Table III. Selected Bond Distances (Å) and Angles (deg) for $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$

U-N(1)	2.35 (1)	U-N(2)	2.32 (2)
U-N(3)	2.38 (2)	U-N(4)	2.37 (2)
U-N(5)	2.26 (3)		
K(1)-O(1)	2.72 (2)	K(1)-O(3)	2.72 (2)
K(2)-O(2)	2.62 (2)	K(2)-O(4)	2.78 (3)
K(1)-C(31)	3.38 (3)	K(1)-C(32)	3.15 (3)
K(1)-C(33)	3.06 (3)	K(1)-C(34)	3.24 (3)
K(1)-C(41)	3.14 (3)	K(1)-C(42)	3.06 (3)
K(1)-C(43)	3.11 (3)	K(1)-C(44)	3.24 (3)
K(1)-C(45)	3.30 (3)	K(1)-C(46)	3.34 (3)
K(2)-C(21)	3.29 (3)	K(2)-C(24)	3.30 (3)
K(2)-C(25)	3.09 (3)	K(2)-C(26)	3.11 (3)
K(2)-C(51)	3.26 (3)	K(2)-C(52)	3.38 (3)
K(2)-C(53)	3.34 (3)	K(2)-C(54)	3.21 (3)
K(2)-C(55)	3.15 (2)	K(2)-C(56)	3.22 (3)
N(1)-U-N(2)	88.1 (6)	N(1)-U-N(3)	129.4 (9)
N(1)-U-N(4)	80.9 (6)	N(1)-U-N(5)	118.3 (9)
N(2)-U-N(3)	87.2 (8)	N(2)-U-N(4)	166.0 (7)
N(2)-U-N(5)	95.9 (9)	N(3)-U-N(4)	92.9 (7)
N(3)-U-N(5)	112.3 (8)	N(4)-U-N(5)	97.1 (9)
U-N(1)-C(11)	148 (1)	U-N(2)-C(21)	156 (2)
U-N(3)-C(31)	141 (2)	U-N(4)-C(41)	152 (2)
U-N(5)-C(51)	149 (2)		

(benzenoid B-band) transition in the anilide ligand. The 290-nm band is assigned to a nitrogen-to-uranium ligand-to-metal charge-transfer (LMCT) excitation.

The infrared spectrum (4000–450 cm^{-1}) shows a weak, broad feature at 3300 cm^{-1}, which we assign as the N–H stretch. A strong band at 1583 cm^{-1} is assigned to the C=C aromatic stretch, and the vibrations at 744 and 684 cm^{-1} are consistent with C–H out of plane bending modes expected for a 1,2,3-trisubstituted arene ring. In addition, infrared absorption bands indicative of coordinated (1041, 884, 838 cm^{-1}) and nonligated (1054, 906 cm^{-1}) THF are observed.[18]

In summary, $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$ has been prepared by metathesis of $UI_3(THF)_4$ with potassium 2,6-diisopropylanilide in THF and structurally characterized. It is our expectation that complexes of the type $\{[K(THF)_2]_2[U(NH\text{-}Ar)_5]\}$ will be useful precursors for further explorations of low- and high-valent uranium chemistry.

Acknowledgment. This work was performed under the auspices of the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy. We are grateful to Dr. John G. Watkin and Dr. David R. Wheeler for technical assistance.

Supplementary Material Available: Tables of crystallographic data, fractional coordinates, bond distances, bond angles, and anisotropic thermal parameters and figures of atomic numbering schemes for uranium and potassium coordination environments (13 pages); a listing of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Technetium Complexes of Tripodal Oxygen Donor Ligands

John Anthony Thomas and Alan Davison*

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Recently, complexes containing the $Re^{VII}O_3^+$ moiety and the monoanionic, tridentate oxygen donor ligand $[(\eta^5\text{-}C_5H_5)Co(P(OR)_2{=}O)_3]^-$ (Figure 1, R is methyl or ethyl) have been synthesized.[1] There is current interest in rhenium and technetium $M^{VII}O_3^+$ complexes because of their scarceness[1-5] and the ability of $Tc^{VII}O_3^+$ complexes to oxidize olefins to diolates.[3-5] Details of the characterization and synthesis of the only reported technetium complex of this ligand, $[((\eta^5\text{-}C_5H_5)Co(P(OMe)_2{=}O)_3)TcO_3]$, are scant.[1] Because of these reasons, and the ability to alter the solubility properties of $[(\eta^5\text{-}C_5H_5)Co(P(OR)_2{=}O)_3]^-$ and its resulting metal complexes,[6] we have prepared several new, high oxidation state technetium complexes of $[(\eta^5\text{-}C_5H_5)Co(P(OR)_2{=}O)_3]^-$, where R is ethyl or butyl. The known complex (R is methyl) has been prepared here for comparison.

