/Cell	4	2
Calculated Density	1.50 g cm^{-3}	1.30 g cm^{-3}
Observed Density[a]	1.50 g cm^{-3}	1.19 g cm^{-3}
Linear Absorption Coefficient, $\mu_{MoK\alpha}$	40.87 cm^{-1}	31.72 cm^{-1}

[a] Measured by flotation in aqueous KI.

Table II. Positional and Anisotropic Thermal Parameters (x 10^3) for Th[*i*-Pr-N(O)-C(O)-*t*-Bu]$_4$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Th	.0000	.2500	.1250	1.73(2)	1.73(2)	2.08(2)	.00	.00	.00
O1	.4183(2)	.1652(2)	.2823(2)	2.81(10)	2.27(9)	3.56(15)	-.37(7)	-1.11(10)	.41(10)
O2	.4161(2)	.3059(2)	.2352(2)	3.38(11)	2.15(10)	4.08(16)	.03(8)	-1.29(11)	.17(10)
N	.3815(2)	.1878(2)	.1915(2)	2.46(11)	2.48(11)	3.08(17)	-.25(9)	-.62(11)	.06(11)
C1	.3809(2)	.2623(2)	.1718(3)	2.03(12)	2.60(13)	2.88(19)	.11(9)	-.28(12)	.22(13)
C2	.3376(2)	.2986(3)	.0775(3)	2.61(14)	3.05(15)	3.43(22)	.06(11)	-.67(14)	.64(15)
C3	.3480(3)	.3861(3)	.0839(4)	3.63(19)	3.30(18)	6.62(32)	.19(14)	-.76(14)	1.74(21)
C4	.2507(3)	.2806(3)	.0851(4)	2.23(14)	4.46(21)	6.27(30)	.15(13)	-1.07(17)	.67(21)
C5	.3710(3)	.2720(3)	.9715(4)	4.27(22)	5.05(24)	3.72(25)	.41(17)	.08(19)	.96(20)
C6	.3552(3)	.1223(3)	.1268(3)	3.32(16)	2.63(14)	4.03(22)	-.45(11)	-.95(17)	-.37(17)
C7	.4248(4)	.0796(3)	.0832(5)	5.06(26)	4.10(23)	6.54(35)	.57(19)	-.60(25)	-1.96(23)
C8	.3023(4)	.0704(3)	.1896(4)	5.28(26)	4.27(22)	6.23(34)	-2.45(20)	-.61(24)	-.05(22)

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Hydrogen Atom Parameters in Th[i-PrN(O)C(O)-t-Bu]$_4$.

Atom	x	y	z	B
H3A	.331(2)	.405(1)	.155(1)	5.3(8)
H3B	.316(2)	.411(1)	.029(2)	5.3(8)
H3C	.404(1)	.399(1)	.072(3)	5.3(8)
H4A	.243(1)	.224(1)	.081(2)	5.9(9)
H4B	.222(2)	.306(1)	.027(3)	5.9(9)
H4C	.232(2)	.300(1)	.154(2)	5.9(9)
H5A	.361(1)	.216(1)	.962(1)	7.2(10)
H5B	.428(1)	.282(1)	.972(4)	7.2(10)
H5C	.347(3)	.301(1)	.912(3)	7.2(10)
H6	.326(3)	.147(2)	.070(4)	2.7(9)
H7A	.456(2)	.116(1)	.039(3)	8.2(12)
H7B	.407(2)	.035(1)	.039(3)	8.2(12)
H7C	.457(2)	.060(1)	.143(2)	8.2(12)
H8A	.290(2)	.023(1)	.148(1)	6.4(10)
H8B	.253(1)	.099(1)	.206(4)	6.4(10)
H8C	.328(2)	.055(2)	.257(2)	6.4(10)

