Contribution from the Department of Chemistry and Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Synthetic and Structural Chemistry of Gadolinium and Holmium Catecholates[1]

GWEN E. FREEMAN and KENNETH N. RAYMOND*[2]

Received December 11, 1984

As part of a study to characterize the complexes formed by catechol (1,2-dihydroxybenzene) with lanthanides in aqueous solution, crystalline samples of three gadolinium(III) complexes and a holmium(III) complex have been prepared and characterized by structural, analytical, and spectroscopic techniques. Only 1:1 complexes are isolated at pH <8, but bis-, tris-, and tetrakis(catecholato)gadolinium complexes have been prepared in basic (pH >11) solutions. The structures of tris- and tetrakis(catecholato)gadolinium compounds have been determined by single-crystal X-ray diffraction methods using counter data. The tetrakis complex in $Na_5[Gd(catecholate)_4]\cdot 19.2H_2O$ has D_{2d} molecular symmetry and is nearly isomorphous with the previously characterized series $Na_4[M^{IV}(catecholate)_4]\cdot 21H_2O$ (M = Th, U, Hf, Ce). It conforms to the space group $I\bar{4}$ with $a = 14.663$ (1) and $c = 9.9526$ (6) Å. For 2536 independent data with $F_o^2 > 3\sigma(F_o^2)$ full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 1.99$ and $R_w = 2.58\%$. The structure of $Na_4[Hf(catecholate)_4]\cdot 21H_2O$ has been newly refined to correct a small error in the previous solution; for 4539 independent data, refinement as above converged to $R = 1.96$ and $R_w = 2.19\%$. The tris(catecholato)gadolinium complex in $Na_6[Gd(catecholate)_3]_2\cdot 20H_2O$ is a dimer in which the metal ion is seven-coordinate. The crystal conforms to the space group $P2_1/n$ with $a = 11.931$ (1), $b = 13.507$ (1), and $c = 17.265$ (2) Å and $\beta = 105.427$ (8)°. For 4652 independent data, $R = 1.65$ and $R_w = 2.14\%$. The analogous holmium complex has been synthesized and characterized. Another stoichiometry has been found in which the complex salt $Na[Gd(catecholate)_2]\cdot 10H_2O$ crystallizes in the space group Cc or $C2/c$ with $a = 16.681$ (2), $b = 19.325$ (3), and $c = 25.868$ (3) Å and $\beta = 94.24$ (1)°. However, the crystals decomposed by desolvation too readily to permit structural characterization.

Introduction

We have been engaged in an effort to develop effective and *specific* complexing agents for the actinides, in part to develop better therapeutic decorporation agents for these toxic elements.[3–7] Much of our early work has focused on the catecholate (1,2-dihydroxybenzene dianion) coordination chemistry of actinides and analogous ions such as cerium in the +4 oxidation state,[3,4] since this is the predominant oxidation state of plutonium in vivo.

Our attention has recently turned to the relatively unknown catecholate coördination chemistry of the trivalent actinides in order to understand the unusual excretion behavior of americium(III) observed in mice and dogs treated with catecholate chelating agents we have developed.[5,8,9] In addition, the redox potentials of the catechol complexes (the metal IV/III oxidation state couple) combined with the stability constants of the metal(III) complexes allow indirect thermochemical determination of the metal(IV) stability constants.[10]

Although transuranium actinides have a wide variety of oxidation states available, in their trivalent state they exhibit ionic radii similar to those of the trivalent lanthanides in the same column of the periodic table, or one column to the left.[11] Since the stability and coordination chemistry of metal catecholate complexes are largely determined by the metal's charge to ionic radius ratio,[5–7] the lanthanide(III) catecholates are excellent models for corresponding transuranium catecholate complexes. We are particularly interested in modeling the behavior of americium(III) catecholates. Europium is in the same column of the periodic table as americium; gadolinium is immediately to the right of europium. The eight-coordinate ionic radii are 1.066 (Eu), 1.053 (Gd), and 1.09 Å (Am).[11] We have examined europium catecholate solution chemistry[12] and the synthetic and structural chemistry of gadolinium catecholates as models of americium(III).

The solution[12,13] and synthetic[14] chemistry of the lanthanide catecholates indicate that below pH 7 a 1:1 lanthanide:catecholate complex is the only species present. At around pH 7, hydrolysis of this complex occurs and an insoluble complex of the stoichiometry $[Ln(cat)(OH)]\cdot 4H_2O$ (cat = catecholate) is the predominant species, regardless of the amount of excess ligand present. As the pH is raised to very basic regions (pH >11), much more complicated behavior is observed and the stoichiometry of the isolated product is dependent on the initial ligand to metal ratio as well as on the method of preparation. Although it is tangential to the chemistry of americium(III) catechol complexes at physiological pH, much of the work in this paper focuses on elucidating the synthetic and structural chemistry of the lanthanide(III) catecholates in the high-pH region.

While structural studies of metal catecholate complexes have been documented for transition metals and the tetravalent actinides,[3,4,15] none have been reported for the trivalent lanthanides or actinides. This paper reports the synthesis of isolated 2:1, 3:1, and 4:1 catechol:metal stoichiometries in $\{Na[Gd(cat)_2]\cdot 10H_2O\}_n$, $Na_6[M(cat)_3]_2\cdot 20H_2O$ (M = Gd, Ho), and $Na_5[Gd(cat)_4]\cdot 19.2H_2O$, respectively. The latter two gadolinium compounds have been structurally characterized.

Also included is the redetermination of a hafnium catecholate crystal structure. Previously we have reported the X-ray crystal structures of the isostructural series $Na_4[M(cat)_4]\cdot 21H_2O$, where M = Th, U, Hf, and Ce.[3,4] During the course of solving the very similar structure of $Na_5[Gd(cat)_4]\cdot 19.2H_2O$, it was noticed that a mathematically reasonable solution to the structure contained a chemically unreasonable catechol oxygen to water oxygen distance of 2.0 Å. The shortest known hydrogen-bonded oxygen–oxygen distance of 2.29 (2) Å is found in the X-ray structure of the bihydroxide ($H_3O_2^-$) anion.[16] The shortest such distance

---

(1) Specific Sequestering Agents for the Actinides. 12. Part 11: Ref. 10.

(2) Address correspondence to this author at the Department of Chemistry, U.C. Berkeley.

(3) Sofen, S. R.; Abu-Dari, K.; Freyberg, D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 7882.

(4) Sofen, S. R.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 1611.

(5) Raymond, K. N.; Freeman, G. E.; Kappel, M. J. *Inorg. Chim. Acta* **1984**, *94*, 193.

(6) Raymond, K. N.; Smith, W. L.; Weitl, F. L.; Durbin, P. W.; Jones, E. S.; Abu-Dari, K.; Sofen, S. R.; Cooper, S. R. *ACS Symp. Ser.* **1980**, *No. 131*, 143.

(7) Raymond, K. N.; Smith, W. L. *Struct. Bonding (Berlin)* **1981**, *43*, 159.

(8) Durbin, P. W.; Jeung, N.; Jones, E. S.; Weitl, F. L.; Raymond, K. N. *Radiat. Res.* **1984**, *99*, 85.

(9) Lloyd, R. D.; Bruenger, F. W.; Mays, C. W.; Atherton, D. R.; Jones, C. W.; Taylor, G. N.; Stevens, W.; Durbin, P. W.; Jeung, N.; Jones, E. S.; Kappel, M. J.; Raymond, K. N.; Weitl, F. L. *Radiat. Res.* **1984**, *99*, 106.

(10) Kappel, M. J. Nitsche, H.; Raymond, K. N. *Inorg. Chem.* **1985**, *24*, 605.

(11) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

(12) Zhu, D.; Kappel, M. J.; Raymond, K. N., manuscript in preparation.

(13) Pakhomova, D. V.; Kumok, V. N.; Serebrennikov, V. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1969**, *14*, 752.

(14) Fernandes, L. *Gazz. Chim. Ital.* **1926**, *56*, 682; *Chem. Abstr.* **1927**, *21*, 866.

(15) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(16) Abu-Dari, K.; Raymond, K. N.; Freyberg, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 3688.

0020-1669/85/1324-1410$01.50/0 © 1985 American Chemical Society

found by neutron diffraction is 2.546 Å.[17] The short distance found in the gadolinium structure and in all of the $Na_4[M(cat)_4]\cdot21H_2O$ structures resulted from assigning one of the water oxygens, O(3), an incorrect position in which its *z* coordinate had the opposite sign from what it should have had relative to the remainder of the structure. We are interested in the results of the redetermination of the hafnium structure as it relates to the uranium tetrakis(catecholate) structure, in which a ligand field effect for the $5f^2$ uranium(IV) ion was inferred from the difference in U–O bond distances for the two catecholate oxygens.