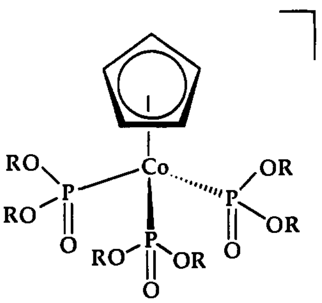

Figure 1. Ligand (L_{OR}) used in this study (R is methyl, ethyl, and butyl).

Experimental Section

Caution! Technetium-99 is a weak β^--emitter (E = 292 keV, $t_{1/2}$ = 2.12 × 10^5 years). All experiments have been done in laboratories approved for low-level radioactive materials following precautions detailed elsewhere.[7]

Ammonium pertechnetate was obtained as a gift from Du Pont/Biomedical Products. Solvents and reagents were used as received unless otherwise indicated. Methylene chloride was distilled over calcium hydride. Tetrahydrofuran was distilled over sodium metal and benzophenone. Pentane and octane were washed with sulfuric acid/nitric acid and water and were distilled over calcium chloride. The ligands, sodium (cyclopentadienyl)tris(diethyl phosphito)cobaltate, $Na(L_{OEt})$,[8] sodium (cyclopentadienyl)tris(dimethylphosphito)cobaltate, $Na(L_{OMe})$,[8] and sodium (cyclopentadienyl)tris(dibutylphosphito)cobaltate, $Na(L_{OBu})$,[9] were prepared by published procedures. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Fast atom bombardment mass spectra (FABMS) were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun that produced a beam of 6–8-keV Xenon neutrals. The samples were dissolved in a *p*-nitrobenzyl alcohol matrix. Infrared spectra were recorded on a Mattson Cygnus 100 FT spectrophotometer. NMR spectra were run on a Varian XL 300-MHz instrument SEP-PAK C_{18} cartridges were obtained from Waters Associates.

Preparation of ((Cyclopentadienyl)tris(diethyl phosphito)cobaltato)-oxodichlorotechnetium(V), $[(L_{OEt})TcOCl_2]$. To 0.45 mL of a 0.22 M aqueous solution of $(NH_4)[TcO_4]$ (0.1 mmol) were added 1 mL of methanol, $Na(L_{OEt})$ (73.41 mg, 0.13 mmol), and 1 mL of concentrated HCl. The orange solution was refluxed for 2.5 h, during which time it became yellow-green, and a yellow-green solid precipitated. The mixture was stored at −20 °C overnight and was filtered onto a fritted glass funnel. A yellow-green solid was collected (40.12 mg), washed with water, and dried overnight in vacuo. A second crop precipitated from

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* Author to whom correspondence should be addressed.

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the filtrate and was collected, washed with water, and dried in vacuo (20.20 mg). Total yield: 60.32 mg (84%). The material was recrystallized by pentane diffusion into a tetrahydrofuran solution of the compound; mp 205–206 °C dec.

Anal. Calcd for $C_{17}H_{35}Cl_2CoO_{12}P_3Tc$: C, 28.33; H, 4.86; Cl, 9.72. Found: C, 28.56; H, 4.90; Cl, 9.96.

FABMS(+): *m/z* 719 $(M - H)^+$, 703 $(M - O - H)^+$, 684 $(M - H - Cl)^+$, 649 $(M - H - 2Cl)^+$. IR (KBr): ν = 3118 w, 2981 m, 2931 m, 2902 m, 2866 w, 1476 w, 1442 m, 1424 m, 1387 m, 1363 w, 1297 w, 1164 m (ν(P=O)), 1105 s (ν(P=O)), 1076 s (ν(COP)), 1015 s (ν(COP)), 965 s, 940 s, 847 s, 744 s, 731 s, 637 m, 601 s, 473 m cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 5.1 (s, 5 H), 4.25 (m, 8 H), 3.89 (quintet, 4 H), 1.35 (m, 12 H), 1.15 (t, 6 H).

