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The Structure and Properties of Tetrakis(tironato)cerate(IV), $Na_{12}[Ce(C_6H_2O_2(SO_3)_2)_4]\cdot9H_2O\cdot6C_3H_7NO$

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Abstract

The title complex, prepared in 1 M NaOH, was crystallized from hot *N,N*-dimethylformamide/ethanol solutions to give $Na_{12}[Ce(C_6H_2O_2(SO_3)_2)_4]\cdot9H_2O\cdot6DMF$. The purple–brown crystals were examined by X-ray diffraction while inside quartz capillaries filled with DMF, (λ_{max} 425 nm, ϵ 3664; λ_{sh} 520 nm, ϵ 2240) and belong to space group *Pbca*, $Z = 8$ with $a = 21.846(4)$, $b = 17.348(2)$, $c = 43.103(6)$ Å, $V = 16.335(7)$ Å^3, $D_c = 1.693$ g cm^{-3}, $D_o = 1.725$ g cm^{-3}. Diffractometer data were collected using Mo Kα radiation to $2\theta = 43°$. For 7331 independent data with $F_o^2 > 3\sigma(F_o^2)$ full matrix least squares refinement converged to unweighted and weighted R factors of 0.072 and 0.110, respectively, with a mixture of anisotropic and isotropic thermal parameters. The disordered DMF atom parameters were not refined. The structure consists of discrete monomeric $Ce(C_6H_2S_2O_8)_4^{12-}$ units with 12 Na^+ counter cations and 10 H_2O molecules (two with half occupancy), and 6 DMF molecules of solvation filling up spaces between cations and anions. Cerium(IV) is in a general position with a coordination polyhedron close to the trigonal-faced dodecahedron, D_{2d}, with the angles between the two BAAB trapezoids of 2.3° and 3.7°. The average Ce–O(A) distance, 2.363(9) Å is longer than the average Ce–O(B) distance, 2.326(15) Å, with the reverse being true for one of the four tironato ligands. The average ring O–Ce–O angle is 67.9(1)°. The cerium(IV) complex is found by cyclic voltammetry to undergo a quasi-reversible one-electron reduction (in strongly basic solution with excess tiron) with $E_f = -497$ mV *vs.* SCE, hence the ratio of the formation constants for tetrakis(tironato)cerate(IV) to that for tetrakis(tironato)cerate(III), K_{IV}/K_{III}, is 10^{33}. Characterization of other tiron salts is reported.

Introduction

Catecholates, including sulfonated catecholates, have been considered as specific sequestering agents for the actinides [1]. Based on the similarities of Pu(IV) and Fe(III), the naturally-occurring Fe(III) sequestering agents produced by microbes, siderophores, were taken as models for synthesizing Pu(IV) sequestering agents. The siderophore enterobactin contains catechoylamide functional groups that form a hexadentate cavity for Fe(III). Octadentate macrocyclic ligands containing catechoylamide functional groups have been prepared and tested for the removal of Pu(IV) from rat body tissue and skeleton [2, 3]. Sulfonation of these macrocyclic catechoylamide ligands improves the water solubility, stability to air oxidation and affinity to Pu(IV) at low pH. The linear catechoylamide sulfonate, 3,4,3-LICAMS [*N,N',N'''*-tetra(2,3-dihydroxy-5-sulfobenzoyl)-1,5,10,14-tetraazatetradecane] was initially screened for Pu(IV) removal from dogs and mice [4–6]. The structure of such complexing agents can be optimized to allow the four catecholate functional groups to encapsulate the tetravalant actinide. In order to establish the shape and dimensions of the cavity into which the tetravalent actinide could be trapped, a series of isostructural tetrakis(catecholato) complexes with the general stoichiometry $Na_4[M(C_6H_4O_2)_4]\cdot21H_2O$ (M = Th, U, Ce, Hf) have been structurally characterized by X-ray diffraction [7, 8]. The preferred eight-coordinate polyhedron has been found to be a dodecahedron, D_{2d}, with a radius near 2.4 Å. The preferred coordination polyhedron for free sulfonated catechol ligand with M(IV), analogous to that in tetrakis(catecholato) complexes, has not been established. With this end in view we undertook the preparation and structural determination of the sulfonated catechol complex with cerium(IV), $Ce[C_6H_2O_2(SO_3)_2]_4^{12-}$.

Experimental

Preparation of $Na_{12}[Ce(C_6H_2S_2O_8)_4]\cdot9H_2O\cdot6C_3H_7NO$

Addition of Ce(IV) to disodium 4,5-dihydroxy-*m*-benzenedisulfonate monohydrate, $Na_2C_6H_4S_2O_8\cdot H_2O$ (commercial name 'Tiron') in basic medium gives a purple–brown solution. Continuous variation