Experimental Section

All work was carried out in an argon atmosphere free of O_2, either on a Schlenk line or in a glovebag or -box whose atmosphere was moist but not saturated with water. $Gd(NO_3)_3\cdot5H_2O$ (Aldrich and Orion, 99.9%), $Ho(NO_3)_3\cdot5H_2O$ (Orion, 99.9%), $Ho_2(SO_4)_3\cdot8H_2O$ (Orion, 99.9%), and NaOH pellets (MCB, ACS reagent) were used without further purification. Catechol (Aldrich, 99+%) was sublimed in vacuo before use. Water was deionized and distilled in glass before use. The IR spectra of the compounds were recorded as Nujol mulls in KBr or CsI plates on a Perkin-Elmer 597 infrared spectrophotometer. Elemental analyses for carbon, hydrogen, and sodium were done by the Microanalytical Laboratory, University of California, Berkeley, CA. Gadolinium was determined by EDTA titration using Eriochrome Black T as an indicator.[18] Density measurements were done by the flotation technique in dibromomethane/toluene solutions. The pH was measured with a Brinkmann Instruments pH meter, Model 102, calibrated with standard buffer solutions at pHs 7.00 and 10.00. Melting points were recorded in sealed argon-filled capillaries.

Syntheses. $Na_5[Gd(cat)_4]\cdot19.2H_2O$. NaOH (1.065 g, 26.63 mmol) was dissolved in 13 mL of water, and the resultant mixture was deoxygenated for 80 min and added by cannula to a deoxygenated solution of $Gd(NO_3)_3\cdot5H_2O$ (1.405 g, 3.242 mmol) and catechol (1.440 g, 13.07 mmol) in 15 mL of water. A white precipitate formed immediately upon addition of the NaOH solution and continued forming until approximately half of the latter was added, at which point the precipitate abruptly went back into solution. The solution [pH 12.8 (1)] was stirred for 20 min and the volume reduced (to 7–8 mL) by vacuum with gentle heating until a precipitate started to form. This was allowed to settle, and the remaining liquid was decanted by cannula into argon-filled vials. Slow cooling of this solution to 3 °C yielded 1.617 g (47.5% yield) of large, colorless crystals that were used for analyses, spectra, and X-ray work. Infrared spectra included peaks at 1565, 1032, 896.7 (w), 866, 780 (m), 745 (sh), 728 (m–s), and 710 (sh) cm^{-1}, which are indicative of a coordinated catechol. No melting or decomposition was observed below 315 °C. Anal. Calcd for $Na_5[Gd(C_6H_4O_2)_4]\cdot19.2H_2O$ (mol wt 1050.50): C, 27.44; H, 5.22; Na, 10.94; Gd, 14.97. Found: C, 27.47; H, 5.11; Na, 11.0; Gd, 13.82. Anal. Calcd for $Na_5[Gd(C_6H_4O_2)_4]\cdot8H_2O$: Gd, 18.53. Found (dried in vacuo at ambient temperature to constant weight): Gd, 18.6.

$Na_6[Gd(cat)_3]_2\cdot20H_2O$. A solution of 1.050 g (26.25 mmol) of NaOH in 9.0 mL of water was deoxygenated for 2 h and added by cannula to deoxygenated solution of 1.404 g (3.240 mmol) of $Gd(NO_3)_3\cdot5H_2O$ and 1.442 g (13.10 mmol) of catechol in 9.0 mL of water. As above, a white precipitate formed and disappeared again as the NaOH was added. The solution (pH 11.8) was stirred and the volume reduced to $5^1/_2$ mL by vacuum with gentle heating, which caused a precipitate to form. The precipitate was almost completely dissolved with stirring and gentle heat by the addition of 9 mL of degassed water. The remaining precipitate was allowed to settle, and the liquid was decanted into argon-filled vials. Slow cooling of this solution to 3 °C yielded 1.196 g (50.5% yield) of large, colorless crystals that were used for analyses, spectra, and X-ray diffraction. When exposed to air overnight, the surface of the crystals would blacken but could be cut away, leaving an unharmed interior. The crystal used for X-ray data collection was cut in air before being sealed in a glass capillary; the surface blackened, but the crystal was still of acceptable quality. From 80 to 90 °C a small amount of dehydration occurs, and from 140 to 180 °C the crystal size decreases slightly, but no further changes or melting are observed below 315 °C. Infrared spectra include peaks at 1570, 1030, 915 (w), 867, 780 (m–w), 768 (m–w), 750 (m), and 742 (w) cm^{-1}. Anal. Calcd for $Na_6[Gd(C_6H_4O_2)_3]_2\cdot20H_2O$ (mol wt 1461.33): C, 29.59; H, 4.41; Na, 9.44; Gd, 21.52. Found: C, 29.99; H, 4.39; Na, 9.39.

Table I. Crystal Data for $Na_5[Gd(C_6H_4O_2)_4]\cdot19.2H_2O$ and $Na_4[Hf(C_6H_4O_2)_4]\cdot21H_2O$

metal	Gd	Hf
fw	1051.2	1081.3
space gp	$I\bar{4}$	$I\bar{4}$
cell const		
a, Å	14.663 (1)	14.486 (1)
c, Å	9.9526 (6)	9.984 (1)
V, $Å^3$	2139.8 (4)	2095.1
Z	2	2
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
d_{calcd}, g/cm^3	1.631	1.71
d_{obsd}, g/cm^3	1.66 (1)	1.69 (1)
μ(Mo Kα), cm^{-1}	17.5	26.0
cryst size	irregular shape	approx sphere
dimens, mm	0.45 × 0.27 × 0.38	radius 0.14
data collcd	*hkl*; $-h,-k,l$	$h,k,\pm l$; $-h,k,\pm l$
2θ range, deg	3–70	3–70
no. of indep data	2605[a]	4573[b]
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2536	4539
final *R*, %	1.99	1.96
final R_w, %	2.58	2.19
GOF	1.0027	0.7869
no. of variables	136	132

[a] After averaging, 5232 reflections collected; *R*(intensity) = 1.7%. [b] After averaging, 8525 reflections collected; *R*(intensity) = 2.4%.

$\{Na[Gd(cat)_2]\cdot10H_2O\}_n$. A solution of 0.899 g (22.48 mmol) of NaOH in 10.0 mL of water was deoxygenated for 2 h and added by cannula to deoxygenated solution of 1.365 g (3.150 mmol) of $Gd(NO_3)_3\cdot5H_2O$ and 1.222 g (11.10 mmol) of catechol (3.523 cat/Gd) in 8.0 mL of water. A white precipitate formed immediately upon addition of NaOH and dissolved completely once all of the NaOH solution was added (pH 12.7). The volume was reduced (to 8 mL) by vacuum with gentle heating until a precipitate formed. This was allowed to settle, and the liquid was decanted by cannula. Slow cooling of this solution to 3 °C yielded 0.385 g (0.668 mmol Gd; 21.2% yield based on Gd) of small, colorless crystals that were used for elemental analyses, density measurements, spectra, and X-ray diffraction. Infrared spectra included peaks at 1570, 1560 (sh), 1028, 908 (w), 872 (m), 788 (m), and 738 (m) cm^{-1}. The melting point was greater than 315 °C. Anal. Calcd for $\{Na[Gd(cat)_2]\cdot10H_2O\}_n$ (mol wt 1153.17): C, 25.00; H, 4.90; Na, 3.99; Gd, 27.27. Found: C, 25.12; H, 4.69; Na, 4.90; Gd, 28.5.

$Na_6[Ho(cat)_3]_2\cdot20H_2O$. Scheme I. A solution of 1.502 g (37.55 mmol) of NaOH was dissolved in 12 mL of water, and the resultant mixture was deoxygenated for 3 h and added by cannula to a deoxygenated solution of 1.397 g (3.168 mmol) of $Ho(NO_3)_3\cdot5H_2O$ and 2.054 g (18.65 mmol) of catechol in 14 mL of water, causing a precipitate to form and disappear again. The solution [pH 13.0 (1)] was stirred for a few minutes, and then the volume was reduced by vacuum with gentle heating until pinkish white precipitate began to form. The solution was filtered by cannula into argon-filled vials. Slow cooling of this solution to 3 °C yielded small crystals that were used for analyses, spectra, and X-ray work. Infrared spectra included peaks at 1560, 1030, 915 (w), 862, 780 (m–w), 768 (m–w), 750 (m–w), and 745 (m) cm^{-1}. Anal. Calcd for $Na_6[Ho(C_6H_4O_2)_3]_2\cdot20H_2O$ (mol wt 1469.01): C, 29.28; H, 4.37; Na, 9.34. Found: C, 29.55; H, 4.47; Na, 9.70.