Preparation of ((Cyclopentadienyl)tris(diethyl phosphito)cobaltato)trioxotechnetium(VII), $[(L_{OEt})TcO_3]$. Method 1. To 0.45 mL of a 0.22 M aqueous solution of $(NH_4)[TcO_4]$ (0.1 mmol) were added $Na(L_{OEt})$ (64.67 mg, 0.12 mmol) and 1 mL of distilled water. On addition of 0.9 mL of concentrated HNO_3 to the orange solution, a pale yellow solid precipitated. The mixture was stirred for 4 h and then filtered onto a fritted glass funnel. The pale yellow solid was washed with 50 mL of distilled water and dried overnight in vacuo. Yield: 66.00 mg (97%). Vapor diffusion of *n*-pentane into a tetrahydrofuran solution of the complex yielded yellow crystals within 24 h; mp 174–175 °C dec.

Anal. Calcd for $C_{17}H_{35}CoO_{12}P_3Tc$: C, 29.91; H, 5.13. Found: C, 29.93; H, 5.07.

FABMS(+): *m/z* 682 $(M)^+$, 666 $(M - O)^+$, 650 $(M - 2O)^+$, 537 $(M - 5\ \text{ethyl})^+$, 513 $(M - 2O - P(O)(OEt)_2)^+$, 485 $(M - 2O - P(O)(OEt)_2 - \text{ethyl} + H)^+$. IR (KBr): ν = 3109 w, 2983 m, 2969 sh, 2931 m, 2905 m, 2867 w, 1444 w, 1385 m, 1363 w, 1297 w, 1105 s (ν(P=O)), 1089 m (ν(P=O)), 1042 s (ν(COP), 1012 s (ν(COP)), 947 s, 929 vs, 901 s, 889 vs, 834 m, 777 m, 732 m, 628 m, 584 s, 502 w, 443 w cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 5.05 (s, 5 H), 4.1 (m, 12 H), 1.25 (t, 18 H). ^{99}Tc NMR(CD_2Cl_2): δ = 320 ppm; line width = 600 Hz [$\delta(TcO_4^-)$ = 0 ppm].

Method 2. To $[(L_{OEt})TcOCl_2]$ (20.26 mg, 0.03 mmol) were added 3 mL of CH_2Cl_2 and 0.3 mL of concentrated HNO_3. The resulting yellow solution was refluxed for 30 min, during which time it became golden and then pale yellow. Subsequently, the reaction mixture was evaporated to dryness under vacuum and dissolved in tetrahydrofuran. Vapor diffusion of *n*-pentane into the solution at room temperature yielded yellow crystals within 48 h. The pale yellow supernatant was decanted off and the crystals were dried in vacuo. Yield: 4.32 mg (23%). Mp: 174–175 °C dec.

The infrared and ^1H NMR spectra of the yellow crystals are identical to those of the product obtained from method 1.

Preparation of ((Cyclopentadienyl)tris(dimethyl phosphito)cobaltato)trioxotechnetium(VII), $[(L_{OMe})TcO_3]$. To 0.62 mL of a 0.4 M aqueous solution of $(NH_4)[TcO_4]$ (0.25 mmol) were added $Na(L_{OMe})$ (159.09 mg, 0.30 mmol) and 1 mL of distilled water. On addition of 1 mL of concentrated HNO_3 to the orange solution, a pale yellow solid precipitated. The reaction conditions, product isolation, and recrystallization are identical to those of $[(L_{OEt})TcO_3]$, Method 1. Yield: 138.00 mg (92%). Mp: 175 °C dec.

Anal. Calcd for $C_{11}H_{23}CoO_{12}P_3Tc$: C, 22.07; H, 3.85. Found: C, 22.18; H, 3.85.