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plot of absorbance at λ_{max} *vs.* mole fraction Ce(IV) establishes that the color is due to a Ce(IV)/Tiron adduct in the ratio of 1/4. The compound $Na_{12}[Ce(C_6H_2S_2O_8)_4]\cdot xH_2O$ is prepared as a paste by heating on a steam bath for 1 h 0.1 mmol of recrystallized [9] ammonium hexanitratocerate(IV), $(NH_4)_2[Ce(NO_3)_6]$, and 0.4 mmol of Tiron dissolved in 10 ml of oxygen free 1 M NaOH. Oxygen is excluded to minimize decomposition of the sulfonated catechol ligand in basic medium. The Na^+ salt can be salted out only as a paste by addition of ethanol. The complex anion $[Ce(C_6H_2S_2O_8)_4]^{12-}$ has a very high electrical charge which produces a strong affinity for water. Attempts to prepare less soluble salts of the complex anion by using larger cations than Na^+, or cations that provide hydrogen bonding (e.g. K^+, NH_4^+, $[(C_2H_5)_4N]^+$, $[(C_4H_9)_4N]^+$, $[C(en)_3]^{3+}$) failed to produce a crystalline product. Addition of Ba^{2+} to solutions containing the complex anion yielded a white crystalline precipitate that analyzed as barium tironate dihydrate, $BaC_2H_4S_2O_8\cdot 2H_2O$. Successful crystallization of the sodium salt of $[Ce(C_6H_2S_2O_8)_4]^{12-}$ was achieved by precipitating the salt from hot *N,N*-dimethylformamide (DMF) with ethanol. The resultant paste was washed twice with 10 ml increments of ethanol and dissolved in 5 ml of water. This solution was filtered and 30 ml of DMF added. Dark purple–brown crystals with approximate octahedral morphology separated after most of the water evaporated in a vacuum oven set at 60 °C after one day. The crystals were filtered quickly, washed on the frit with a small portion DMF, placed in the vacuum oven at 60 °C for 10 min and stored in a sealed container. The crystals although air stable, are extremely hygroscopic and are best handled underneath DMF. *Anal.* Calc. for $Na_{12}[Ce(C_6H_2S_2O_8)_4]\cdot 9H_2O\cdot 6C_3H_7NO$: C, 24.24; H, 3.29; N, 4.04; S, 12.32. Found: C, 24.44; H, 3.22; N, 4.34; S, 12.43%.

Infrared spectra were recorded on a Perkin-Elmer 238 spectrophotometer as KBr pellets, visible spectra in aqueous media on a Varian-Cary 118 spectrophotometer, and ^1H NMR spectra on a Varian T 60-A spectrophotometer. Cyclic voltammetric examinations were performed under argon using a three electrode configuration: a hanging mercury drop working electrode, a platinum wire auxiliary electrode, and a saturated calomal reference electrode. The medium was 5 M NaOH, 1 M ligand, and 0.05 M cerium(III) oxalate. Microanalyses were performed by the Microanalytical Laboratory, University of California, Berkeley.

Unit Cell and Diffraction Data

Crystals of the title compound, opaque purple–brown in color and approximately octahedral in shape, were inserted while under dry DMF in quartz capillaries filled with DMF and the capillaries were sealed with a microtorch. Weissenberg and precession photographs revealed mmm Laue symmetry. The systematic absences $0kl, k \neq 2n; h0l, l \neq 2n; hk0, h \neq 2n$ and consistent uniquely with the orthohombic space group *Pbca*. Crystal data obtained by a least-squares fit of 25 high-angle reflections recorded by a Nonius CAD-4 automated four-circle diffractometer [8] are listed in Table I*.

TABLE I. Crystal Data for $Na_{12}[Ce(C_6H_2S_2O_8)_4]\cdot 9H_2O\cdot 6C_3H_7NO$

Formula weight	2081.53
Crystallographic system	orthorhombic
Space group	*Pbca* (D_{2h}^{15}) (#61)
Cell constants[a]	
a (Å)	21.846(4)[b]
b (Å)	17.348(2)
c (Å)	43.103(6)
Volume ($Å^3$)	16335(7)
Formula units per cell	8
Calculated density (g cm^{-3})	1.693
Observed density[c] (g cm^{-3})	1.725
λ(Mo Kα_1) (Å)	0.70930
λ(Mo Kα) (cm^{-1})	9.337
Crystal shape	approximate octahedron 0.50 mm vertex to vertex
μR	0.23

[a] Ambient temperature of 25 °C. [b] The standard deviation of the least significant figures are given here and elsewhere in parentheses. [c] Measured by flotation in dimethylformamide and dibromomethane.

The best diffraction data were obtained from a crystal of approximately octahedral morphology inserted in a DMF filled quartz capillary with the spindle along the $\bar{1}0\bar{2}$ direction. The intensity data

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*The crystal dimensions were 0.26 mm between 112 and $\bar{1}\bar{1}\bar{2}$, 0.25 mm between $\bar{1}1\bar{2}$ and $1\bar{1}2$, and 0.28 mm between $1\bar{1}\bar{2}$ and $\bar{1}12$, and 0.30 mm between $11\bar{2}$ and $\bar{1}\bar{1}2$. In addition to the eight faces mentioned a tiny 010 face was apparent. The intensities of 10656 reflections corresponding to one equivalent set of *h, k, l* with $3° < 2\theta < 43°$ were measured employing the ω scan technique of the automated CAD-4 diffractometer using graphite monochromatized Mo Kα radiation (λ(Mo Kα_1) = 0.70930 Å). The ω scan technique was chosen in preference to the $\theta - 2\theta$ technique to improve peak resolution as well as peak/background ratios. For each reflection the scan angle was extended 25% on either side to estimate the background count. The scan time was variable, with a maximum of 40 s. The orientation was checked every 200 reflections and there was less than 0.1% change in the setting angles. The intensity of three standard reflections were measured every 6000 s of X-ray exposure and showed no significant decay. A Zirconium attenuator decreasing the intensity of the diffracted beam by a factor of 18.17 was automatically inserted into the beam when the prescan indicated an intensity too high for accurate counting.