Table IV. Positional and Anisotropic Thermal Parameters (x 10^4) for Th[i-Pr-N(O)-C(O)-neopentyl]$_4$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Th	.09004(2)	.36624(1)	.33844(1)	101.1(3)	44.0(1)	25.98(7)	-12.5(1)	6.49(9)	-11.35(6)
O11	-.0781(4)	.3544(3)	.4344(2)	119(5)	74(3)	30(1)	-37(3)	6(2)	-15(2)
O12	.1433(4)	.4052(3)	.4511(2)	125(5)	63(3)	31(1)	-38(3)	19(2)	-17(1)
N1	-.0377(5)	.3526(3)	.5055(2)	111(6)	63(3)	26(2)	-26(4)	7(2)	-11(2)
C11	.0789(6)	.3799(4)	.5108(3)	110(7)	40(3)	32(2)	-17(4)	8(3)	-12(2)
C12	.1417(6)	.3789(4)	.5844(3)	126(8)	56(4)	34(2)	-28(4)	12(3)	-22(2)
C13	.2737(6)	.2935(5)	.6142(3)	122(8)	72(4)	34(2)	-18(5)	0(3)	-21(2)
C14	.2384(10)	.1948(6)	.6295(6)	211(15)	68(5)	112(6)	-14(7)	-31(8)	-10(4)
C15	.3922(8)	.2956(8)	.5580(5)	138(11)	161(9)	56(4)	2(8)	11(5)	-14(4)
C16	.3265(10)	.3062(7)	.6855(5)	249(15)	140(8)	55(4)	-6(9)	-34(6)	-38(4)
C17	-.1340(7)	.3212(5)	.5641(3)	139(9)	71(4)	30(2)	-41(5)	18(3)	-12(2)
C18	-.2738(8)	.3986(5)	.5517(4)	152(10)	78(5)	57(3)	-45(6)	37(5)	-22(3)
C19	-.1509(8)	.2221(5)	.5657(4)	201(12)	65(5)	58(3)	-63(6)	23(5)	-10(3)
O21	.3257(4)	.3720(3)	.3448(2)	118(5)	82(3)	29(1)	-27(3)	20(2)	-20(2)
O22	.2254(5)	.3624(5)	.2243(3)	119(7)	175(6)	42(2)	-37(5)	20(3)	-50(3)
N2	.4153(5)	.3598(4)	.2893(3)	122(7)	94(4)	31(2)	-21(4)	14(3)	-18(2)
C21	.3575(8)	.3586(6)	.2267(4)	166(12)	120(7)	38(3)	-25(7)	21(4)	-30(3)
C22	.4404(9)	.3595(7)	.1556(5)	188(13)	127(7)	54(3)	-40(8)	28(5)	-35(4)
C23	.4452(8)	.2743(7)	.1251(4)	167(11)	149(8)	45(3)	-26(8)	27(5)	-46(4)
C24	.5530(10)	.2651(10)	.0666(5)	221(15)	254(14)	45(3)	-7(12)	32(6)	-59(6)
C25	.3017(11)	.2767(9)	.0925(5)	235(17)	223(12)	61(4)	-74(12)	30(7)	-73(6)
C26	.4891(14)	.1775(9)	.1935(6)	435(28)	131(10)	63(5)	-5(13)	24(9)	-16(5)
C27	.5620(6)	.3543(5)	.3096(4)	85(8)	93(5)	44(3)	-16(5)	8(3)	-17(3)
C28	.5720(8)	.4394(7)	.3341(5)	156(11)	121(8)	73(4)	-65(8)	7(5)	-25(4)
C29	.6205(8)	.2582(6)	.3702(4)	171(11)	103(7)	54(3)	-9(7)	-4(5)	-11(4)
O31	-.0901(4)	.4479(3)	.2442(2)	136(6)	65(3)	37(2)	-23(3)	-3(2)	0(2)
O32	.0618(5)	.5460(3)	.2816(2)	164(6)	56(3)	33(1)	-18(3)	7(3)	-9(2)
N3	-.0834(6)	.5370(4)	.1968(3)	149(8)	62(3)	30(2)	-7(4)	2(3)	2(2)
C31	-.0040(7)	.5842(5)	.2198(4)	160(10)	53(4)	35(2)	-10(5)	21(4)	-9(2)
C32	.0033(9)	.6869(5)	.1736(4)	218(13)	60(4)	45(3)	-15(6)	20(5)	-4(3)
C33	.1445(11)	.6946(6)	.1388(6)	258(16)	69(5)	74(4)	-39(8)	57(7)	-7(4)
C34	.1322(13)	.7981(7)	.0907(6)	421(24)	81(7)	91(6)	-71(10)	84(9)	-4(5)
C35	.1805(16)	.6248(8)	.0883(8)	550(34)	117(9)	144(9)	-100(14)	206(15)	-57(7)
C36	.2593(14)	.6649(12)	.1945(10)	241(22)	221(16)	165(12)	-113(15)	4(13)	58(11)
C37	-.1651(8)	.5598(6)	.1251(4)	196(12)	89(6)	32(2)	-5(6)	-4(4)	-4(3)
C38	-.3193(10)	.5839(8)	.1388(5)	179(14)	179(10)	45(3)	-17(10)	-21(5)	-6(4)
C39	-.1206(12)	.4757(7)	.0914(5)	377(21)	116(8)	43(3)	-9(10)	-18(6)	-31(4)
O41	.1998(5)	.1997(3)	.3943(3)	179(7)	49(3)	64(2)	-11(4)	-41(3)	-13(2)
O42	-.0130(4)	.2435(3)	.3054(2)	140(6)	56(3)	47(2)	-12(3)	-13(3)	-20(2)
N4	.1524(6)	.1260(3)	.3783(3)	183(9)	41(3)	54(2)	-21(4)	-8(4)	-17(2)
C41	.0421(7)	.1538(4)	.3324(3)	144(9)	52(4)	40(2)	-22(5)	3(4)	-18(2)
C42	-.0226(8)	.0811(5)	.3104(4)	173(11)	72(5)	48(3)	-48(6)	12(4)	-20(3)
C43	.0072(9)	.0696(6)	.2310(4)	242(15)	79(5)	49(3)	-46(7)	5(5)	-32(3)
C44	-.0468(12)	.1706(9)	.1724(5)	382(23)	153(10)	45(3)	-93(13)	-23(7)	-11(5)
C45	.1625(12)	.0325(7)	.2233(5)	289(20)	132(8)	68(4)	-25(10)	34(7)	-53(5)
C46	-.0750(12)	.0012(8)	.2180(6)	368(23)	140(9)	83(5)	-105(12)	9(8)	-62(6)
C47	.2364(9)	.0275(5)	.4195(4)	216(13)	46(4)	58(3)	-9(6)	-19(5)	-8(3)
C48	.2147(12)	.0111(7)	.5019(6)	333(20)	102(7)	56(4)	-26(9)	-12(7)	-2(4)
C49	.3892(11)	.0165(7)	.4003(6)	216(17)	96(7)	90(5)	50(8)	-8(7)	-18(5)

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table V. Positional and Isotropic Atom Parameters for Th[*i*-Pr-N(O)-C(O)-neopentyl]$_4$.