Scheme II. A solution of 0.904 g (22.6 mmol) of NaOH was dissolved in 10 mL of water, and the resultant mixture was deoxygenated for 2.5 h and added by cannula to a deoxygenated solution of 1.20 g (3.15 mmol of Ho) of $Ho_2(SO_4)_3\cdot8H_2O$ and 1.224 g (11.12 mmol) of catechol in 7 mL of water. The usual precipitate formed as the NaOH solution was added but did not dissolve completely when all of the NaOH was transferred. This precipitate was allowed to settle, and the liquid [pH 12.9 (1)] was decanted by cannula into another argon-filled Schlenk flask. The volume in the fresh Schlenk flask was reduced somewhat, causing further precipitation, thus indicating that the reaction was run near the solubility limit of the compound. The precipitate was allowed to settle, and the liquid was decanted by cannula into argon-filled vials. Slow cooling to 3 °C yielded single crystals that were used for analyses. spectra, and X-ray work. The IR spectrum was the same as above. Anal. Found: C, 29.15; H, 4.25; Na, 11.0.

X-ray Diffraction Studies. $Na_5[Gd(cat)_4]\cdot19.2H_2O$. The crystal was mounted in a glass capillary under moist argon. Photographic examination showed the crystal to be of good quality. Precession photography showed the crystal to have tetragonal symmetry and systematic absences *hkl* ($h + k + l = 2n + 1$) consistent with a body-centered tetragonal

---

(17) Chiari, G.; Ferraris, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2331.

(18) Schwarzenbach, G.; Flashka, H. "Complexiometric Titrations", 2nd ed.; Methuen: London, 1969; p 194.

Table II. Positional and Thermal Parameters for the Non-Hydrogen Atoms in $Na_5[Gd(C_6H_4O_2)_4]\cdot 19.2H_2O$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Gd	0.000	0.000	0.000	2.052 (1)
Na(1)	−0.04052 (9)	0.18548 (9)	0.2573 (1)	4.03 (2)
Na(2)	0.000	0.500	0.250	6.9 (1)
Na(3)	0.000	0.000	0.441 (1)	4.9 (2)
O(1)	0.0411 (1)	0.1524 (1)	0.0612 (2)	3.01 (3)
O(2)	0.0303 (1)	0.0940 (1)	−0.1950 (2)	2.80 (3)
OW(1)	0.0665 (2)	0.0949 (2)	0.3862 (3)	4.79 (5)
OW(2)	0.2758 (2)	0.3618 (2)	0.0445 (3)	5.16 (5)
OW(3)	0.2729 (2)	0.1658 (2)	−0.1465 (3)	5.55 (6)
OW(4)	0.0313 (2)	0.3262 (2)	0.3619 (3)	5.86 (7)
OW(5)	0.2155 (2)	0.1817 (2)	0.1411 (3)	5.13 (5)
C(1)	0.0463 (2)	0.2140 (1)	−0.0375 (2)	2.65 (3)
C(2)	0.0430 (1)	0.1833 (1)	−0.1727 (2)	2.53 (3)
C(3)	0.0548 (2)	0.2464 (2)	−0.2768 (3)	3.22 (4)
C(4)	0.0693 (2)	0.3386 (2)	−0.2491 (3)	3.78 (5)
C(5)	0.0683 (2)	0.3689 (2)	−0.1183 (4)	4.03 (5)
C(6)	0.0573 (2)	0.3075 (1)	−0.0115 (5)	3.72 (4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

space group. The crystal was mounted on an Enraf-Nonius CAD-4 diffractometer for data collection. Crystal data obtained by a least-squares fit to 24 high-angle reflections are listed in Table I along with other crystallographic data. Intensities were measured by the θ–2θ scan technique. Three intensity standards were measured every 2 h of X-ray exposure time, and three orientation standards were checked every 250 reflections.

The raw data were processed as previously described.[19] An isotropic decrease in intensity of 4.0% was observed in the intensity standards during the 82.0 h of data collection, and decay corrections were applied accordingly. The crystal orientation was also redetermined four times during the course of data collection. An empirical absorption correction, based on ψ scans of five reflections having high χ (>80°) angles and spanning a range of $4.53° < \theta < 27.50°$, was also applied. The minimum and maximum correction factors were 0.9467 and 0.9991, respectively. Systematically absent reflections were not collected. Averaging the 5232 data collected yielded 2605 data, 2536 of which had $F_o^2 > 3\sigma(F_o^2)$.

Structure Solution and Refinement. The structure was solved by standard heavy-atom methods. The fifth sodium proved to be disordered between two special positions in the unit cell, one position [Na(2)] on the crystallographic $\bar{4}$ axis at 0, $^1/_2$, $^1/_4$ and the other position [Na(3)] on the crystallographic twofold axis at 0, 0, 0.4408. The latter position placed constraints on the occupancy of water molecule OW(1) (see Discussion), which resulted in the value of 19.2 waters. The distribution of the sodium atom between the two special positions was varied until the lowest *R* factor and most plausible thermal parameters for Na(2), Na(3), and OW(1) were achieved at Na(2)/Na(3) = 0.62/0.38. All catecholate hydrogens and 32 water hydrogens were located following full anisotropic refinement of the non-hydrogen atoms. Catecholate hydrogen atoms were assigned idealized coordinates with C–H distances of 0.95 Å[20] and isotropic thermal factors of $B = 5.0$ Å^2. The water hydrogens were given the coordinates of their associated peaks in the difference Fourier and assigned isotropic thermal factors of $B = 6.5$ Å^2 (or 7.0 Å^2), depending on the thermal factors of their associated oxygens. One of the two hydrogen atoms for water OW(2) was disordered as a result of the disorder of the fifth sodium. A value of 0.03 was used for the parameter *p* in the weighting function. Examination of the most intense reflections showed a systematic trend of $F_o < F_c$, indicating secondary extinction. The final least-squares cycle, in which the secondary extinction coefficient was also refined,[21] converged to $R = 1.99$ and $R_w = 2.58\%$ with the extinction coefficient 6.589×10^{-7} e^2. The largest parameter shift was 2% of its associated esd, and the largest peak in the final difference Fourier was 0.580 e/Å^3. The error in an observation of unit weight (GOF) for 136 variables was 1.003. Positional parameters are listed in Table II.

Table III. Crystal Data for $Na_6[M(C_6H_4O_2)_3]_2\cdot 20H_2O$ (M = Gd, Ho)

metal	Gd	Ho
fw	1461.33	1469.01
space gp	$P2_1/n$	$P2_1/n$
cell const		
a, Å	11.931 (1)	11.84 (5)
b, Å	13.507 (1)	13.49 (5)
c, Å	17.265 (2)	17.21 (5)
β, deg	105.427 (8)	105.4
V, Å^3	2682.1 (8)	2651 (10)
Z	2	2
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
d_{calcd}, g/cm^3	1.809	1.840
d_{obsd}, g/cm^3	1.795	1.841 (8)
μ(Mo Kα), cm^{-1}	26.0	
cryst size	irregular shape	
dimens, mm	0.40 × 0.17 × 0.21	
no. of data collcd	$+h, \pm k, \pm l$	
2θ range, deg	3–55	
no. of indep data	6169[a]	
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	4652	
final *R*, %	1.65	
final R_w, %	2.14	
GOF	1.023	
no. of variables	344	

[a] After averaging, 129 32 reflections collected; *R*(intensity) = 2.1%.

$Na_6[Gd(cat)_3]_2\cdot 20H_2O$. The crystal was mounted in air in a glass capillary. Brief photographic examination showed the crystal to be of good quality. Intensity data collection was on an Enraf-Nonius CAD-4 diffractometer. Accurate cell dimensions were derived from least-squares refinement of 24 high-angle reflections and are listed in Table III along with other crystallographic data. Intensities were measured by the θ–2θ scan technique. Three intensity standards were measured every 2 h of X-ray exposure time, and three orientation standards were checked every 250 reflections.

The raw data were processed as previously described.[19] An isotropic decrease in intensity of 23% was observed in the intensity standards during the 166 h of data collection, and decay corrections were applied accordingly. The crystal orientation was also redetermined three times during the course of data collection. An empirical absorption correction, based on ψ scans of five reflections having high χ angles (>80°) and spanning a range of $6.3° < \theta < 23.1°$, was also applied. The minimum and maximum correction factors were 0.934 and 1.000, respectively. The space group $P2_1/n$ was verified by the systematic absence of all reflections $0k0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$). After systematically absent reflections were rejected, the remaining data were averaged to yield 4652 data for which $F_o^2 > 3\sigma(F_o^2)$.

Structure Solution and Refinement. The structure was solved by heavy-atom methods. All hydrogen atoms were located following full anisotropic refinement of the non-hydrogen atoms. Hydrogen atoms were assigned isotropic thermal factors of $B = 5.0$ Å^2. Where possible, hydrogen atoms were assigned idealized coordinates with C–H or O–H distances of 0.95 Å.[20] Due to the extensive water–sodium network (vide infra), hydrogen atoms for OW(3), OW(4), OW(6), OW(7), and OW(8), which are all bridging water molecules, could be assigned idealized locations assuming tetrahedral geometry for the ONa_2H_2 unit. All other water protons were given the coordinates of their associated peaks in the difference Fourier. A value of 0.02 was used for the parameter *p* in the weighting function. Examination of the most intense reflections showed a systematic trend of $F_o < F_c$, indicating secondary extinction. The final least-squares cycle, in which a secondary extinction coefficient was also refined,[21] converged to $R = 1.65$ and $R_w = 2.14\%$ with the extinction coefficient $1.63\ (5) \times 10^{-7}$ e^2. The largest parameter shift was 26% of its associated esd, and the largest positive and negative peaks in the final difference Fourier were 0.30 and −0.41 e/Å^3. The GOF, with 344 variables, was 1.023. Positional parameters are listed in Table IV.