TABLE II. Positional and Thermal Parameters ($\times 10^4$) for the Non-hydrogen Atoms that were Refined Anisotropically

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ce	0.02870(3)	0.18774(4)	0.13844(2)	7.1(1)	10.8(2)	1.9(0)	1.0(4)	0.7(1)	−1.1(2)
S1A[b]	−0.0121(2)	0.4439(2)	0.20473(8)	18.8(9)	13.0(1)	2.6(2)	3.0(2)	−0.1(7)	1.2(8)
S2A	0.0110(2)	0.2490(2)	0.30399(8)	16.0(9)	23.0(1)	2.1(2)	0.0(2)	0.0(7)	−1.2(9)
S1B	−0.0217(2)	0.4485(2)	0.08054(9)	16.7(8)	13.0(1)	3.8(2)	7.0(2)	−2.6(8)	−2.0(8)
S2B	0.0205(2)	0.2856(2)	−0.02515(8)	19.2(9)	21.0(1)	2.4(2)	0.0(2)	−1.7(7)	2.2(8)
S1C	0.1545(2)	−0.0723(2)	0.12232(9)	9.9(7)	11.0(1)	5.8(2)	−1.0(2)	0.2(8)	−0.7(9)
S2C	0.3530(2)	0.1191(2)	0.12797(9)	6.7(7)	20.0(1)	6.1(3)	1.0(2)	0.7(7)	−2.0(1)
S1D	−0.0917(2)	−0.0681(2)	0.10707(8)	11.5(8)	16.0(1)	3.9(2)	−7.0(2)	−1.7(7)	−0.5(9)
S2D	−0.2899(2)	0.1299(3)	0.10653(10)	9.1(8)	39.0(2)	6.5(3)	0.0(2)	−2.2(9)	6.0(1)
Na1	0.0379(2)	0.0362(3)	0.0849(1)	15.0(1)	16.0(2)	3.4(3)	−3.0(3)	1.0(1)	−3.0(1)
Na2	−0.0728(2)	0.3429(3)	0.1416(1)	14.0(1)	19.0(2)	4.5(3)	4.0(3)	1.0(1)	3.0(1)
Na3	−0.0971(3)	0.0871(3)	0.3037(1)	23.0(2)	29.0(2)	5.9(4)	−1.0(3)	−1.0(1)	0.0(2)
Na4	0.0228(3)	−0.0393(3)	0.1569(1)	14.0(1)	31.0(2)	4.2(3)	1.0(3)	−2.0(1)	−3.0(2)
Na5	0.0756(3)	0.4134(3)	0.1414(1)	16.0(1)	27.0(2)	4.9(4)	4.0(3)	1.0(1)	0.0(2)
Na6	0.1330(3)	0.2274(4)	−0.0620(1)	22.0(2)	31.0(2)	4.4(4)	−2.0(3)	1.0(1)	−3.0(2)
Na7	−0.1278(3)	0.5686(4)	0.0529(2)	24.0(2)	38.0(3)	16.8(8)	7.0(4)	8.0(2)	16.0(3)
Na8	−0.1323(3)	0.2909(4)	0.3226(2)	32.0(2)	23.0(2)	9.5(5)	−5.0(4)	9.0(2)	−2.0(2)
Na9	−0.1152(3)	0.5215(4)	0.1479(2)	25.0(2)	36.0(3)	7.1(5)	9.0(4)	−6.0(2)	6.0(2)
Na10	−0.1355(3)	−0.2097(4)	0.1448(2)	25.0(2)	44.0(3)	7.4(5)	−10.0(4)	−2.0(2)	7.0(2)
Na11	−0.0672(4)	0.4291(4)	−0.0617(2)	36.0(2)	44.0(3)	10.0(6)	−22.0(4)	−14.0(2)	12.0(2)
Na12	−0.0427(3)	0.1425(4)	−0.0671(2)	21.0(2)	32.0(2)	7.2(4)	−9.0(3)	−1.0(1)	−9.0(2)
O1A	0.0304(4)	0.1602(5)	0.1907(2)	22.0(2)	14.0(3)	2.4(5)	−2.0(5)	2.0(2)	−3.0(2)
O2A	0.0201(4)	0.3007(5)	0.1695(2)	15.0(2)	17.0(3)	1.7(5)	2.0(5)	2.0(2)	0.0(2)
O3A	0.0448(5)	0.4688(6)	0.1902(3)	20.0(3)	21.0(4)	7.3(8)	−7.0(5)	7.0(2)	7.0(3)
O4A	−0.0603(5)	0.4342(5)	0.1815(2)	31.0(3)	17.0(3)	4.1(6)	12.0(6)	−8.0(2)	−1.0(3)
O5A	−0.0302(5)	0.4942(5)	0.2299(2)	29.0(3)	16.0(3)	3.3(6)	15.0(6)	0.0(2)	−5.0(2)
O6A	−0.0168(5)	0.1729(6)	0.3092(2)	29.0(3)	30.0(4)	3.6(6)	−24.0(6)	0.0(2)	3.0(3)
O7A	0.0753(4)	0.2484(6)	0.3131(2)	16.0(2)	37.0(4)	3.5(6)	−2.0(6)	−4.0(2)	−1.0(3)
O8A	−0.0234(5)	0.3103(6)	0.3188(2)	21.0(3)	36.0(4)	2.6(5)	18.0(6)	2.0(2)	−4.0(3)
O1B	0.0371(4)	0.1686(5)	0.0842(2)	23.0(2)	11.0(3)	2.1(5)	19.0(5)	2.0(2)	2.0(2)
O2B	0.0193(4)	0.3030(5)	0.1105(2)	15.0(2)	16.0(3)	1.8(4)	3.0(5)	−2.0(2)	−3.0(2)
O3B	−0.0722(4)	0.4322(6)	0.1013(2)	14.0(2)	26.0(4)	5.8(7)	12.0(5)	4.0(2)	2.0(3)
O4B	−0.0370(5)	0.5032(5)	0.0566(2)	25.0(3)	15.0(3)	5.0(6)	11.0(5)	−4.0(2)	1.0(3)
O5B	0.0326(5)	0.4746(6)	0.0980(2)	21.0(3)	22.0(4)	4.8(6)	−7.0(6)	−4.0(2)	−2.0(3)
O6B	0.0769(5)	0.3267(6)	−0.0330(2)	27.0(3)	28.0(4)	5.9(7)	−3.0(6)	9.0(3)	3.0(3)
O7B	−0.0334(5)	0.3231(7)	−0.0367(2)	28.0(3)	45.0(5)	3.7(6)	7.0(7)	−3.0(2)	6.0(3)
O8B	0.0255(5)	0.2065(6)	−0.0341(2)	32.0(3)	24.0(4)	2.6(5)	−2.0(6)	0.0(2)	2.0(2)
O1C	0.1323(4)	0.2135(5)	0.1404(2)	9.0(2)	10.0(3)	5.0(6)	4.0(4)	0.0(2)	−3.0(2)
O2C	0.0877(3)	0.0744(4)	0.1350(2)	6.0(2)	12.0(3)	2.4(5)	−1.0(4)	0.0(2)	2.0(2)
O3C	0.1094(4)	−0.0641(5)	0.0976(3)	14.0(2)	17.0(3)	8.8(8)	5.0(5)	−11.0(2)	−5.0(3)