FABMS(+): *m/z* 599 $(M + H)^+$, 582 $(M - O)^+$, 566 $(M - 2O)^+$, 489 $(M - P(O)(OMe)_2)^+$, 472 $(M - H - O - P(O)(OMe)_2)^+$, 457 $(M - 2O - P(O)(OMe)_2)^+$, 1197 $(2M + H)^+$, 1180 $(2M - O)^+$, 1164 $(2M - 2O)^+$, 1148 $(2M - 3O)^+$. IR (KBr): ν = 3094 w, 2998 w, 2950 m, 2839 w, 1457 m, 1426 m, 1374 w, 1174 w, 1121 s (ν(P=O)), 1113 s (ν(P=O)), 1029 s (ν(COP)), 990 s (ν(COP)), 903 s, 891 vs, 842 m, 835 m, 783 s, 735 s, 631 m, 589 s, 473 w, 419 m cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 5.1 (s, 5 H), 3.7 (quartet, 18 H). ^{99}Tc NMR (CD_2Cl_2): δ = 320 ppm; line width = 485 Hz [$\delta(TcO_4^-)$ = 0 ppm].

Preparation of ((Cyclopentadienyl)tris(dibutyl phosphito)cobaltato)trioxotechnetium(VII), $[(L_{OBu})TcO_3]$. To 0.62 mL of a 0.4 M aqueous solution of $(NH_4)[TcO_4]$ (0.25 mmol) were added 1 mL of distilled water and 1.5 mL of a yellow solution of $Na(L_{OBu})$ (178.30 mg, 0.25 mmol) in octane. Concentrated HNO_3 (0.5 mL) was added to the mixture. The two phases were stirred together at room temperature for 1 day and then separated. The octane layer was washed with distilled water and evaporated to dryness under high vacuum to give a yellow, waxy solid. The solid was dissolved in CH_2Cl_2 and eluted through a C_{18} SEP-PAK. The yellow eluant was dried under high vacuum. Yield of ($[(L_{OBu})TcO_3]$): 113.52 mg (53%). Mp: 100–102 °C.

Anal. Calcd for $C_{29}H_{59}CoO_{12}P_3Tc$: C, 40.94; H, 6.94. Found: C, 40.89; H, 7.01. FABMS(+): *m/z* 850 $(M)^+$, 834 $(M - O)^+$, 818 $(M - 2O)^+$, 793 $(M - \text{butyl})^+$, 777 $(M - O - \text{butyl})^+$, 762 $(M - 2O - \text{butyl} + H)^+$, 705 $(M - 2OBu)^+$. IR (KBr): ν = 3122 w, 2959 s, 2934 s, 2874 s, 2737 w, 1646 w, 1558 w, 1457 m, 1427 w, 1384 m, 1278 w, 1232 w, 1124 s (ν(P=O)), 1112 s (ν(P=O)), 1061 s (ν(COP)), 1026 s (ν(COP)), 972 s, 954 sh, 900 sh, 897 s, 836 w, 787 w, 719 w, 627 sh, 589 m cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 5.05 ppm (s, 5 H), 4.0 (m, 12 H), 1.65 (m, 12 H), 1.45 (m, 12 H), 0.95 (t, 18 H). ^{99}Tc NMR(CD_2Cl_2): δ = 320 ppm; line width = 950 Hz [$\delta(TcO_4^-)$ = 0 ppm].

Results and Discussion

The reaction of $(NH_4)[TcO_4]$ in the presence of aqueous methanol, HCl, and $Na(L_{OEt})$ gives $[(L_{OEt})TcOCl_2]$ in high yield. This method is similar to that used to prepare $[(HB(pz)_3)TcOCl_2]$ and and $[(HB(pz)_3)ReOCl_2]$ ($(HB(pz)_3)^-$ is hydrotris(1-pyrazolyl)borate).[10] The FAB(+) mass spectrum indicates a parent peak less one proton at *m/z* 719; therefore, in the mass spectrometer, the original complex is oxidized to a monocation. A readily assignable fragmentation pattern is observed. The ^1H NMR spectrum of $[(L_{OEt})TcOCl_2]$ shows that two of the ligand's PO groups are equivalent and the third, coordinated trans to the oxo group, is unique.