$\{Na[Gd(cat)_2]\cdot 10H_2O\}_n$. The crystal was mounted in a glass capillary under moist argon. Photographic examination showed the crystal to be of good quality. Precession photography showed the crystal to have monoclinic symmetry and systematic absences $hk0$ ($h + k = 2n + 1$) and $h0l$ ($l = 2n + 1$) consistent with space groups *Cc* or *C*2/*c*. The crystal was mounted on an Enraf-Nonius CAD-4 diffractometer for data collection. Crystal data obtained by least-squares fit to 24 high-angle reflections are listed in Table V along with density data. This examination also indicated that the crystal had a small fracture or twin of unknown orientation and thus was not suitable for data collection. Other crystals of good quality were mounted in glass capillaries under moist

---

[19] Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653.

[20] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

[21] The correction for secondary extinction follows the equation $F_c = F_o(1 + gI_c)$, according to: Stout, G. H.; Jensen, L. H. "X-Ray Structure Determination"; Macmillan: New York, 1968; p 412.

Table IV. Positional and Thermal Parameters for the Non-Hydrogen Atoms in $Na_6[Gd(C_6H_4O_2)_3]_2 \cdot 20H_2O$[a]

atom	x	y	z	B_{eq}, Å^2
Gd	0.02610 (1)	0.09519 (1)	−0.07593 (1)	1.411 (2)
Na(1)	−0.2046 (1)	0.26344 (9)	−0.22029 (7)	3.26 (2)
Na(2)	−0.06700 (9)	0.53801 (9)	−0.20899 (7)	3.23 (2)
Na(3)	−0.0040 (1)	0.5526 (1)	−0.39646 (7)	4.05 (3)
OW(1)	−0.0162 (2)	0.2679 (2)	−0.2518 (1)	3.69 (5)
OW(2)	0.1371 (2)	0.1671 (2)	0.1878 (1)	3.64 (4)
OW(3)	−0.1059 (2)	0.3962 (2)	−0.1305 (1)	3.27 (4)
OW(4)	−0.2504 (2)	0.6087 (1)	−0.2063 (1)	2.71 (4)
OW(5)	−0.4872 (2)	0.1882 (2)	−0.2366 (1)	4.43 (5)
OW(6)	0.0706 (2)	0.4527 (2)	−0.2745 (2)	4.19 (5)
OW(7)	−0.1756 (2)	0.5044 (1)	−0.3507 (1)	3.02 (4)
OW(8)	−0.1279 (2)	0.5019 (2)	−0.5272 (1)	3.54 (4)
OW(9)	0.0345 (2)	0.6223 (2)	−0.0808 (1)	4.60 (5)
OW(10)	0.1358 (2)	0.6900 (2)	−0.3661 (1)	4.29 (5)
O(11)	−0.0584 (1)	0.0683 (1)	0.03210 (9)	1.91 (3)
O(12)	−0.1643 (1)	0.1577 (1)	−0.10685 (9)	1.90 (3)
O(21)	0.2100 (1)	0.1219 (1)	0.0151 (1)	2.29 (3)
O(22)	0.0517 (1)	0.2639 (1)	−0.0436 (1)	2.49 (4)
O(31)	−0.0560 (1)	0.0185 (1)	−0.20103 (9)	2.11 (3)
O(32)	0.1367 (1)	0.1294 (1)	−0.1684 (1)	2.46 (3)
C(11)	−0.1420 (2)	0.1351 (2)	0.0329 (1)	1.71 (4)
C(12)	−0.1980 (2)	0.1820 (2)	−0.0406 (1)	1.90 (4)
C(13)	−0.2876 (2)	0.2483 (2)	−0.0420 (2)	2.95 (5)
C(14)	−0.3203 (2)	0.2710 (2)	0.0275 (2)	3.56 (6)
C(15)	−0.2646 (2)	0.2259 (2)	0.0996 (2)	3.14 (5)
C(16)	−0.1754 (2)	0.1583 (2)	0.1021 (1)	2.27 (5)
C(21)	0.2449 (2)	0.2170 (2)	0.0217 (1)	1.94 (4)
C(22)	0.1617 (2)	0.2914 (2)	−0.0090 (1)	2.06 (4)
C(23)	0.1959 (2)	0.3909 (2)	−0.0024 (2)	2.62 (5)
C(24)	0.3111 (2)	0.4168 (2)	0.0345 (2)	2.96 (5)
C(25)	0.3925 (2)	0.3448 (2)	0.0636 (2)	2.84 (5)
C(26)	0.3599 (2)	0.2452 (2)	0.0564 (2)	2.58 (5)
C(31)	0.0153 (2)	0.0100 (2)	−0.2498 (1)	1.95 (4)
C(32)	0.1168 (2)	0.0688 (2)	−0.2325 (1)	2.00 (4)
C(33)	0.1889 (2)	0.0638 (2)	−0.2834 (2)	2.72 (5)
C(34)	0.1642 (2)	0.0000 (2)	−0.3494 (2)	3.34 (6)
C(35)	0.0675 (3)	−0.0581 (2)	−0.3650 (2)	3.26 (6)
C(36)	−0.0078 (2)	−0.0532 (2)	−0.3154 (2)	2.61 (5)

[a] Anisotropically refined atoms are given in the form of B_{eq}, the isotropic equivalent thermal parameter, defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table V. Crystal Data for $\{Na[Gd(C_6H_4O_2)_2]\cdot 10H_2O\}_n$

formula	$\{Na[Gd(C_6H_4O_2)_2]\cdot 10H_2O\}_n$
fw (monomer)	576.58
space gp	Cc or $C2/c$
cell const	
a, Å	16.681 (2)
b, Å	19.325 (3)
c, Å	25.868 (3)
β, deg	94.24 (1)
V, Å^3	8315.93
Z	16
d_{obsd}, g/cm^3	1.84 (2)
d_{calcd}, g/cm^3	1.84

argon, but subsequent photographic examination showed that they crumbled into a powder within a few days and thus were not suitable for data collection. Visual examination indicated that they had not oxidized. The crystals are not severely air sensitive but desolvate and fracture quite readily.

$Na_6[Ho(cat)_3]_2 \cdot 20H_2O$. The crystal was mounted in a glass capillary under moist argon. Photographic examination showed the crystal to be of acceptable quality. Due to the large number of reflections present and the inconvenient orientation of the crystal within the capillary, only one primary zone (b^*c^*) was located. It showed systematic absences $0k0$ ($k = 2n + 1$) and $00l$ ($l = 2n + 1$). From this b^* and c^* were determined directly. The precession photography, via a primary and nonprimary zone, indicated a cell volume of 2651 (8) Å^3. This was sufficient to show that the crystal is isomorphous with $Na_6[Gd(cat)_3]_2 \cdot 20H_2O$. By assuming that β is the same for both the Ho and Gd complexes, the unit cell constants a and c could be calculated. These values and other crystallographic data are listed in Table III with the analogous Gd values.

Table VI. Positional and Thermal Parameters for the Non-Hydrogen Atoms in $Na_4[Hf(C_6H_4O_2)_4]\cdot 21H_2O$[a]

atom	x	y	z	B, Å^2
Hf	0.000	0.000	0.000	1.5931 (9)
Na	0.04317 (7)	−0.18385 (7)	−0.2585 (1)	3.30 (2)
O(1)	−0.0374 (1)	−0.14025 (9)	−0.0631 (1)	2.38 (2)
O(2)	−0.0240 (1)	−0.08510 (8)	0.1821 (1)	2.20 (2)
O(3)	−0.0607 (1)	−0.0943 (1)	−0.3916 (2)	3.76 (3)
O(4)	−0.0281 (2)	−0.3254 (2)	−0.3616 (2)	4.82 (4)
O(5)	0.1329 (2)	−0.2204 (2)	−0.4549 (2)	4.73 (4)
O(6)	0.1665 (2)	−0.2731 (2)	−0.1444 (2)	4.56 (4)
O(7)	−0.2192 (1)	−0.1816 (1)	−0.1493 (2)	4.35 (4)
O(8)	0.000	−0.500	−0.250	5.08 (7)
C(1)	−0.0432 (1)	−0.2064 (1)	0.0315 (2)	2.19 (3)
C(2)	−0.0372 (1)	−0.1758 (1)	0.1652 (2)	2.00 (2)
C(3)	−0.0470 (1)	−0.2392 (1)	0.2697 (2)	2.58 (3)
C(4)	−0.0612 (2)	−0.3323 (1)	0.2406 (2)	3.11 (3)
C(5)	−0.0642 (2)	−0.3624 (1)	0.1090 (3)	3.47 (4)
C(6)	−0.0553 (1)	−0.2997 (1)	0.0030 (6)	3.04 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

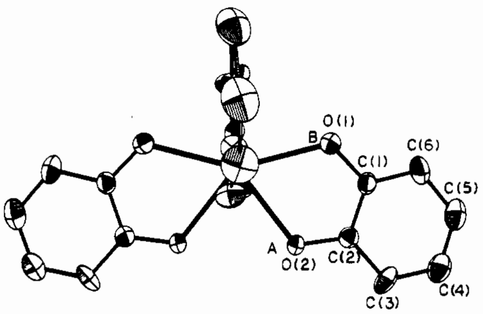

Figure 1. ORTEP drawing of $[Gd(C_6H_4O_2)_4]^{5-}$ and $[Hf(C_6H_4O_2)_4]^{4-}$ viewed along the molecular mirror plane with the $\bar{4}$ axis vertical, showing the crystallographic numbering scheme.