(Continued)

TABLE II. *(continued)*

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O4C	0.2041(4)	−0.1254(5)	0.1151(3)	11.0(2)	18.0(3)	8.6(8)	2.0(5)	−3.0(2)	−6.0(3)
O5C	0.1244(5)	−0.0930(6)	0.1506(2)	23.0(3)	19.0(4)	7.1(7)	−4.0(5)	11.0(2)	5.0(3)
O6C	0.3647(5)	0.1870(7)	0.1468(3)	11.0(2)	45.0(5)	17.0(1)	4.0(6)	−4.0(3)	−34.0(4)
O7C	0.3813(4)	0.0516(6)	0.1416(2)	11.0(2)	36.0(4)	6.3(7)	15.0(5)	2.0(2)	8.0(3)
O8C	0.3704(5)	0.1305(7)	0.0960(3)	15.0(3)	59.0(5)	6.8(8)	9.0(7)	5.0(2)	18.0(3)
O1D	−0.0761(4)	0.2116(5)	0.1388(2)	11.0(2)	11.0(3)	7.4(7)	−1.0(4)	0.0(2)	−7.0(3)
O2D	−0.0291(4)	0.0736(5)	0.1302(2)	8.0(2)	14.0(3)	3.5(5)	4.0(4)	−1.0(2)	−1.0(2)
O3D	−0.0695(5)	−0.0956(5)	0.1367(2)	20.0(2)	21.0(3)	4.1(6)	−6.0(5)	−5.0(2)	6.0(3)
O4D	−0.1399(4)	−0.1189(5)	0.0946(2)	15.0(2)	19.0(3)	5.5(7)	−11.0(5)	−4.0(2)	−4.0(3)
O5D	−0.0416(4)	−0.0573(6)	0.0852(2)	12.0(2)	27.0(4)	5.3(6)	−4.0(5)	7.0(2)	−5.0(3)
O6D	−0.3100(6)	0.1742(10)	0.1336(3)	25.0(3)	140.0(9)	8.6(9)	77.0(8)	−3.0(3)	−37.0(5)
O7D	−0.2956(5)	0.1740(8)	0.0785(3)	17.0(3)	71.0(6)	6.7(8)	10.0(7)	−3.0(3)	18.0(4)
O8D	−0.3213(5)	0.0591(7)	0.1056(3)	13.0(2)	34.0(5)	16.0(1)	−8.0(6)	−12.0(3)	8.0(4)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The letter designation refers to the appropriate tironate ligand.

were reduced to F^2 and $=(F^2)^*$ but no absorption correction was applied, since μR is only 0.23 and azimuthal scans revealed little variation due to absorption. A p-factor of 0.04 was chosen to prevent overweighting the strong reflections [10].

Solution and Refinement of the Structure

The positions of all non-hydrogen atoms were obtained routinely by heavy atom techniques. The location and refinement of the solvent molecules, however, proved to be difficult. It was apparent that the carbon atoms of the DMF molecules are disordered. Attempts to assign an equally occupied two-position model were not successful. The problem was by-passed by treating the carbon atoms of DMF as fixed atoms. The assigned coordinates were obtained from a difference Fourier map phased by all other non-hydrogen atoms in the structure. An isotropic thermal parameter of 15 Å^2 was assigned to each carbon atom in DMF, estimated from the B_{iso} for oxygen of DMF (10.8) and of nitrogen (12.8 Å^2). This gave a final $R = 0.0719$, $R_w = 0.1096$ and an error in an observation of unit weight = 3.4 [10] for the 7331 reflections $[(F_o{}^2 > 3\sigma(F_o{}^2)]$ refined**.