The nitric acid oxidation of $[(HB(pz)_3)TcOCl_2]$ and $[(HB(pz)_3)ReOCl_2]$ yield $[(HB(pz)_3)TcO_3]$ and $[(HB(pz)_3)ReO_3]$, respectively.[3] The analogous compound, $[(L_{OEt})TcO_3]$, is formed in low yield (23% based on Tc) by the nitric acid oxidation of $[(L_{OEt})TcOCl_2]$. However, $[(L_{OEt})TcO_3]$ can be prepared in excellent yield (97%) by the reaction of an aqueous solution of $(NH_4)[TcO_4]$, $[L_{OEt}]^-$, and concentrated HNO_3. The FAB(+) mass spectrum shows the parent ion at *m/z* 682 and fragments corresponding to loss of one oxo group (666) two oxo groups (650), and several lower mass peaks which represent successive break-up of the ligand. The three phosphito groups of the ligand are equivalent, as determined by the ^1H NMR spectrum. The known compound $[(L_{OMe})TcO_3]$[1] has been synthesized here in a manner analogous to $[(L_{OEt})TcO_3]$, and its ^1H NMR spectrum shows the six methyl groups of the ligand are equivalent and are split into a quartet by virtual coupling to the ligand's three phosphorus nuclei. The FAB(+) mass spectrum of $[(L_{OMe})TcO_3]$ shows the parent peak plus one proton at *m/z* 599. This monocation can be formulated as $[(L_{OMe})Tc^{VII}O_2(OH)]^+$

Other analogues of the ligand $(L_{OR})^-$ can be synthesized by varying the phosphito groups, and these analogues exhibit a range of solubility properties.[6] For example, $Na(L_{OBu})$ is insoluble in water but is very soluble in hydrocarbons.[9] In the presence of concentrated nitric acid, the two-phase stoichiometric reaction of $Na(L_{OBu})$ in octane and aqueous $(NH_4)[TcO_4]$ gives $[(L_{OBu})TcO_3]$ in good yield (53%). The compound, $[(L_{OBu})TcO_3]$, is very soluble in hydrocarbons, acetone, and CH_2Cl_2. The solubility properties of $[(L_{OBu})TcO_3]$ are unique among complexes of the polar core $[Tc^{VII}O_3^+]$.[3-5] This fact may prove useful in isolating and separating technetium by complexation with $(L_{OBu})^-$ by a two-phase water/hydrocarbon reaction in the presence of nitric acid.

The FAB(+) mass spectrum of $[(L_{OBu})TcO_3]$ indicates a parent peak at *m/z* 850 and an extensive, assignable fragmentation pattern. The ^1H NMR spectrum shows the equivalence of the three arms of the ligand. The compound, $[(L_{OBu})TcO_3]$, shows strong infrared absorbances at 1124, 1112, 1061, and 1026 cm^{-1}. The peaks at 1124 and 1112 cm^{-1} are assigned as ν(P=O) bands, and the two lower energy bands originate from ν(COP) vibrations. All compounds presented in this work show similar resonances in this region of their infrared spectra. These assignments are based on infrared data from compounds such as $[(L_{OEt})_2Cu]$.[11]

Varying the ligand's alkyl groups does little to perturb the Tc nucleus, because $[(L_{OBu})TcO_3]$, $[(L_{OEt})TcO_3]$, and $[(L_{OMe})TcO_3]$, show peaks at 320 ppm vs TcO_4^- in their ^{99}Tc NMR spectra. These signals are in the region where other Tc(VII) complexes resonate, such as $[(HB(pz)_3)TcO_3]$.[3,12,13] The line width of $[(L_{OMe})TcO_3]$ is the smallest (485 Hz), followed by $[(L_{OEt})TcO_3]$ (600 Hz), and $[(L_{OBu})TcO_3]$ (950 Hz) shows the broadest tech-

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netium signal. This follows from the relationship of line width to the radius of the molecule; the bulkier the molecule, the greater the line width.[12]

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Contribution from the Westinghouse Savannah
River Laboratory, Aiken, South Carolina 29802,
and Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Chemical Applications of Topology and Group Theory. 27. Covalent Bonding in Actinide Derivatives[1a]