$Na_4[Hf(cat)_4]\cdot 21H_2O$. The raw data for $Na_4[Hf(cat)_4]\cdot 21H_2O$ were retrieved from archival storage. (Neither raw nor processed data could be retrieved for the isostructural Th, U, or Ce structures.) The $Na_4[Hf(cat)_4]\cdot 21H_2O$ data were processed as previously described.[19] No decay was observed. The initial p factor was chosen as 0.04 to duplicate the previous refinement of this structure.[4] As before, a spherical absorption correction was applied: minimum, maximum, and average correction factors (% transmission) were 1.77 (56.5), 1.80 (55.6), and 1.78 (56.1), respectively, for μR of 0.4.[22]

Structure Solution and Refinement. The structural refinement began with the final positional parameters published previously[4] using the opposite sign for the z coordinate of the water oxygen OW(3). After three cycles of least-squares refinement, it became apparent that the y position for carbon C(6) contained a typographical error. The refinement was started over again with a C(6) y position of 0.29 instead of 0.2297. After several cycles of isotropic refinement of all non-hydrogen atoms, a catechol proton was observed on a difference Fourier map. All carbon protons were included with idealized coordinates with C–H distances of 0.95 Å and isotropic thermal factors of $B = 5.0$ Å^2. Full anisotropic refinement of all non-hydrogen atoms converged to $R = 5.13$ and $R_w = 6.67\%$, and GOF was 2.06. Refining the inverse converged to $R = 2.11$ and $R_w = 2.58\%$. All water hydrogens were located and assigned the coordinates of their associated peaks in the difference Fourier. They were assigned thermal factors of $B = 6.0$ or 7.0 Å^2, depending on the thermal motion of their oxygens. Examination of the most intense low-angle reflections showed systematic trends of $F_o < F_c$, indicating secondary extinction. The final least-squares cycle, in which a secondary extinction coefficient was also refined,[21] converged to $R = 1.96$ and $R_w = 2.19\%$, with the secondary extinction coefficient 1.88002×10^{-7} e^2. The largest parameter shift was 3% of its associated esd. The four largest peaks in the final difference Fourier (from 0.544 to 0.338 e/Å^3) were all within 0.73 Å of the metal atom. The GOF, for 132 variables, was 0.787. Crystallographic data from this redetermination are listed in Table I.

---

(22) Kasper, J. S., Lonsdale, K., Eds. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1959; Vol. II, Table 5.3.6B, p 302.

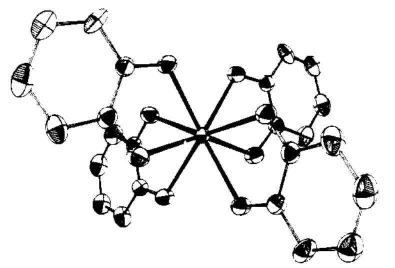

Figure 2. ORTEP drawing of $[Gd(C_6H_4O_2)_4]^{5-}$ and $[Hf(C_6H_4O_2)_4]^{4-}$ viewed down the molecular twofold axis. The $\bar{4}$ axis is vertical.

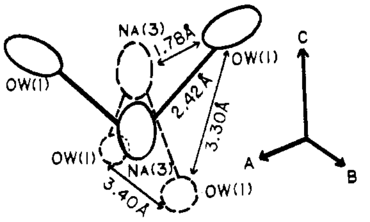

Figure 3. Diagram of the symmetry-related position of Na(3) and OW-(1) and their interatomic distances. The $\bar{4}$ axis runs vertically through the two Na(3) positions. When the disordered sodium atom does not occupy the Na(3) position (62% of the time), there are no excessively close contacts between water molecules and all OW(1) positions are occupied [OW(1) has full occupancy]. When one of the Na(3) positions is occupied, the sodium is too close to its symmetry-related position and to two of the OW(1) positions. When occupied, the sodium positions at any given time are either those marked by the solid line or those marked by the dashed line.

Table VIII. Structural Parameters for $Na_5[Gd(C_6H_4O_2)_4]\cdot19.2H_2O$ and $Na_4[M(C_6H_4O_2)_4]\cdot21H_2O$ (M = Hf, Ce, U, Th)

metal	ionic R,[a] Å	$[(M-O_A)-(M-O_B)]$, Å	O_A-O_A, Å
Gd	1.053	0.029 (3)	2.896 (3)
Hf (redet struct)	0.83	0.029 (1)	2.562 (3)
Hf (prev struct)	0.83	0.026 (4)	2.554 (5)
Ce	0.97	0.005 (5)	2.831 (7)
U	1.00	0.027 (5)	2.883 (7)
Th	1.05	0.004 (5)	2.972 (6)

[a] Reference 11.

Positional parameters are listed in Table VI.

Discussion

$Na_5[Gd(cat)_4]\cdot19.2H_2O$. The gadolinium tetrakis(catecholate) complex is isomorphous with the Th, U, Ce, and Hf tetrakis(catecholate) structures characterized previously.[3,4] Again, the crystal structure consists of discrete, eight-coordinate $[Gd(cat)_4]^{5-}$ dodecahedra, sodium ions and waters of crystallization that are involved in a hydrogen-bonded network throughout the crystal (see Figures 1 and 2). However, the difference in charges for the M(IV) and M(III) complexes obviously requires a corresponding change in counterions. For the Gd complex the fifth sodium ion is disordered over several sites in the cell. The sodium position Na(3) on the crystallographic twofold axis is close to the $\bar{4}$ position (at 0, 0, $^1/_2$), which generates a symmetry-related atom only 1.18 Å away. Each of these two sodium positions is unrealistically close to two of the four symmetry-related positions of OW(1) (see Figure 3). The OW(1) position can only have half-occupancy when the sodium is located in the Na(3) position. When the sodium is located in Na(2) on the crystallographic $\bar{4}$ axis (at 0, $^1/_2$, $^1/_4$) OW(1) has full occupancy. Consequently, the total occupancy of OW(1) is given by the equation % occupancy = 100% − $x/2$ where x is the percentage occupancy of the sodium Na(3). Since x = 38%, OW(1) is present 81% of the time and contributes 3.2 waters (instead of 4) to the structure. The analytical data from elemental analyses and measured density are not sufficient to give more accurate values for the total number of waters present.

Table IX. Selected Bond Distances (Å) in $Na_5[Gd(C_6H_4O_2)_4]\cdot19.2H_2O$ and $Na_4[Hf(C_6H_4O_2)_4]\cdot21H_2O$

atom 1	atom 2	Gd	Hf
M	O(1)	2.393 (2)	2.195 (1)
M	O(2)	2.422 (2)	2.224 (1)
O(1)	C(1)	1.337 (3)	1.348 (2)
O(2)	C(2)	1.341 (3)	1.339 (2)
C(1)	C(2)	1.420 (3)	1.410 (3)
C(2)	C(3)	1.400 (3)	1.397 (3)
C(3)	C(4)	1.397 (4)	1.394 (3)
C(4)	C(5)	1.376 (5)	1.386 (4)
C(5)	C(6)	1.402 (8)	1.401 (7)
C(6)	C(1)	1.404 (3)	1.393 (3)
Na(1)	O(1)	2.341 (2)	2.360 (2)
Na(1)	O(2)	2.485 (2)	2.512 (2)
Na(1)	OW(1)	2.423 (3)	
Na(1)	OW(2)	2.503 (3)	
Na(1)	OW(3)	2.497 (3)	
Na(1)	OW(4)	2.539 (4)	
Na(3)	OW(1)	1.784 (5)	
Na(3)	OW(1)	2.419 (9)	
Na(3)	O(2)	2.843 (10)	
Na(3)	Na(3)	1.178 (23)	
Na(2)	OW(4)	2.819 (3)	
Na	O(3)		2.390 (3)
Na	O(4)		2.515 (3)
Na	O(5)		2.411 (3)
Na	O(6)		2.483 (3)