The largest peak in the final difference Fourier map (0.92 e Å^{-3}) corresponds to a hydrogen of water O2. The second largest peak (0.85 e Å^{-3}) is a ripple near cerium. Tables II and III give the positional and thermal parameters for the anisotropically refined and for the isotropically refined atoms, respectively. Table IV gives the assigned positional and thermal parameters for the fixed carbon atoms of DMF.

Results and Discussion

Physical Studies

The absorption spectrum of the purple–brown tetrakis(tironato)cerate(IV) complex anion, $[\mathrm{Ce}(\mathrm{C_6H_2S_2O_8})_4]^{12-}$ (Fig. 1) exhibits a maximum at 425 nm (ϵ 3664) and a shoulder at ~520 nm (ϵ ~ 2240). The intensity of the color is greater than for the analogous deep red complex of Ce(IV) with catechol,

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*Data reduction and structure solution and refinement were performed on the Lawrence Berkeley Laboratory CDC 7600 computer. The following programs or modifications were used: Zalkin's FORDAP Fourier program, Ibers' NUCLS, a group least-squares version of the Busing-Levy ORFLS program; ORFFE, a function and error program by Busing and Levy; Johnsons's ORTEP, a thermal ellipsoid plot program. See ref. 10 for further experimental details.

**The discrepancy indicators are $R = \Sigma||F_o| - |F_c||/\Sigma F_o$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$ where $w = 4F_o{}^2/[\sigma(F_o{}^2)]^2$. The error in an observation of unit weight is defined as $[\Sigma w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o is the number of observations and n_v is the number of variables and $w = 4F_o{}^2/[\sigma(F_o{}^2)]^2$.

TABLE III. Positional and Isotropic Temperature Factors for the Non-hydrogen Atoms that were Refined Isotropically

Atom	x	y	z	B (Å^2)
OH201	−0.1779(6)	0.3970(8)	0.1420(3)	6.3(3)
OH202	0.1691(8)	0.3563(10)	0.1347(4)	9.4(5)
OH203	−0.1263(6)	0.5913(7)	0.1962(3)	6.0(3)
OH204	−0.0393(6)	0.2225(8)	−0.1119(3)	6.1(3)
OH205	0.0736(6)	0.2747(8)	−0.1052(3)	6.1(3)
OH206	−0.1404(8)	0.2186(10)	−0.0631(4)	9.7(5)
OH207	0.0151(6)	0.0136(8)	0.2050(3)	6.0(3)
OH208	−0.0261(5)	0.5946(6)	0.1369(2)	3.7(2)
OH209[a]	−0.1191(12)	0.5121(16)	−0.0305(6)	6.8(7)
OH2010[a]	−0.2340(14)	0.3334(17)	0.3104(7)	7.6(8)
ODMF1	−0.1834(10)	−0.1955(12)	0.0141(5)	10.2(6)
ODMF2	−0.0603(8)	0.0180(11)	−0.0347(4)	6.3(5)
ODMF3	−0.1701(10)	0.4661(12)	0.0253(5)	13.2(6)
ODMF4	−0.2083(10)	−0.1224(13)	0.1692(5)	9.3(6)
ODMF5	−0.1468(10)	0.2065(12)	0.2788(5)	13.3(6)
ODMF6	−0.3179(10)	0.5303(12)	0.2837(5)	12.3(6)
NDMF1	−0.197(1)	−0.215(2)	−0.0369(6)	13.6(7)
NDMF2	−0.129(1)	0.028(2)	0.0022(6)	13.4(7)
NDMF3	−0.171(1)	0.331(2)	0.0396(6)	11.4(7)
NDMF4	−0.163(1)	−0.023(2)	0.1966(6)	10.9(7)
NDMF5	−0.193(1)	0.235(2)	0.2298(6)	14.1(7)
NDMF6	−0.211(1)	0.522(2)	0.2774(6)	13.5(7)
C1A	0.0204(6)	0.2157(8)	0.2118(3)	2.2(3)
C2A	0.0139(5)	0.2915(7)	0.1999(3)	1.7(2)
C3A	0.0004(6)	0.3527(7)	0.2203(3)	1.9(2)
C4A	−0.0021(6)	0.3387(7)	0.2530(3)	2.1(3)
C5A	0.0094(6)	0.2651(7)	0.2636(3)	2.1(3)
C6A	0.0195(6)	0.2022(8)	0.2438(3)	2.5(3)
C1B	0.0272(6)	0.2273(7)	0.0654(3)	1.7(2)
C2B	0.0159(6)	0.2992(7)	0.0798(3)	2.2(3)
C3B	−0.0007(6)	0.3626(7)	0.0616(3)	2.0(3)
C4B	−0.0007(6)	0.3588(8)	0.0292(3)	2.2(3)
C5B	0.0149(6)	0.2883(8)	0.0164(3)	2.2(3)
C6B	0.0272(6)	0.2217(8)	0.0336(3)	2.2(3)
C1C	0.1724(6)	0.1574(7)	0.1363(3)	1.9(2)
C2C	0.1472(5)	0.0820(7)	0.1329(3)	1.4(2)
C3C	0.1871(6)	0.0196(7)	0.1274(3)	1.7(2)
C4C	0.2507(6)	0.0296(8)	0.1251(3)	2.1(2)
C5C	0.2732(6)	0.1056(7)	0.1293(3)	1.9(3)
C6C	0.2359(6)	0.1695(7)	0.1345(3)	2.1(3)
C1D	−0.1136(6)	0.1581(8)	0.1287(3)	2.2(3)
C2D	−0.0876(6)	0.0820(7)	0.1240(3)	1.7(2)
C3D	−0.1255(6)	0.0237(7)	0.1130(3)	2.0(3)
C4D	−0.1888(6)	0.0371(8)	0.1073(3)	2.3(3)
C5D	−0.2118(7)	0.1079(8)	0.1124(3)	2.7(3)
C6D	−0.1755(7)	0.1701(8)	0.1231(3)	2.8(3)

[a] Site with 0.5 occupancy.