Atom	x	y	z	B	Atom	x	y	z	B
C51A	.4828(4)	.0066(4)	.95835(2)	36.1(11)	C51C	.4994(10)	.0426(4)	.9647(2)	36.1(11)
C51B	.4460(9)	.0493(4)	.9840(4)	36.1(11)	C51D	.4294(2)	.0133(7)	.9777(2)	36.1(11)
C52A	.3747(19)	.1052(10)	.9263(7)	36.1(11)	C52C	.3581(11)	.0692(13)	.9200(5)	36.1(11)
C52B	.4115(13)	.0625(10)	.9007(3)	36.1(11)	C52D	.4281(20)	.0984(8)	.9070(5)	36.1(11)
C53A	.3403(22)	.1183(16)	.8430(7)	36.1(11)	C53C	.3569(30)	.1543(13)	.8493(9)	36.1(11)
C53B	.3035(29)	.1611(16)	.8686(11)	36.1(11)	C53D	.2869(21)	.1251(19)	.8623(9)	36.1(11)
H12A	.068	.373	.622	6.6(5)	H32A	-.070	.710	.132	6.6(5)
H12B	.169	.442	.578	6.6(5)	H32B	-.018	.731	.207	6.6(5)
H14A	.156(8)	.194(3)	.663(5)	10.3(7)	H34A	.040(6)	.824(4)	.062(5)	10.3(7)
H14B	.214(12)	.184(4)	.581(1)	10.3(7)	H34B	.139(13)	.841(2)	.124(1)	10.3(7)
H14C	.322(5)	.142(1)	.655(6)	10.3(7)	H34C	.211(8)	.799(2)	.055(5)	10.3(7)
H15A	.388(8)	.250(7)	.527(5)	10.3(7)	H35A	.165(13)	.556(2)	.119(2)	10.3(7)
H15B	.380(8)	.364(3)	.525(5)	10.3(7)	H35B	.106(7)	.644(6)	.047(4)	10.3(7)
H15C	.486(1)	.274(9)	.586(1)	10.3(7)	H35C	.274(7)	.628(7)	.066(6)	10.3(7)
H16A	.345(12)	.373(4)	.676(2)	10.3(7)	H36A	.234(6)	.703(7)	.233(5)	10.3(7)
H16B	.254(6)	.299(9)	.724(2)	10.3(7)	H36B	.277(9)	.593(3)	.220(6)	10.3(7)
H16C	.416(7)	.255(6)	.704(4)	10.3(7)	H36C	.346(5)	.679(9)	.169(2)	10.3(7)
H17	-.091	.313	.615	6.6(5)	H37	-.141	.617	.088	6.6(5)
H18A	-.255(1)	.465(1)	.540(7)	10.3(7)	H38A	-.345(3)	.525(3)	.173(6)	10.3(7)
H18B	-.329(6)	.394(6)	.509(4)	10.3(7)	H38B	-.342(3)	.639(6)	.163(6)	10.3(7)
H18C	-.329(6)	.388(5)	.598(3)	10.3(7)	H38C	-.374(1)	.604(9)	.090(1)	10.3(7)
H19A	-.197(11)	.226(2)	.517(3)	10.3(7)	H39A	-.016(2)	.459(6)	.088(6)	10.3(7)
H19B	-.056(2)	.174(2)	.573(7)	10.3(7)	H39B	-.151(12)	.418(3)	.124(4)	10.3(7)
H19C	-.212(10)	.200(4)	.608(4)	10.3(7)	H39C	-.166(10)	.495(4)	.040(3)	10.3(7)
H22A	.540	.358	.168	6.6(5)	H42A	-.127	.102	.314	6.6(5)
H22B	.397	.421	.116	6.6(5)	H42B	.014	.015	.347	6.6(5)
H24A	.553(9)	.332(2)	.033(4)	10.3(7)	H44A	-.150(4)	.196(5)	.178(5)	10.3(7)
H24B	.649(3)	.233(8)	.092(1)	10.3(7)	H44B	.005(10)	.218(3)	.181(4)	10.3(7)
H24C	.530(8)	.224(8)	.036(5)	10.3(7)	H44C	-.030(12)	.163(2)	.121(7)	10.3(7)
H25A	.231(4)	.278(9)	.132(2)	10.3(7)	H45A	.211(3)	.086(3)	.221(7)	10.3(7)
H25B	.270(7)	.337(5)	.049(4)	10.3(7)	H45B	.202(3)	-.025(6)	.267(4)	10.3(7)
H25C	.311(4)	.217(5)	.075(6)	10.3(7)	H45C	.178(2)	.012(8)	.176(4)	10.3(7)
H26A	.587(6)	.170(5)	.213(5)	10.3(7)	H46A	-.032(8)	-.067(2)	.250(5)	10.3(7)
H26B	.422(8)	.182(4)	.235(3)	10.3(7)	H46B	-.175(4)	.023(5)	.232(6)	10.3(7)
H26C	.487(13)	.119(2)	.176(2)	10.3(7)	H46C	-.072(11)	.002(7)	.164(2)	10.3(7)
H27	.621	.351	.265	6.6(5)	H47	.204	-.023	.402	6.6(5)
H28A	.533(11)	.501(1)	.293(3)	10.3(7)	H48A	.286(9)	.035(8)	.524(2)	10.3(7)
H28B	.516(10)	.441(5)	.380(4)	10.3(7)	H48B	.117(5)	.047(7)	.510(1)	10.3(7)
H28C	.673(2)	.434(5)	.346(6)	10.3(7)	H48C	.228(13)	-.061(2)	.526(2)	10.3(7)
H29A	.552(6)	.250(5)	.411(3)	10.3(7)	H49A	.395(1)	.047(8)	.345(2)	10.3(7)
H29B	.635(12)	.202(1)	.348(2)	10.3(7)	H49B	.435(4)	.050(8)	.430(5)	10.3(7)
H29C	.713(6)	.260(4)	.391(5)	10.3(7)	H49C	.439(4)	-.055(1)	.413(6)	10.3(7)

Table VI. Bond Lengths and Angles in Th[*i*-PrN(O)C(O)-*t*-Bu]$_4$.

Bond Distances, Å					
Th–O1	2.357(3)	N–C1	1.316(5)	C2–C4	1.543(6)
Th–O2	2.492(3)	N–C6	1.475(5)	C2–C5	1.538(6)
O1–O2	2.512(4)	C1–C2	1.547(5)	C6–C7	1.512(7)
O1–N	1.376(4)	C2–C3	1.528(7)	C6–C8	1.520(8)
O2–C1	1.261(5)				
Bond Angles, Degrees					
O1–Th–O2	62.32(9)	O2–C1–N	117.6(3)	C3–C2–C4	108.2(4)
Th–O1–N	121.4(2)	O2–C1–C2	119.0(3)	C3–C2–C5	107.5(4)
Th–O2–C1	120.3(2)	N–C1–C2	123.4(3)	C4–C2–C5	111.2(4)
O1–N–C1	116.3(3)	C1–C2–C3	107.8(4)	N–C6–C7	109.5(4)
O1–N–C6	113.0(3)	C1–C2–C4	110.1(3)	N–C6–C8	110.5(4)
C1–N–C6	130.4(3)	C1–C2–C5	111.9(4)	C7–C6–C8	112.7(5)

Table VII. Shape Parameters[a] for Th[*i*-PrN(O)C(O)R]$_4$.

Parameter	R = *t*-Bu[b]	R = Neopentyl	Dodecahedron[c]	Cube[c]
ϕ	10.3	1.1,10.1	0.0	0.0
δ_a	33.2	67.6,70.2	51.3	0.0
δ_b	11.3	35.5,36.5,41.5,48.4	29.5	0.0
δ_g	80.5	42.3,45.4,46.9,51.0 54.0,55.6,58.9,62.7	62.5	90.0
$\delta_{g'}$	69.3		62.5	90.0
δ_m	87.9	70.2,76.2,79.7,85.5	51.3	90.0
Θ_A	44.5	32.9,33.6,35.3,38.8	36.9	54.7
Θ_B	60.0	78.8,82.4,84.0,84.4	69.5	54.7
$M\text{-}O_A/r$[d]	1.06	0.96,0.97,0.99,1.02	1.00	1.00
a/r	1.48	1.11,1.16	1.20	1.63
b/r	1.58	1.32,1.36,1.41,1.60	1.50	1.63
g/r	1.07	1.23,1.27,1.29,1.32 1.34,1.37,1.39,1.40	1.20	1.16
g'/r	1.26		1.20	1.16
m/r	1.27	1.03,1.04,1.04,1.04	1.20	1.16

[a] The shape parameters are defined in references 16 and 18; ϕ is the twist in the BAAB trapezoid, Θ is the angle between the M-O vector and the principal axis, δ_{edge} is the dihedral angle between the faces containing the edge as labeled in Figures 5 and 9.