Table X. Selected Bond Angles (deg) in $Na_5[Gd(C_6H_4O_2)_4]\cdot19.2H_2O$ and $Na_4[Hf(C_6H_4O_2)_4]\cdot21H_2O$

	cat angle,[a] deg	Gd	Hf
O(1)-M-O(2)		68.05 (6)	71.51 (5)
O(1)-M-O(2)	90	79.86 (7)	76.89 (6)
O(1)-M-O(2)	180	141.40 (6)	141.84 (5)
O(1)-M-O(1)	90	93.71 (2)	94.72 (2)
O(1)-M-O(1)	180	150.52 (9)	146.65 (8)
O(2)-M-O(2)	90	129.97 (5)	131.93 (5)
O(2)-M-O(2)	180	73.45 (8)	70.33 (7)
M-O(1)-C(1)		117.28 (15)	118.19 (12)
M-O(2)-C(2)		116.64 (15)	117.61 (12)
O(1)-C(1)-C(2)		118.66 (19)	115.87 (17)
O(1)-C(1)-C(6)		122.1 (4)	123.7 (3)
O(2)-C(2)-C(1)		118.16 (20)	115.88 (17)
O(2)-C(2)-C(3)		122.67 (24)	124.45 (19)
C(1)-C(2)-C(3)		119.17 (22)	119.66 (19)
C(2)-C(3)-C(4)		120.8 (3)	119.66 (22)
C(3)-C(4)-C(5)		119.8 (3)	120.46 (22)
C(4)-C(5)-C(6)		120.7 (3)	120.6 (3)
C(5)-C(6)-C(1)		120.0 (6)	119.1 (5)
C(6)-C(1)-C(2)		119.3 (4)	120.4 (3)

[a] Angle between catechols containing the two oxygens.

The dodecahedral shape parameters[23] for the Gd, Th, U, Ce, and Hf complexes[3,4] are given in Table VII (supplementary material). The experimentally determined differences in metal–oxygen distances are given in Table VIII for the A and B sites of the Hoard and Silverton dodecahedron.[24] Tables IX and X contain selected bond lengths and bond angles, respectively, for this complex. The metal–oxygen bond distance expected from simple ionic radii considerations is 2.403 Å.[11] The Gd–O(2) bond distance is 0.019 Å longer than this value, presumably due to coordination by Na(3). This could also explain the relatively large difference in the gadolinium–oxygen bond distances. Based on their similar ionic radii,[11] the Gd and Th complexes would otherwise be expected to be very similar. Further commentary on the M(IV) tetrakis(catecholates) follows below.

$Na_6[Gd(cat)_3]_2\cdot20H_2O$. The structure of the dimeric tris(catecholate) complex consists of discrete units of $[Gd(cat)_3]_2^{6-}$. Each

---

(23) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

(24) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235.

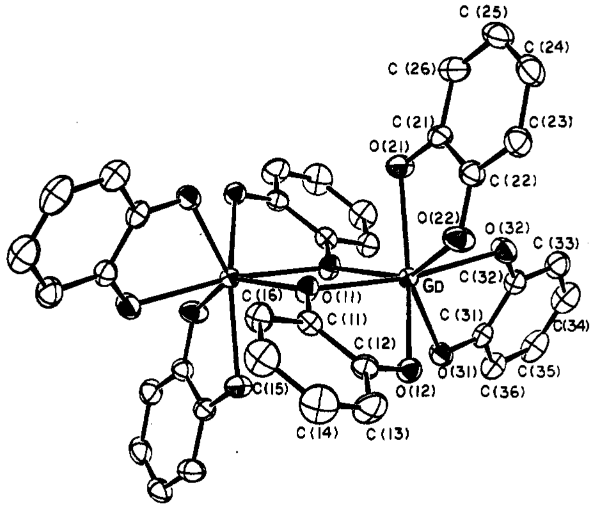

Figure 4. ORTEP drawing of the $[Gd(C_6H_4O_2)_3]_2^{6-}$ molecule that shows the crystallographic numbering scheme.

Table XI. Selected Bond Distances (Å) in $Na_6[Gd(C_6H_4O_2)_3]_2 \cdot 20H_2O$

atom 1	atom 2	dist	atom 1	atom 2	dist
Gd	Gd	3.840 (1)	Na(1)	OW(1)	2.450 (3)
			Na(1)	OW(2)	2.318 (2)
Gd	O(11)	2.372 (2)	Na(1)	OW(3)	2.456 (2)
Gd	O(11)	2.333 (2)	Na(1)	OW(4)	2.429 (2)
Gd	O(12)	2.348 (2)	Na(1)	O(12)	2.367 (2)
Gd	O(21)	2.362 (2)			
Gd	O(22)	2.346 (2)	Na(2)	OW(3)	2.461 (2)
Gd	O(31)	2.361 (2)	Na(2)	OW(4)	2.399 (2)
Gd	O(32)	2.372 (2)	Na(2)	OW(5)	2.397 (2)
			Na(2)	OW(6)	2.508 (3)
O(11)	C(11)	1.348 (3)	Na(2)	OW(7)	2.486 (2)
O(12)	C(12)	1.350 (3)	Na(2)	OW(9)	2.498 (3)
O(21)	C(21)	1.346 (3)			
O(22)	C(22)	1.342 (3)	Na(3)	OW(6)	2.459 (3)
O(31)	C(31)	1.351 (3)	Na(3)	OW(7)	2.469 (2)
O(32)	C(32)	1.346 (3)	Na(3)	OW(8)	2.444 (3)
			Na(3)	OW(8)	2.422 (2)
C(11)	C(12)	1.416 (3)	Na(3)	OW(10)	2.457 (3)
C(21)	C(22)	1.413 (4)			
C(31)	C(32)	1.413 (3)			

gadolinium atom is seven-coordinate via dimer formation through two bridging catecholates. The sodium atoms and 20 waters of crystallization are in infinite bridging chains running diagonally across the unit cell and involve some of the catecholate oxygens (see Figures 4 and 5). These chains lock all of the molecules in place and generate a highly stable crystal structure, which explains the resistance to air oxidation found for this complex in the solid state.

Although several metal dimers with bridging catecholates are known,[15] seven-coordinate lanthanide complexes are relatively uncommon[25] and difficult to parametrize.[23,26] The coordination geometry of the oxygens about the gadolinium (Figure 4) can be viewed as a distorted bicapped trigonal bipyramid or as a distorted capped octahedron. Selected bond lengths and angles for this complex are listed in Tables XI and XII. The Gd–O bond lengths average 2.356 (2) Å, which is a reasonable value, but it is interesting that the shortest distance, 2.333 (2) Å, belongs to the monodentate catecholate–Gd interaction.

$Na_6[Ho(cat)_3]_2 \cdot 20H_2O$. The smaller unit cell constants and higher density for the holmium compound are consistent with the smaller ionic radius and greater atomic weight of holmium. An analogous contraction is found for the series $Na_4[M(cat)_4] \cdot 21H_2O$ (M = Th, U, Ce, Hf).[3,4]

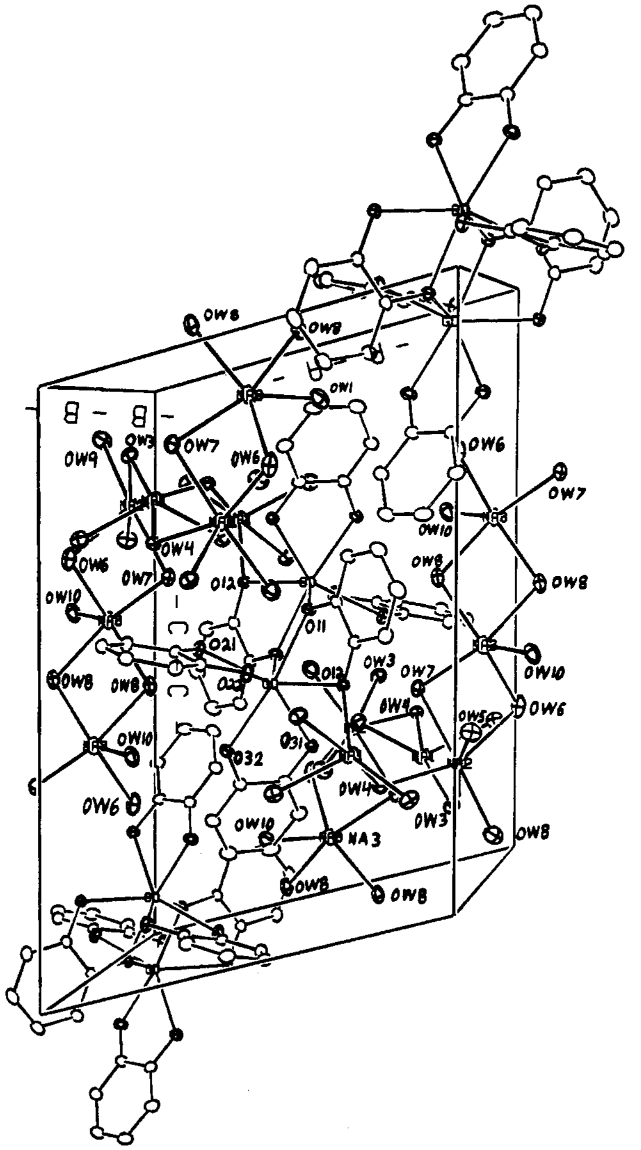

Figure 5. $Na_6[Gd(C_6H_4O_2)_3]_2 \cdot 20H_2O$ packing diagram showing the sodium–water bridging network.