$[Ce(C_6H_4O_2)_4]^{4-}$ (ϵ 2350 at λ_{max} 517 nm) [9]. Cyclic voltammetric examination of Ce(IV)/Ce(III) in strongly basic aqueous medium containing excess Tiron revealed a quasi-reversible, one-electron wave with a formal potential $E_f = -497$ mV *vs.* saturated calomal electrode (SCE), $E_f = -253$ mV *vs.* normal hydrogen electrode (NHE), and a peak potential separation of 71 mV (Fig. 2). As the examination proceeded, the initially colorless solution containing tetrakis(tironato)cerate(III) complex gradually changed to purple–brown due to the formation of the tetrakis(tironato)cerate(IV) complex. Taking the standard potential Ce(IV)/Ce(III) as 1.70 V *vs.* NHE [11] it is possible to calculate [12] that the formation constant for the cerium(IV)–Tiron complex is about 10^{33} times that for the cerium(III)–Tiron complex. More detailed electrochemical examination of other catecholate ligands are reported elsewhere [13].

TABLE IV. Positional and Isotropic Temperature Factors for the Non-hydrogen Atoms that were not Refined[a]

Atom	*x*	*y*	*z*	*B* (Å^2)[b]
C1DMF1	−0.1797	−0.2461	−0.0059	15.0
C2DMF1	−0.2070	−0.1348	−0.0449	15.0
C3DMF1	−0.1797	−0.2871	−0.0605	15.0
C1DMF2	−0.0840	0.0000	−0.0059	15.0
C2DMF2	−0.1816	0.0605	−0.0215	15.0
C3DMF2	−0.1660	0.0079	0.0312	15.0
C1DMF3	−0.1555	0.3880	0.0206	15.0
C2DMF3	−0.2058	0.3690	0.0693	15.0
C3DMF3	−0.1522	0.2546	0.0391	15.0
C1DMF4	−0.1994	−0.0465	0.1766	15.0
C2DMF4	−0.1208	−0.0769	0.2145	15.0
C3DMF4	−0.1498	0.0573	0.2031	15.0
C1DMF5	−0.1406	0.2187	0.2500	15.0
C2DMF5	−0.2500	0.2187	0.2129	15.0
C3DMF5	−0.1543	0.2695	0.2051	15.0
C1DMF6	−0.2655	0.5505	0.2901	15.0
C2DMF6	−0.2108	0.4694	0.2501	15.0
C3DMF6	−0.1522	0.5521	0.2876	15.0

[a] All above atoms were treated as fixed atoms. Positions obtained from a final difference Fourier synthesis with F_{calc} including all other non-hydrogen atoms. [b] Value used for isotropic temperature factor is the average of values obtained for carbon atoms of DMF upon refinement, and is consistent with B_{iso} for oxygen and nitrogen atoms of DMF.

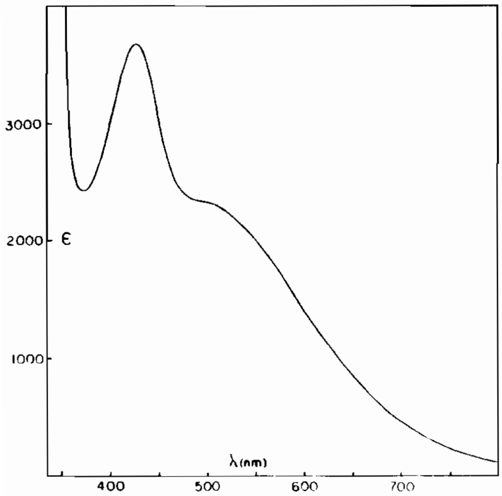

Fig. 1. Absorption spectrum of $[Ce(C_6H_2S_2O_8)_4]^{12-}$ in 1 M NaOH solution containing excess Tiron, tironate/Ce(IV) = 20/1.

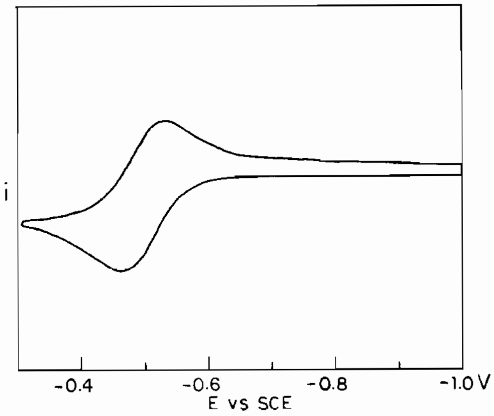

Fig. 2. Cyclic voltammogram of $[Ce(C_6H_2S_2O_8)_4]^{12-}$ in 5 M NaOH, 1 M Tiron aqueous solution at 100 mV/s scan rate.