[b] The dodecahedral g edges are divided into edges spanned by the ligands and those which are not, designated g and g′ respectively.

[c] Calculated using the Hard Sphere Model.

[d] r = average M-O$_B$ distance.

Table VIII. Bond Lengths and Angles in Th[i-PrN(O)C(O)neopentyl]$_4$.

	Ligand 1	Ligand 2	Ligand 3	Ligand 4	Average[a]
			Bond Distances, Å		
Th-O1	2.387(4)	2.334(4)	2.353(4)	2.355(4)	2.359(11)
Th-O2	2.410(4)	2.468(4)	2.498(4)	2.479(4)	2.464(19)
O1-O2	2.507(5)	2.514(6)	2.530(6)	2.530(6)	2.520(6)
O1-N	1.376(6)	1.352(6)	1.373(6)	1.377(6)	1.370(6)
O2-C1	1.267(6)	1.281(9)	1.245(7)	1.252(7)	1.261(8)
N-C1	1.313(7)	1.311(9)	1.305(8)	1.303(8)	1.308(3)
C1-C2	1.505(8)	1.524(10)	1.529(9)	1.512(9)	1.518(6)
C2-C3	1.543(8)	1.495(12)	1.524(11)	1.536(10)	1.526(12)
C3-C4	1.518(10)	1.500(10)	1.509(12)	1.551(13)	1.525(3)
C3-C5	1.536(10)	1.531(12)	1.524(11)	1.498(13)	
C3-C6	1.506(10)	1.593(14)	1.540(15)	1.499(11)	
N-C7	1.468(7)	1.459(8)	1.482(8)	1.476(8)	1.474(4)
C7-C8	1.521(10)	1.463(11)	1.492(12)	1.496(12)	1.499(7)
C7-C9	1.492(9)	1.528(10)	1.495(11)	1.506(13)	
			Bond Angles, Degrees		
O1-Th-O2	63.0(1)	63.1(2)	62.7(2)	63.1(2)	63.0(1)
Th-O1-N	118.6(3)	122.7(3)	118.7(3)	121.4(3)	120.4(10)
Th-O2-C1	121.0(3)	119.2(3)	117.5(3)	119.9(3)	119.4(8)
O1-N-C1	115.8(4)	115.7(5)	116.8(5)	116.2(5)	116.1(3)
O1-N-C7	114.4(4)	113.1(5)	111.8(5)	112.3(5)	112.9(6)
C1-N-C7	129.8(5)	131.1(6)	131.3(6)	131.5(6)	130.9(4)
O2-C1-C2	119.0(5)	119.3(7)	120.1(7)	118.5(6)	119.2(4)
O2-C1-N	117.9(5)	118.6(6)	118.9(6)	119.4(6)	118.7(3)
N-C1-C2	123.0(5)	122.0(7)	120.9(6)	122.1(6)	122.0(5)
C1-C2-C3	114.3(4)	114.6(7)	115.6(6)	115.8(6)	115.1(4)
C2-C3-C4	111.2(6)	113.0(8)	109.4(8)	109.3(7)	110.1(6)
C2-C3-C5	111.7(6)	112.8(8)	108.5(9)	110.5(7)	
C2-C3-C6	107.3(6)	107.1(7)	112.7(9)	107.5(7)	
C4-C3-C5	108.0(7)	108.7(7)	108.5(9)	109.3(8)	108.8(4)
C4-C3-C6	110.2(7)	107.5(9)	110.8(11)	108.3(8)	
C5-C3-C6	108.4(7)	107.3(8)	106.8(12)	112.0(8)	
N-C7-C8	109.4(5)	111.5(6)	109.5(6)	109.5(7)	109.8(3)
N-C7-C9	110.5(5)	108.9(6)	109.4(6)	109.8(7)	
C8-C7-C9	112.8(6)	111.6(7)	112.9(9)	113.0(8)	112.6(4)

[a] $\bar{x} = (1/n)\Sigma\, x_i$; $\sigma_{(\bar{x})} = [(\Sigma\,(x_i - \bar{x})^2)/n\,(n-1)]^{1/2}$.

Table IX. Average Bond Distances (Å) in Hydroxamic Acids, Hydroximic Acids and Their Complexes.

Compound	$M{-}O_C - M{-}O_N$	N–O	C=O	C–N	Ref.
MeC(O)N(OH)H		1.393(5)	1.234(6)	1.321(6)	27
o-Ph(OH)C(O)N(OH)H		1.390(4)	1.258(4)	1.316(4)	28
[*i*-PrN(OH)C(CH$_2$)$_2$-]$_2$		1.396(2)	1.241(2)	1.328(2)	29
NH$_2$C(O)N(OH)H		1.396(4)	1.253(4)	1.334(4)	30
Average[a]		1.394(1)	1.247(6)	1.325(4)	
Z-MeC(OMe)=NOH		1.410(4)	1.336(3)	1.274(5)	31
Z-PhC(OEt)=NOH		1.420	1.326	1.277	32
E-PhC(OEt)=NOH		1.410	1.342	1.257	32
Average[a]		1.413(3)	1.335(5)	1.269(6)	
Th(*t*-BuC(O)N(O)*i*-Pr)$_4$	0.135	1.376(4)	1.261(5)	1.316(5)	b
Th(*t*-BuCH$_2$C(O)N(O)*i*-Pr)$_4$	0.105	1.370(6)	1.261(8)	1.308(3)	b
Hf(PhC(O)N(O)Ph)$_4$	0.142	1.375(1)	1.266(3)	1.325(2)	33
Cr(PhC(O)N(O)H)$_3$	0.024	1.374(6)	1.273(2)	1.305(7)	26
Fe(PhC(O)N(O)H)$_3$	0.08	1.37(1)	1.28(1)	1.32(1)	34
Ferrioxamine E	0.096	1.381(7)	1.275(6)	1.307(7)	35
Ferrichrome A	0.06	1.38(1)	1.28(1)	1.32(1)	36
Zn(PhC(O)N(O)H)$_2$[NH$_2$CH$_2$-]$_2$	0.133	1.36(3)	1.27(5)	1.26(3)	37
cis-Sn(Me)$_2$(MeC(O)N(O)Me)$_2$	0.263	1.376(6)	1.257(7)	1.308(8)	38
cis-Sn(Me)$_2$(MeC(O)N(O)H)$_2$	0.122	1.362(5)	1.277(6)	1.307(5)	39
trans-Sn(Me)$_2$(MeC(O)N(O)H)$_2$	0.25	1.39(1)	1.25(1)	1.33(2)	39
cis-SnCl$_2$(PhC(O)N(O)Ph)$_2$	0.07	1.39(2)	1.28(3)	1.34(3)	40
SnPh$_3$(PhC(O)N(O)Ph)	0.217	1.384(6)	1.265(9)	1.304(9)	41
Average[a]	0.13(2)	1.376(3)	1.269(3)	1.312(5)	
cis-[Cr(PhC(O)N(O))$_3$]$^{3-}$	0.012	1.443(4)	1.308(4)	1.298(4)	42
trans-[Cr(PhC(O)N(O))$_3$]$^{3-}$	0.032	1.421(3)	1.317(3)	1.301(4)	42
Average[a]	0.022(10)	1.432(11)	1.313(5)	1.300(2)	

[a] Defined in Table VIII.