$Na_4[Hf(cat)_4] \cdot 21H_2O$. The basic structure remains the same as it was previously (see Figures 1 and 2), except that the water oxygen OW(3) is now more than 2.7 Å from any other oxygen atom and the sodium atom has a mildly distorted octahedral coordination geometry. Selected bond lengths and angles for the redetermined strucutre are listed in Tables IX and X. The new average Hf–O bond length is 2.200 (1) Å, an increase of 0.003 Å.

Conclusions

Lanthanide Catecholates. The observation that a 1:1 lanthanide:catecholate complex is the only species present at neutral pH[12,13] is supported by other recent studies from these laboratories,[10] which investigated the Pu(III) and Am(III) electrochemistry with various catecholate ligands and found catecholate to metal ratios well below 4:1. Solution chemistry studies[12] with multicatecholate ligands we have developed as actinide(IV) chelating agents[5-7] have shown that only 1.5 catecholate arms are bound per lanthanide(III) at neutral pH.

The chemistry of lanthanide catecholates at high pH is completely different from that at the neutral-pH region. Since catechol is a weak acid, the lanthanides cannot compete effectively with protons at low or neutral pH and the multicatecholate lanthanide species are only observed in the high-pH region. We have characterized several of the species present in this region, but the synthetic chemistry has complications that are still being inves-

---

(25) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 985–6.

(26) Kepert, D. L. *J. Chem. Soc., Dalton Trans.* **1974**, 617.

Table XII. Selected Bond Angles (deg) in $Na_6[Gd(C_6H_4O_2)_3]_2 \cdot 20H_2O$

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Gd	O(11)	C(11)	133.58 (15)	OW(1)	Na(1)	OW(2)	117.81 (9)
Gd	O(11)	C(11)	112.10 (14)	OW(1)	Na(1)	OW(3)	78.94 (8)
Gd	O(12)	C(12)	112.52 (13)	OW(1)	Na(1)	OW(4)	89.64 (8)
Gd	O(21)	C(21)	114.50 (14)	OW(1)	Na(1)	O(12)	101.65 (7)
Gd	O(22)	C(22)	115.14 (15)	OW(2)	Na(1)	OW(3)	107.66 (8)
Gd	O(31)	C(31)	115.48 (14)	OW(2)	Na(1)	OW(4)	87.95 (8)
Gd	O(32)	C(32)	115.30 (14)	OW(2)	Na(1)	O(12)	139.46 (9)
				OW(3)	Na(1)	OW(4)	163.66 (8)
O(11)	C(11)	C(12)	117.62 (20)	OW(3)	Na(1)	O(12)	87.72 (7)
O(12)	C(12)	C(11)	118.37 (20)	OW(4)	Na(1)	O(12)	83.15 (7)
O(21)	C(21)	C(22)	118.38 (21)				
O(22)	C(22)	C(21)	118.48 (22)	OW(3)	Na(2)	OW(4)	89.58 (8)
O(31)	C(31)	C(32)	117.87 (21)	OW(3)	Na(2)	OW(6)	97.63 (8)
O(32)	C(32)	C(31)	117.98 (21)	OW(3)	Na(2)	OW(9)	89.14 (8)
				OW(4)	Na(2)	OW(5)	90.77 (9)
O(11)	C(11)	C(16)	122.76 (22)	OW(4)	Na(2)	OW(7)	81.52 (7)
O(12)	C(12)	C(13)	122.86 (23)	OW(4)	Na(2)	OW(9)	91.77 (8)
O(21)	C(21)	C(26)	122.95 (23)	OW(5)	Na(2)	OW(6)	86.24 (9)
O(22)	C(22)	C(23)	122.13 (23)	OW(5)	Na(2)	OW(7)	83.85 (8)
O(31)	C(31)	C(36)	122.70 (23)	OW(5)	Na(2)	OW(9)	81.00 (9)
O(32)	C(32)	C(33)	123.26 (23)	OW(6)	Na(2)	OW(7)	72.82 (7)
				OW(6)	Na(2)	OW(9)	112.83 (9)
O(11)	Gd	O(11)	70.64 (6)	OW(3)	Na(2)	OW(7)	105.94 (8)
Gd	O(11)	Gd	109.36 (6)	OW(3)	Na(2)	OW(5)	170.14 (9)
O(11)	Gd	O(12)	69.26 (5)	OW(4)	Na(2)	OW(6)	154.34 (9)
O(21)	Gd	O(22)	69.76 (6)	OW(7)	Na(2)	OW(9)	163.35 (9)
O(31)	Gd	O(32)	68.86 (6)				
O(11)	Gd	O(21)	90.82 (6)	OW(5)	Na(3)	OW(6)	75.82 (8)
O(11)	Gd	O(22)	90.96 (6)	OW(5)	Na(3)	OW(7)	73.25 (7)
O(11)	Gd	O(31)	119.50 (6)	OW(5)	Na(3)	OW(8)	138.80 (9)
O(11)	Gd	O(32)	171.15 (6)	OW(5)	Na(3)	OW(8)	140.58 (9)
O(11)	Gd	O(12)	118.73 (6)	OW(5)	Na(3)	OW(10)	61.92 (8)
O(11)	Gd	O(21)	83.39 (6)	OW(6)	Na(3)	OW(7)	73.96 (8)
O(11)	Gd	O(22)	147.37 (6)	OW(6)	Na(3)	OW(8)	128.95 (10)
O(11)	Gd	O(31)	82.75 (6)	OW(6)	Na(3)	OW(8)	99.17 (9)
O(11)	Gd	O(32)	109.22 (6)	OW(6)	Na(3)	OW(10)	99.25 (9)
O(12)	Gd	O(21)	140.12 (6)	OW(7)	Na(3)	OW(8)	82.67 (7)
O(12)	Gd	O(22)	76.20 (6)	OW(7)	Na(3)	OW(8)	143.94 (10)
O(12)	Gd	O(31)	78.98 (6)	OW(7)	Na(3)	OW(10)	134.79 (9)
O(12)	Gd	O(32)	117.04 (6)	OW(8)	Na(3)	OW(8)	74.51 (6)
O(21)	Gd	O(31)	139.63 (6)	OW(8)	Na(3)	OW(10)	128.23 (9)
O(21)	Gd	O(32)	80.42 (6)	OW(8)	Na(3)	OW(10)	80.95 (8)
O(22)	Gd	O(31)	129.80 (6)				
O(22)	Gd	O(32)	84.88 (6)				

tigated. A variety of initial reaction stoichiometries were examined, in addition to those reported here, in order to map out the conditions that yield the different gadolinium products. Although there is no sharp boundary, as expected from mass action $[Gd(cat)_4]^{5-}$ is generally favored by large amounts of base and $[Gd(cat)_2]_n^{n-}$ by low catechol:Gd ratios. The formation of the compound $Na_6[Gd(cat)_3]_2 \cdot 20H_2O$ was variable: although a 3:1 catecholate:lanthanide complex is the predominant species in millimolar solutions at pH 12,[12] most reaction conditions in this study yielded either $Na_5[Gd(cat)_4]$ or $Na[Gd(cat)_2]$, both of which are *more* soluble than the tris(catecholate)Gd complex. However, the holmium analogue is readily synthesized under conditions that, for gadolinium, yield the latter two compounds. These species must be in equilibrium as

$$2[Ln(cat)_3]_2^{6-} = [Ln(cat)_2^-]_n + 2[Ln(cat)_4^{5-}]$$

where *n* is assumed to be 2. This equilibrium appears to be in a delicate balance, with solubility and crystallization rates determining the isolated product. The stability of these complexes in solution is significantly less than the M(IV) analogues.

In conclusion, we have found that lanthanide(III) catecholates have a complex aqueous coordination chemistry. Complete encapsulation of these metal ions at near-neutral pH can only be accomplished via more acidic chelating groups than catechol.

$Na_4[M(cat)_4] \cdot 21H_2O$. Although it was the unreasonably short oxygen–oxygen distance that first indicated an error in these four structures, our published thorium structure contains a suspiciously large 2.6 e/Å^3 peak in the final difference Fourier; inspection of the catecholate ring showed an unusually long C(5)–C(6) distance and a large variation in C–C–C angles.