The infrared spectrum of $Na_{12}[Ce(C_6H_2S_2O_8)_4]$, obtained by vacuum drying the title compound at 120 °C, is similar to that of Tiron, $Na_2C_6H_4S_2O_8 \cdot H_2O$. In the 4000–3000 cm^{-1} region, the spectrum of Tiron differs from that of the cerium complex by the C–O and H_2O stretching bands. The 1660 cm^{-1} strong and broad band of the cerium complex corresponds to the two bands 1638 and 1592 cm^{-1} of Tiron. Similarly, the 1463 cm^{-1} band corresponds to that at 1480, 1470 and 1438 cm^{-1} bands of Tiron, and the 864 cm^{-1} band to that at 890, 880 and 860 cm^{-1} bands of Tiron. Otherwise, there is a 1:1 correspondence between the bands in the two spectra. IR $Na_{12}[Ce(C_6H_2S_2O_8)_4]$ (4000–600 cm^{-1}): 3450(b, s), 1660(b, s), 1568(w), 1463(b, s), 1398(ms), 1278(s), 1260(sh), 1185(b, s), 1094(s), 1053(s),1032(s), 961(s), 864(m), 780(sh), 775(w), 665(m), 612(m). IR $Na_2C_6H_4S_2O_8 \cdot H_2O$ (4000–600 cm^{-1}): 3550(s), 3500(s), 3480(s), 3270(s), 3080(w), 1638(s), 1592(s), 1480(sh), 1470(s), 1438(s), 1380(b, m), 1295(s), 1210(b, s), 1108(s), 1058(sh), 1048(s), 952(s), 890(sh), 880(s), 860(s), 756(m), 740(s), 655(w), 632(sh), 605(m). The corresponding infrared spectrum of sodium bitironate hydrate $Na_3[C_6H_2O(OH)(SO_3)_2] \cdot H_2O$ [14], is similar: IR $Na_3[C_6H_2O(OH)(SO_3)_2] \cdot H_2O$ (4000–600 cm^{-1}): 3400(b, s), 3300(sh), 1695(b, w), 1640(b, w), 1597(s), 1568(w), 1560(w), 1495(sh), 1486(s), 1475(sh), 1440(s), 1386(s), 1375(b, s), 1306(s), 1254(s), 1210(b, s), 1180(b, s) 1110(s), 1060(s), 1038(s), 953(s), 862(s), 780(sh), 770(s), 665(sh), 660(s), 615(b, s). (The weak band at 1695 cm^{-1} is due to the –OH bending mode.)

Description of the Structure

The crystal structure consists of discrete, eight-coordinate anionic clusters $[Ce(C_6H_2S_2O_8)_4]^{12-}$, sodium cations, and waters and dimethylformamides of crystallization. The sodium ions are surrounded by 6 to 8 oxygen atoms from the anionic clusters, water or DMF of crystallization. Average bond distance and angle values for the four cerium bonded tironate ligands are shown in Fig. 3 which also shows the numbering scheme. A stereoview of the anionic cluster, $[Ce(C_6H_2S_2O_8)_4]^{12-}$, is shown in Fig. 4. See also 'Supplementary Material'. The coordination polyhedron is close to a perfect triangular faced dodecahedron (D_{2d}) with the bidentate ligands spanning

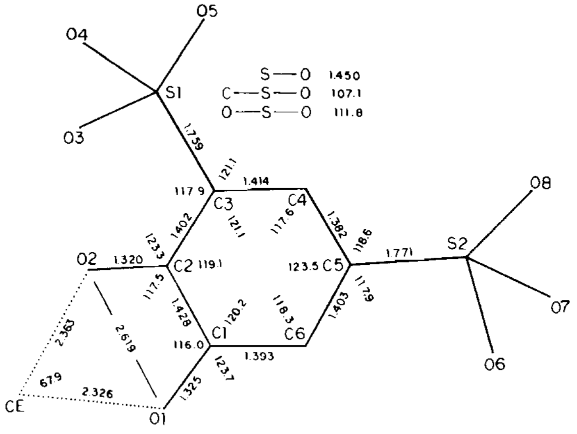

Fig. 3. Average interatomic distances (Å) and angles (°) of the four Ce(IV) coordinated tironato ligands. The atom labeling scheme used in the text is also shown. The O1 and O2 are bonded at the B and A sites, respectively, of the BAAB trapezoids of the dodecahedron, Fig. 5.

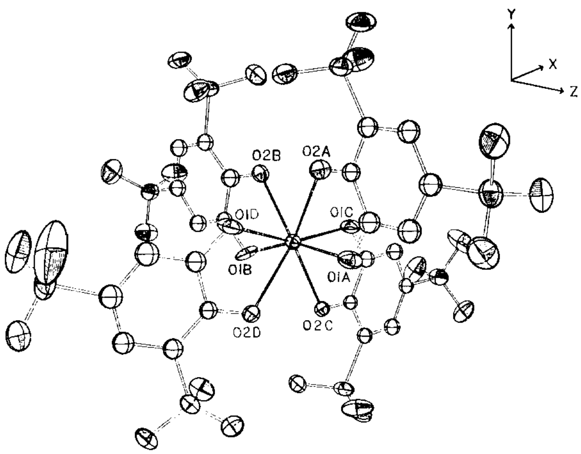

Fig. 4. A stereoscopic ORTEP drawing of the complex anion $[Ce(C_6H_2S_2O_8)_4]^{12-}$.

the m edges (Fig. 5). The O2 atoms of the tironate ligands bond consistently at the A site while the O1 atom bonds at the B site of the BAAB trapezoids.