[b] This work.

Table X. Average Bond Distances (Å) in Complexes of Thiohydroxamic and Thiohydroximic Acids.

Compound	N–O	C=S	C–N	Ref.
cis-Ni(MeC(S)N(O)H)$_2$	1.35(2)	1.730(10)	1.290(13)	43
trans-Ni(MeC(S)N(O)H)$_2$	1.370(10)	1.710(10)	1.300(13)	44
Cr(PhC(S)N(O)Me)$_3$	1.350(3)	1.710(3)	1.303(3)	45
Co(PhC(S)N(O)Me)$_3$	1.354(3)	1.718(2)	1.301(2)	45
Fe(PhC(S)N(O)Me)$_3$	1.348(4)	1.703(3)	1.307(2)	45
Fe(MeC(S)N(O)Me)$_3$	1.342(2)	1.681(2)	1.295(2)	46
Mn(PhC(S)N(O)Me)$_3$	1.349(8)	1.707(6)	1.306(4)	45
Hf(*p*-MePhC(S)N(O)Me)$_4$	1.355(4)	1.700(3)	1.303(7)	47
Average[a]	1.352(3)	1.707(5)	1.301(2)	
$[\mathrm{Cr(PhC(S)N(O))_3}]^{3-}$	1.398(10)	1.739(8)	1.280(10)	48

[a] Defined in Table VIII.

Table XI. Bond Orders in Hydroxamic Acids and Related Compounds.

Compound	Bond Order[a]			%II[b]
	C-X, X=O,S	C(X)-N	C-X + C-N	
Amide	1.86	1.57	3.43	37%
Hydroxamic acid	1.79	1.59	3.38	41%
Hydroxamate complex	1.66	1.68	3.34	51%
Hydroximate complex	1.44	1.75	3.19	65%
Thiohydroxamate complex	1.43	1.74	3.17	65%
Hydroximic acid	1.34	1.93	3.27	77%
Thiohydroximate complex	1.29	1.87	3.16	78%

[a] Bond Order = EXP[(D_1 - D_x)/0.308] (Ref. 49), where, D_1 = 1.426 Å for C-O, 1.472 Å for C-N, and 1.817 Å for C-S bonds (Ref. 14), and D_x is the average bond length in Tables IX and X, except that data for amides is taken from Ref. 14.

[b] %II = [B_{C-N} x 3/(B_{C-N} + B_{C-X}) -1] x 100%, where B is the bond order.

Figure Captions

Figure 1. Structural formulas of the thorium hydroxamate complexes described in this paper.

Figure 2. Packing diagram of Th[i-PrN(O)C(O)-t-Bu]$_4$ (1) viewed down the c ($\bar{4}$) axis with the b axis vertical.

Figure 3. A view of the Th[i-PrN(O)C(O)-t-Bu]$_4$ viewed down the $\bar{4}$ axis. In this and subsequent figures, thermal ellipsoids are drawn at the 50% probability level except for those of the substituent carbon atoms which are at the 8% probability level. Nitrogen and nitrogen oxygen atoms are shaded and hydrogen atoms are omitted for clarity.

Figure 4. Stereopair of Th[i-PrN(O)C(O)-t-Bu]$_4$ viewed down the dodecahedral mirror plane, perpendicular to c.

Figure 5. The coordination polyhedron of Th[I-PrN(O)C(O)-t-Bu]$_4$ compared to a cube and to a dodecahedron.

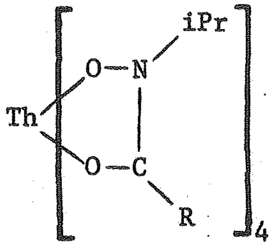
Figure 6. Packing diagram of Th[i-PrN(O)C(O)neopentyl]$_4$ (2) viewed down the b axis with the c axis horizontal. Note the hexane molecule.

Figure 7. Th[i-PrN(O)C(O)neopentyl]$_4$ viewed down what would be the $\bar{4}$ axis of the D_{2d} dodecahedron.

Figure 8. A view down what would be the dodecahedral mirror plane in Th[i-PrN(O)C(O)neopentyl]$_4$, seen perpendicular to the $\bar{4}$ axis.

Figure 9. Stereopair of Th[i-PrN(O)C(O)neopentyl]$_4$ viewed down what would be the twofold axis of the D_{2d} dodecahedron.

Figure 10. Schematic structure of Th[i-PrN(O)C(O)neopentyl]$_4$ emphasizing its relationship to a dodecahedron.