R. B. King[1b]

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The d-block transition metals are characterized by forming strong covalent bonds involving the d orbitals in a nine-orbital spherical sp^3d^5 manifold thereby leading to the familiar "18-electron rule" for the stable electronic configurations of transition metal coordination and organometallic complexes.[2] On the other hand the 4f orbitals in the lanthanides appear to participate very little in covalent bond formation so that the chemistry of the lanthanides is governed largely by electrostatic considerations similar to the chemistry of the alkali and alkaline earth metals but with a predominant +3 oxidation state. The chemistry of the actinides from at least uranium through americium exhibits some features of both the predominantly covalent bonding of the d-block transition metals and the predominantly electrostatic bonding of the lanthanides since both the 5f and 6d orbitals of the actinides can function as valence orbitals leading to an unusual 12-orbital spherical d^5f^7 manifold.[3,4] This paper uses elementary group theory to explore how such a d^5f^7 manifold can participate in the types of covalent bonding prevalent in actinide chemistry. The d^5f^7 valence orbital manifold is also of interest in violating the frequent assumption of "minimum valence orbital nodality" by using binodal d orbitals and trinodal f orbitals in preference to uninodal p orbitals; this assumption, for example, was implicit in a survey of coordination polyhedra by the author[5] about 20 years ago in the first paper of this series. This work also represents an extension of some ideas first outlined by Eisenstein[6] in 1956.

Covalently bonded actinide derivatives have been subjects of a number of computational studies.[7] The actinyl ions, particularly UO_2^{2+}, have been treated by a number of diverse methods including ligand field theory,[8] relativistic extended Hückel methods,[9-12] relativistic $X\alpha$ methods,[13-15] and ab initio Hartree–Fock methods using Slater[16] or Gaussian[17,18] orbitals including relativistic effects in the latter, much more modern, computations. In addition, cyclopentadienylactinide compounds have been studied by Tatsumi and collaborators[19-23] using the extended Hückel method and by Bursten and co-workers[24-27] using $X\alpha$–SW molecular orbital calculations with quasirelativistic corrections. The uranium–uranium bonding in the dimer U_2 has been studied by both relativistic $X\alpha$–SW molecular orbital calculations[28] and relativistic Gaussian ab initio methods.[29] Quasirelativistic $X\alpha$–SW

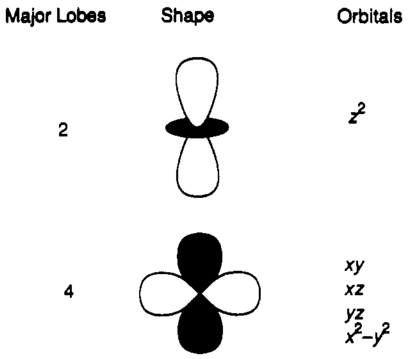

Figure 1. Shapes of the d orbitals showing the number of major lobes. The total number of major lobes in the standard set of five d orbitals is (1)(2) + (4)(4) = 18.

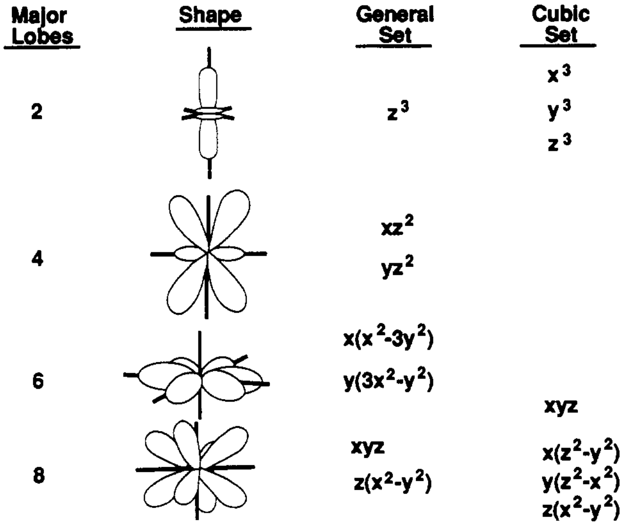

Figure 2. General shapes of both the general and cubic sets of f orbitals showing the numbers of major lobes. The total number of major lobes in either set of seven f orbitals is (1)(2) + (2)(4) + (2)(6) + (2)(8) = (3)(2) + (4)(8) = 38.

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