The average Ce–O2 bond distance is 0.037(15) Å longer than the average Ce–O1, however the trend is not consistent within rings. The Ce–O distance for the A site of the BAAB trapezoid is effectively the same as that bonded at the B site in tetrakis(catecholato)cerate(IV) [8]. In the catecholato case the complex has 4 site symmetry as all B sites are equivalent. In this case Ce(IV) is in a general position in *Pbca* and both the complex and the individual ligands lack any symmetry. As explained for tetrakis(catecholato)hafnate(IV) [8], the M–O distance at A site lengthens relative to M–O at B site to avoid the unfavorable interactions occasioned by further decrease in the $O_A\cdots O_A$ distance.

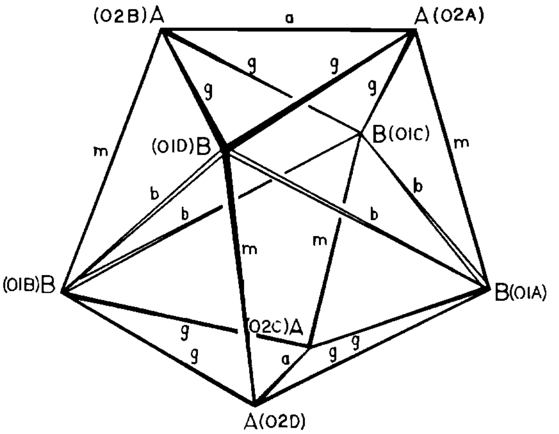

Fig. 5. Schematic representation of the eight-coordinate trigonal-faced dodecahedron (D_{2d}). Edges and vertices (ligand sites) are according to Hoard and Silverton [16].

The Ce(IV) coordination polyhedron is approximately D_{2d}. Of the seven idealized eight-coordinate geometries, the most often encountered highly symmetrical geometries are: the trigonal-faced dodecahedron, D_{2d}; the square antiprism, D_{4d}; and the cube, O_h. Shape parameters [15–17] are the most useful way to describe these coordination polyhedra [18]. In Fig. 5 the edges are sorted into symmetry equivalent groups of the D_{2d} structure, and the corners are labeled A or B and belong to two equivalent and mutually perpendicular BAAB trapezoids. Deviation from the dodecahedron to the antiprism will cause a twist, ϕ, in the BAAB trapezoids to an idealized value of 24.5°. The twist angle, ϕ, is defined to be the dihedral angle between the planes A, A, and the centroid of the two B positions, and B, B, and the centroid of the two A positions; for the two BAAB trapezoids the value is 2.3° and 3.7°, in close agreement to the dodecahedral angle of 0.0°. The dihedral angle for the two planes meeting along the b edge, δ_b, is 29.5° for the dodecahedron. As the symmetry is changed from dodecahedral to square antiprismatic two of the four δ_b angles become 52.4° while the other two become 0.0°, *i.e.* coplanar. The δ_b values for this structure are 26.8°, 37.3°, 41.3°, and 41.6°, near the dodecahedral angle of 29.5°.

The twelve sodium cations, Na^+, per asymmetric unit are surrounded irregularly (2.255 to 3.454 Å) by a varying number (5 to 8) of oxygen atoms. The oxygen atoms are either phenolic or sulfonic from the tironato ligands, or from water or *N*,*N*-dimethylformamide of solvation. Except for water oxygen O8, 3.7 Å^2, the isotropic thermal parameters for the waters' oxygen atoms are relatively high (6.0 to 9.6 Å^2) (Table V). Disordered DMF is not unusual [18–22]. The type of DMF disorder is like that reported for co-crystallized DMF [18], where the N and O atoms are ordered while the carbon atoms alternate between two sets of sites each with half occupancy. Another type of disorder reported for DMF is where the oxygen atom of the formyl group is disordered [19]. However, the average bond distances and angles observed here agree with the reported values for planar DMF [22, 23].

Supplementary Material

The following are available from the authors on request. Table V: Interatomic distances (Å) and angles (degrees). Table VI: Least squares planes and deviation therefrom. Table VII: Shape parameters of the coordination sphere compared to idealized eight coordination polyhedra. Table VIII: F_{obs} and F_{calc} reflections in $Na_{12}[Ce(C_6H_2S_2O_8)_4]\cdot 9H_2O\cdot 6C_3H_7NO]$. Figure S1: The IR spectrum as KBr mull of $Na_{12}[Ce(C_6H_2S_2O_8)_4]$, (A); $Na_2(C_6H_4S_2O_8)\cdot H_2O$, Tiron, (B); and $Na_3[C_6H_2O(OH)(SO_3)_2\cdot H_2O$, (C). Figure S2: An ORTEP drawing of the complex anion $[Ce(C_6H_2S_2O_8)_4]^{12-}$ projected on the *yz*-plane]. Figure S3: An ORTEP drawing of the complex anion $[Ce(C_6H_2S_2O_8)_4]^{12-}$ projected on the *xy*-plane. Figure S4: The disposition of the six DMF molecules of solvation per asymmetric unit relative to the coordination polyhedron; Ce(1V) at height $x = 0.0287$ while the six DMF at height $x = -0.211$ to -0.129]. Figure S5: ORTEP drawing of the coordination polyhedron projected on the *yz*-plane, showing BAAB1 trapezoid (O1A, O2A, O2B, O1B)]. Figure S6: [ORTEP drawing of the coordination polyhedron projected on the *xy*-plane, showing BAAB2 trapezoid (O1C, O2C, O2D, O1D)], (48 pages).

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