1 R = $C(CH_3)_3$

2 R = $CH_2C(CH_3)_3$

Fig. 1

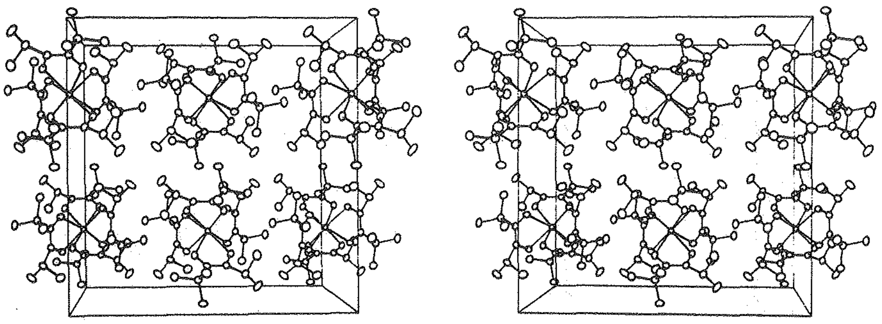


Fig. 2

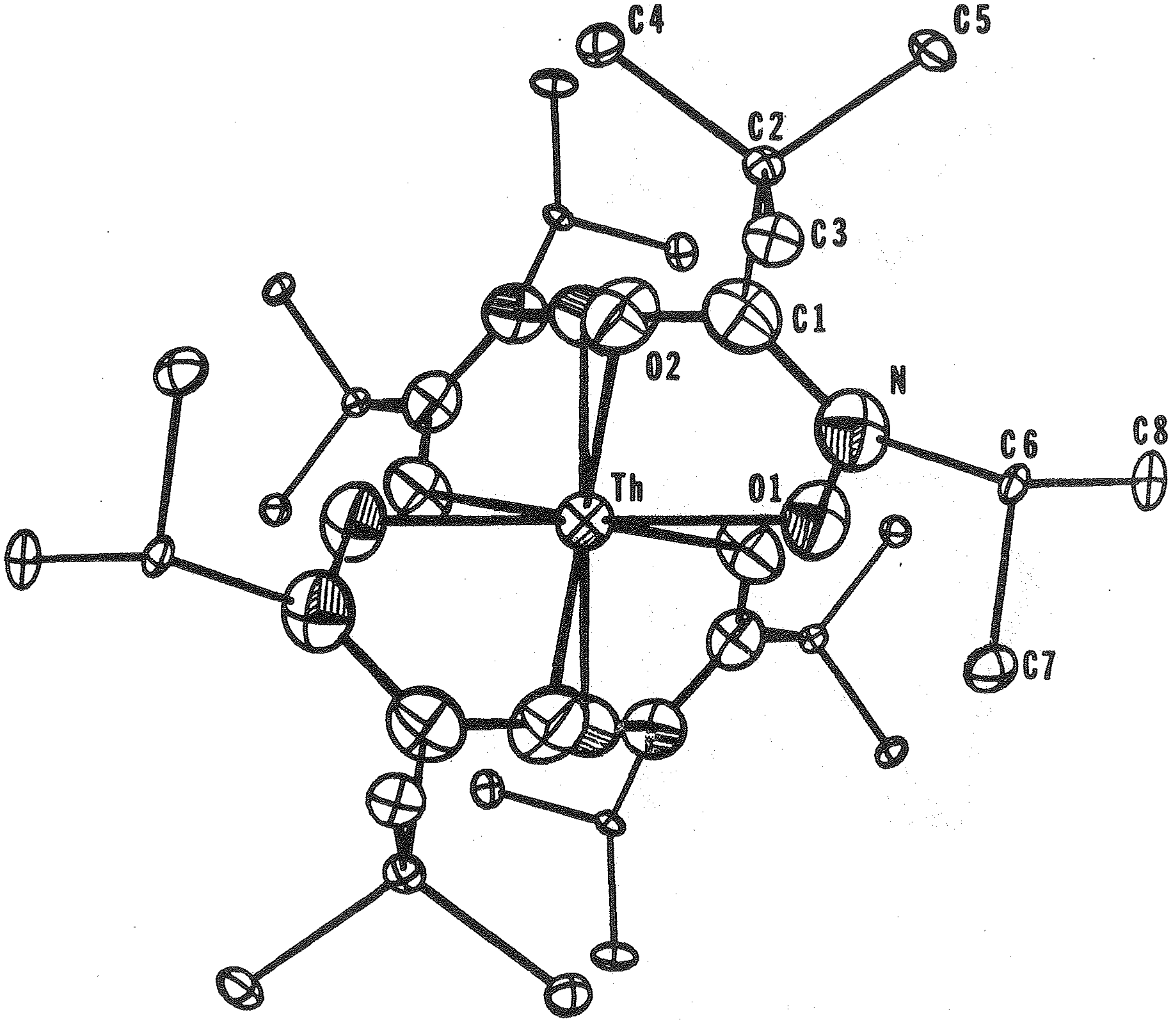
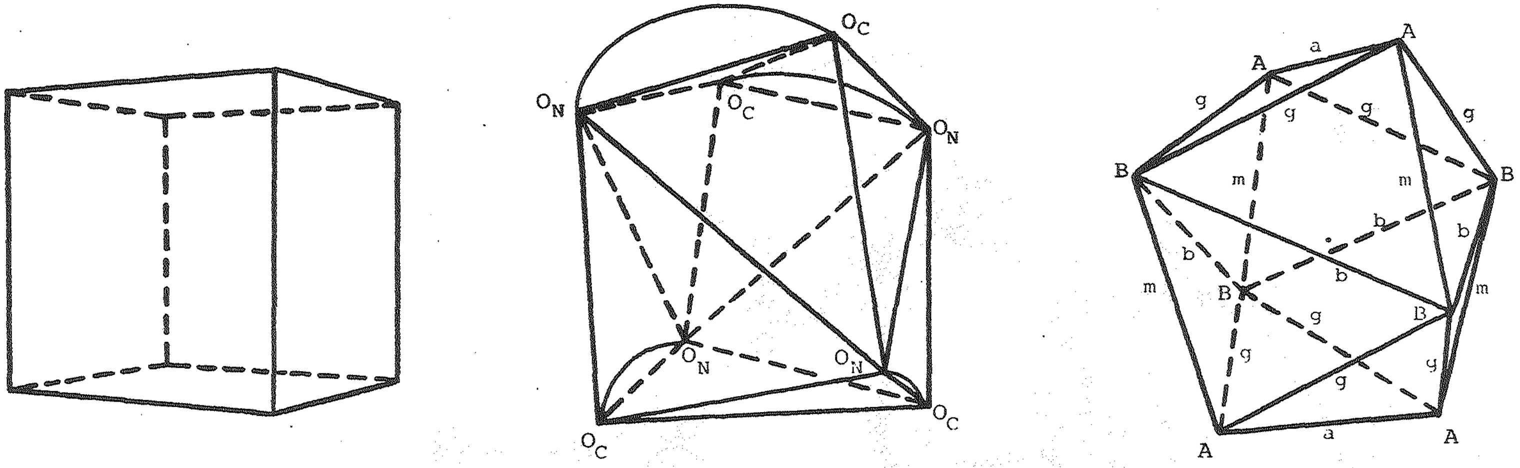