Refinement with the water OW(3) in the correct position results in an improved structure with acceptable oxygen–oxygen distances and catecholate ring parameters. The Hf–O bond distances both increased a small amount, and the difference between them (Table VIII) increased by 0.003 Å to 0.029 Å, resulting in an increase of the O(2)–O(2) distance by 0.008 Å. If the uranium tetrakis(catecholate) structures shows analogous changes, then this alone would not affect the proposal of a ligand field effect. Furthermore, even the larger Hf–O bond distance change of 0.004 (3) Å would not be sufficient to remove the 0.027 (5) Å difference in U–O bond distances. It is interesting to note that the sodium tetrakis(catecholato)gadolinate(III) structure shows a comparable M–O bond distance difference of 0.029 (3) Å which, for the f^7 lanthanide, cannot be attributed either to a ligand field effect or to interligand repulsion. However, this difference can be attributed to the lengthening affect of the coordination of the fifth sodium Na(3), to the ligand oxygen O(2).

The previous and revised dodecahedral shape parameters for these complexes and for the gadolinium complex are given in Table VII. The experimentally determined differences in metal–oxygen distances are given in Table VIII for the A and B sites of the Hoard and Silverton dodecahedron.

Acknowledgment. We gratefully acknowledge the assistance of B. A. Borgias in the X-ray diffraction studies of $Na_6[Gd(cat)_3]_2 \cdot 20H_2O$ and Dr. F. J. Hollander of the U.C. Berkeley X-ray Diffraction Facility (CHEXRAY) for assistance in the other diffraction studies. The CHEXRAY facility was partially funded by NSF Grant No. CHE-79-07027. We also thank Dr. Robert S. McDowell for experimental assistance. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy, under Contract Number DE-AC03-76SF00098.

Registry No. $Na_5[Gd(cat)_4]\cdot 19.2H_2O$, 95531-51-4; $Na_6[Gd(cat)_3]_2\cdot 20H_2O$, 95531-52-5; $Na[Gd(cat)_2]\cdot 10H_2O$, 95531-53-6; $Na_6[Ho(cat)_3]_2\cdot 20H_2O$, 95531-54-7; $Na_4[HF(cat)_4]\cdot 21H_2O$, 69855-29-4.

Supplementary Material Available: Listings of shape parameters, anisotropic thermal parameters, hydrogen atom positions, and observed and calculated structure factors (Tables VII and XIII–XXI) for $Na_5[Gd(cat)_4]\cdot 19.2H_2O$ and $Na_4[M(cat)_4]\cdot 21H_2O$ (M = Hf, Ce, U, Th (72 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Department of Chemistry,
Louisiana State University, Baton Rouge, Louisiana 70803

Quenching of Photosubstitution in Ruthenium Polypyridine Complexes

Mario Ollino and William R. Cherry*

Received May 7, 1984

The photochemical behavior of ruthenium polypyridine complexes has become a topic of intense interest.[1] Extensive investigations of the photophysical properties of tris(bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, has led to the model shown in Figure 1.[2] In this model, the triplet metal-to-ligand charge-transfer state (^{3}MLCT) is populated with unit quantum efficiency. Once formed, the ^{3}MLCT undergoes three decay processes: radiative decay (k_r), radiationless decay (k_{nr}), and thermal population of a higher excited state ($k_0e^{-\Delta E/RT}$). This higher excited state has been identified as a ligand field state (LF) on the basis of the facts that it undergoes efficient radationless decay, is not luminescent, and results in a low-yield photosubstitution reaction.

Recently, the quenchings of both the luminescence and photosubstitution reaction have been investigated.[4] The specific system examined was $Ru(bpy)_3^{2+}$ in dimethylformamide (DMF) with 0.1 M tetrabutylammonium bromide present. The quencher selected was ferrocene. The resulting two linear Stern–Volmer plots were found to have substantially different slopes. In fact, the slope for the quenching of the photosubstitution was found to be 3-fold larger than the slope for the luminescence quenching. These results suggest that the ^{3}MLCT and LF states are not in thermal equilibrium. Furthermore, the lifetime of the LF states appears to be much longer than the ^{3}MLCT state.

These conclusions did not agree with some related results obtained in our laboratory so we decided to investigate the equivalent chloride system. The corresponding Stern–Volmer plots for the ferrocene quenching of both the luminescent lifetime and photosubstitution reaction of $Ru(bpy)_3Cl_2$ in DMF (0.1 M tetrabutylammonium chloride) are shown in Figure 2. The lifetime quenching plot yields a slope of 3070 ± 600 M^{-1}. The quenching rate constant is then evaluated as 4.0×10^9 L/(mol s), in good agreement with 5.9×10^9 L/(mol s) reported for the quenching in ethanol by Wrighton et al.[5] Evaluating the slope for quenching of the substitution process was much more difficult. The ferrocene absorbed a substantial fraction of the incident radiation, and itself undergoes a photoreaction.[4] Considering these difficulties, the difference in these two slopes (3070 ± 600 M^{-1} (τ_0/τ) vs. 1780 ± 700 M^{-1} (ϕ_0/ϕ)) is probably not significant, and in any case the trend is in contrast to the previous result in which the emission quenching had the smaller slope.

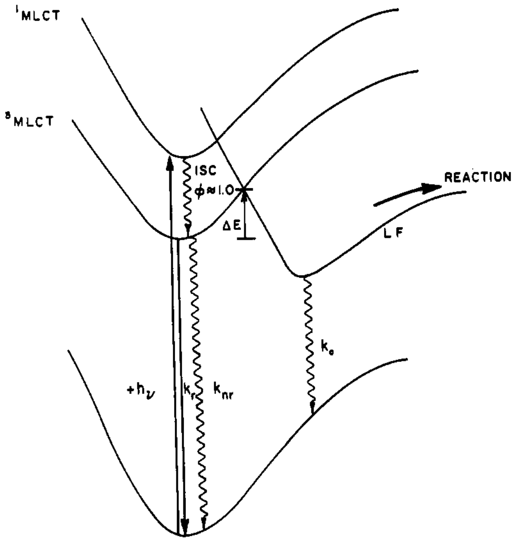

Figure 1. Photophysical processes of $Ru(bpy)_3^{2+}$.

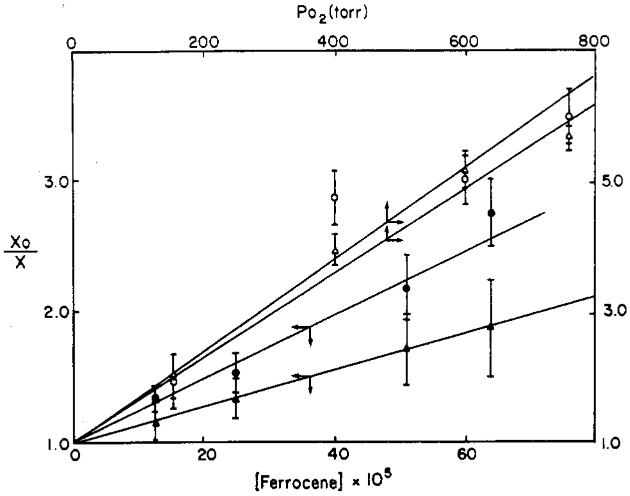

Figure 2. Stern-Volmer plots for the quenching of $Ru(bpy)_3^{2+}$ emission (triangles) and photosubstitution (circles) by ferrocene (solid) and oxygen (open). The progress of photosubstitution was monitored by the disappearance of $Ru(bpy)_3^{2+}$.

In order to avoid the problems associated with using ferrocene as a quencher, the quenchings of both the luminescence and photosubstitution by oxygen have been investigated. Oxygen is a good quencher but does not absorb any incident radiation. The same system ($Ru(bpy)_3^{2+}$ + Cl^-) in CH_3CN has been investigated.

---

(1) The important references are too numerous to list here but the interested reader is referred to the following reviews: Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834. Seddon, K. R. *Coord. Chem. Rev.* **1982**, *41*, 79. Kalyanasundarau, K. *Coord. Chem. Rev.* **1982**, *41*, 159. Ford, P. C. *Rev. Chem. Intermed.* **1979**, *2*, 267. Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. Balzani, V.; Boletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.

(2) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 3843; **1976**, *98*, 4853. Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583. Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803.

(3) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 3722. Bolleta, F.; Juris, A.; Maestri, M.; Sandrini, D. *Inorg. Chim. Acta* **1980**, *44*, L175.

(4) Fasano, R.; Hoggard, P. E. *Inorg. Chem.* **1983**, *22*, 566.

(5) Wrighton, M. S.; Pdungsap, L.; Morse, D. L. *J. Phys. Chem.* **1975**, *79*, 66.

0020-1669/85/1324-1417$01.50/0 © 1985 American Chemical Society