Fig. 3

XBL 796-10274A



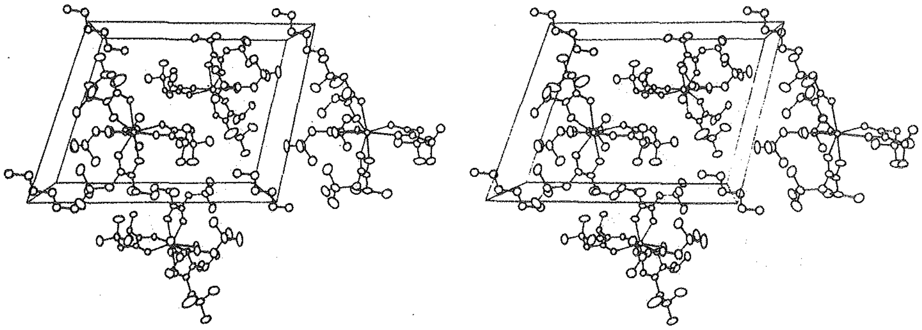
CUBE

Th(i-PrN(O)C(O)-t-Bu)$_4$

DODECAHEDRON

Fig. 4

XBL 796-10271



XBL 7912-13660

Fig. 5

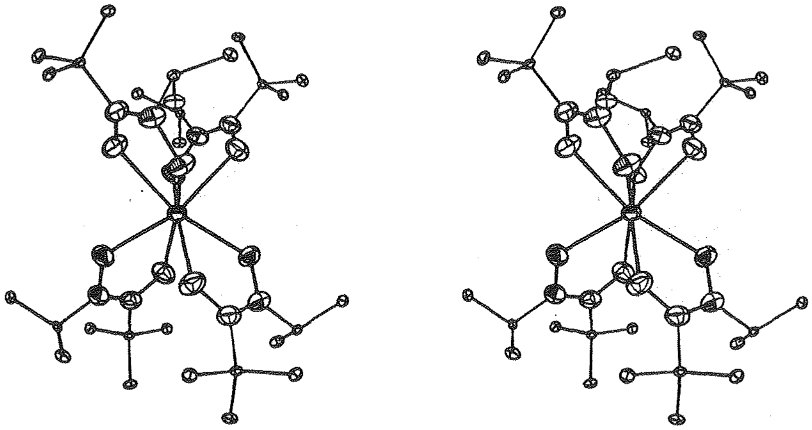


Fig. 6

XBL 7912-13662

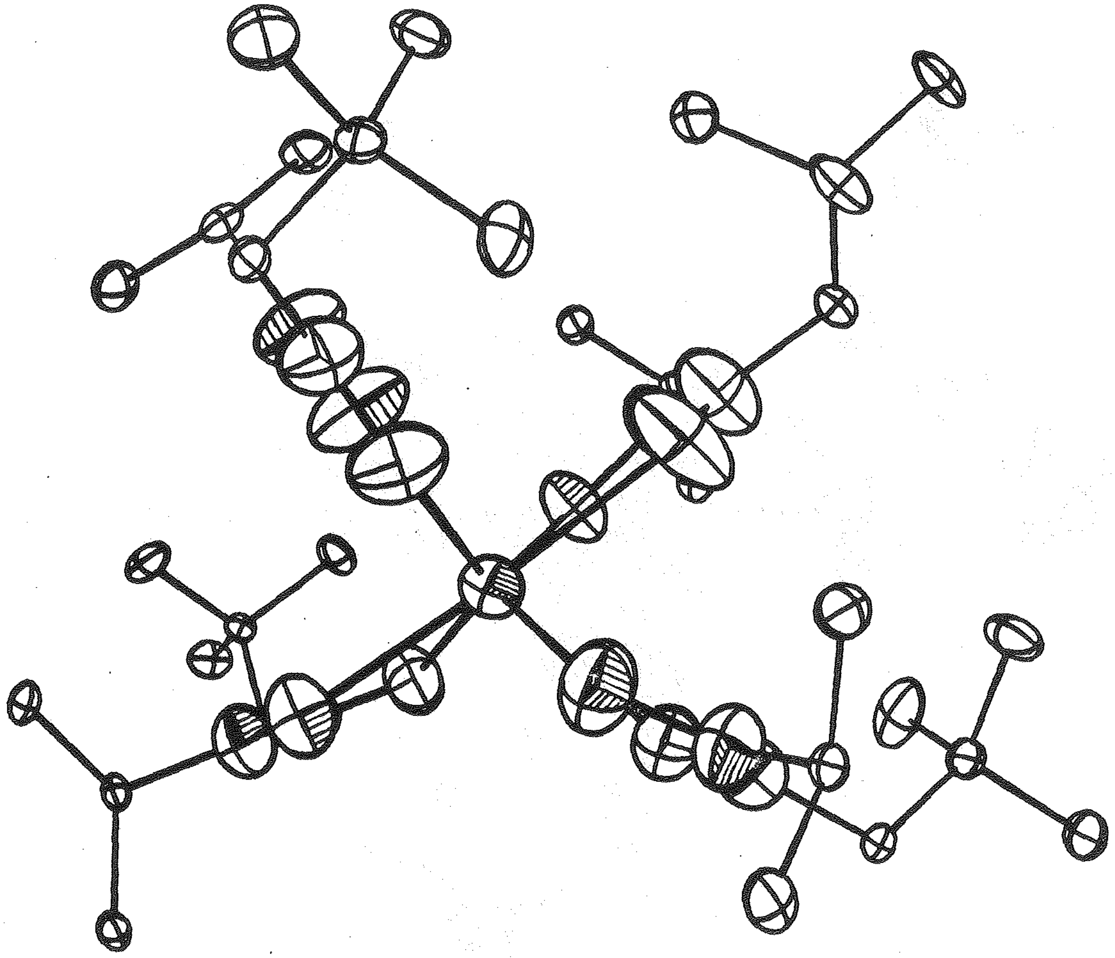


Fig. 7

XBL 799-11354

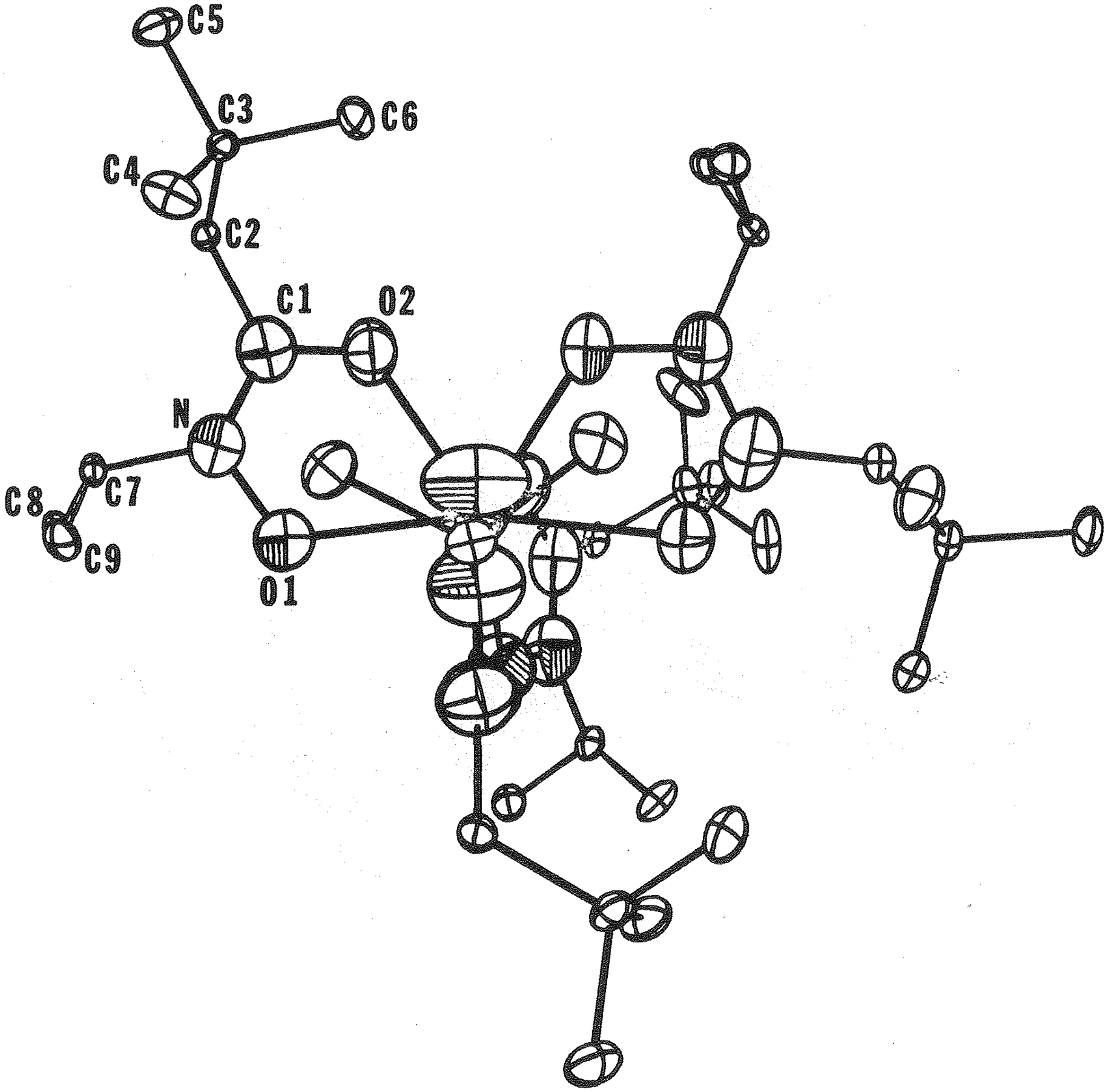


Fig. 8

XBL 7912-13537

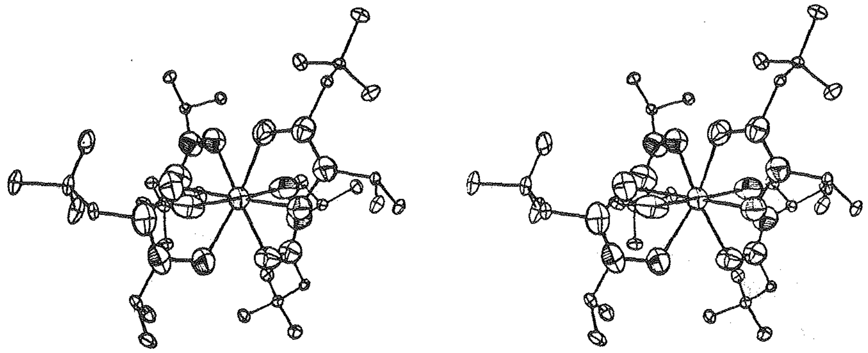


Fig. 9

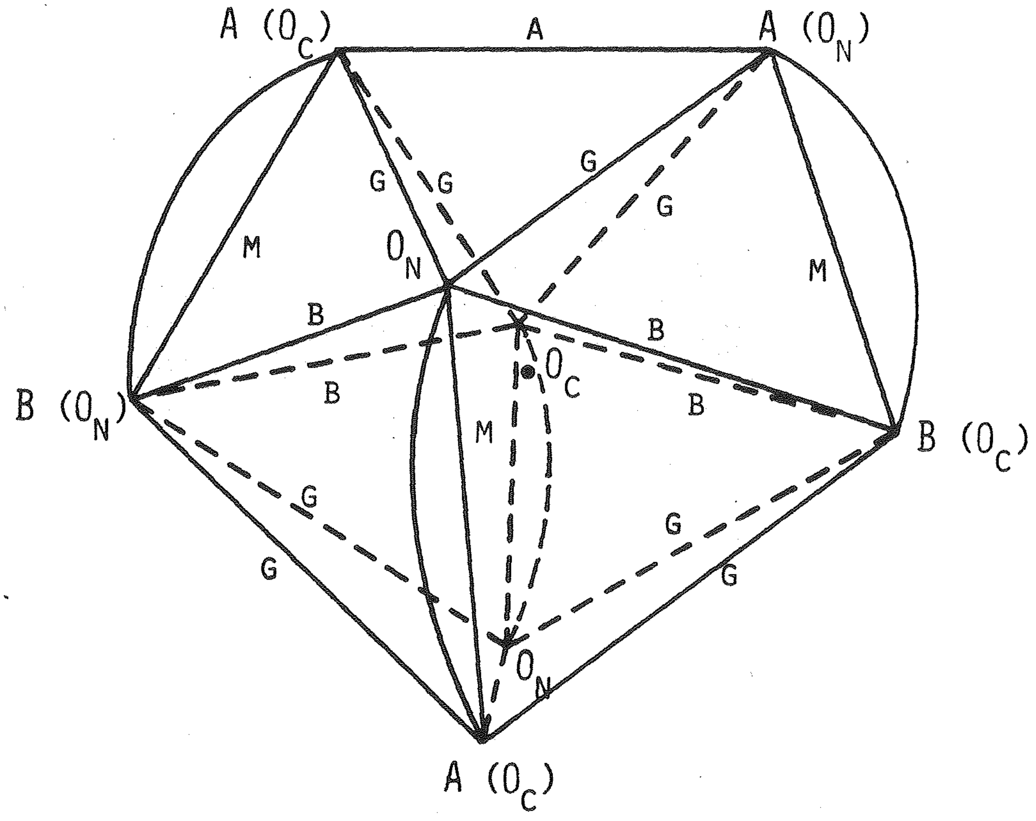


Fig. 10

XBL 7910-12169