well documented,[19,20] this behavior has not been previously exploited to prepare linear oxo-bridged Cr(III) dimers. Our observation of single hydroxo bridge displacement by two thiocyanate ions in $[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+}$ opens the door to the synthesis of an extensive class of $[(tmpa)(L)Cr^{III}OCr^{III}(L)(tmpa)]$ complexes through direct nucleophilic attack by a variety of incoming groups (L) on an easily obtained chromium(III) diol precursor. For example, the oxo-bridged compounds with L = Cl^- and CN^- are obtained in excellent yield by refluxing NaCl and NaCN, respectively, with I in acetonitrile, the solvent of choice to avoid dimer hydrolysis side reactions.[21] The generality of nonoxidative Cr(III)–O–Cr(III) complex synthesis is indicated by the conversion of another chromium(III) diol with aromatic amine ligands, $[(bpy)_2Cr(OH)_2Cr(bpy)_2](ClO_4)_4{\cdot}2H_2O$ (V), to oxo-bridged dimers through nucleophilic attack by pseudohalide incoming groups. Dark brown compounds with elemental analyses corresponding to $[\{Cr(bpy)_2(SCN)\}_2O](ClO_4)_2{\cdot}H_2O$ (VI)[22] and $[\{Cr(bpy)_2(N_3)\}_2O](ClO_4)_2{\cdot}H_2O$ (VII)[23] are obtained from V[24] and NaSCN or NaN_3 by the same procedure used to synthesize II. Oxo-bridged dimers VI and VII exhibit Cr–O–Cr asymmetric stretching bands at 855, 845, and 835 and 850, 825, and 810 cm^{-1}, respectively, and UV–visible spectra (CH_3CN) dominated by a single, extremely intense peak: 301 nm (VI) (ϵ 52 300 M^{-1} cm^{-1}) and 300 nm (VII) (ϵ 56 000 M^{-1} cm^{-1}).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of research at Texas Tech University.

Supplementary Material Available: Positional and thermal parameters for $[\{Cr(tmpa)(NCS)\}_2O](NCS)_2$ (4 pages). Ordering information is given on any current masthead page.

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(22) Anal. Calcd for $[\{Cr(bpy)_2(SCN)\}_2O](ClO_4)_2{\cdot}H_2O$: Cr, 9.64; C, 46.80; H, 3.18; N, 12.99. Found: Cr, 9.63; C, 46.81; H, 2.91; N, 12.83.

(23) Anal. Calcd for $[\{Cr(bpy)_2(N_3)\}_2O](ClO_4)_2{\cdot}H_2O$: Cr, 9.94; C, 45.94; H, 3.28; N, 18.75. Found: Cr, 9.91; C, 46.58; H, 3.03; N, 18.79.

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Department of Chemistry
and Biochemistry
Texas Tech University
Lubbock, Texas 79409

Boyd G. Gafford
Robert A. Holwerda*

Department of Chemistry
Rutgers, The State University
of New Jersey
New Brunswick, New Jersey 08903

Harvey J. Schugar
Joseph A. Potenza

Received September 30, 1987

Pentacoordinate Iron–Sulfur Complexes. Structure and Spectroscopic and Electrochemical Properties of Phenoxy- and Thiophenoxy-Bridged Binuclear Complexes

Sir:

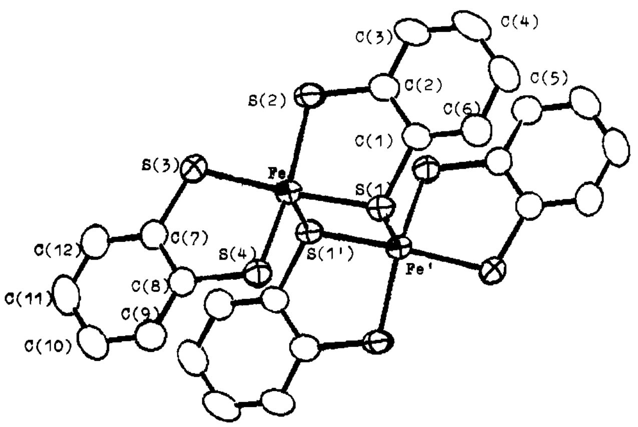

Figure 1. Structure of the anion of $(Et_4N)_2[Fe_2(BDT)_4]$.

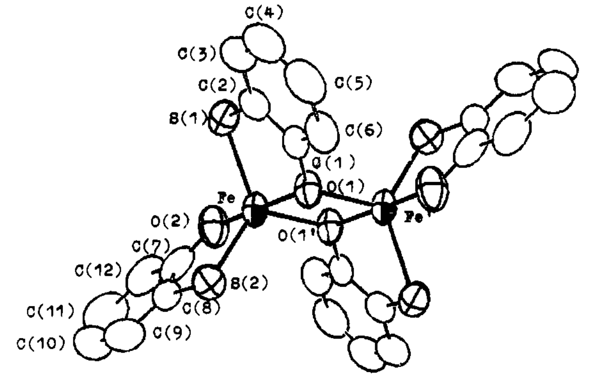

Figure 2. Structure of the anion of $(Et_4N)_2[Fe_2(MP)_4]{\cdot}2CH_3CN$.

The importance of iron–sulfur compounds in biochemical processes has been known for many years since they are the active center of many iron–sulfur proteins and also have been related to the function of redox enzymes. The simulation of the active sites of rubredoxin, 2Fe- and 4Fe-ferredoxins, etc, by synthesizing iron–sulfur compounds, has become an important branch of inorganic chemistry. Among the many kinds of iron–sulfur compounds, 5-coordinate dinulcear thiolato-bridged systems with 1,2-dithiolene ligands have been known[1] while the structurally related phenoxy-bridged analogue is scarce in the literature. We wish to report here a comparison of structures and ^1H NMR, Mössbauer, magnetic, and electrochemical properties of two pentacoordinate thiophenoxy- and phenoxy-bridged diiron complexes $(Et_4N)_2[Fe_2(XSC_6H_4)_4]$ (X = S or O). Differences induced by oxygen or sulfur atom at the bridging position are revealed for the first time.

Results and Discussion. Compounds $(Et_4N)_2[Fe_2(XSC_6H_4)_4]$ (**1**, X = S, $C_6H_4S_2^{2-}$ = BDT^{2-}; **2**·$2CH_3CN$, X = O, $C_6H_4OS^{2-}$ = MP^{2-}) were obtained from reaction of anhydrous $FeCl_3$ with Na_2BDT (**1**) or Na_2MP (**2**) in ethanolic solution on addition of Et_4NBr and recrystallization from CH_3CN.[1f,2] Although both anions of **1** and of **2** have 5-coordinate iron atoms bridged by X atoms of two individual 1,2-dithiolene ligands (X = S in **1**, X = O in **2**), they have quite different structures mainly due to different hybridizations of bridging atoms as shown in Figures 1 and 2. The oxygen atom in **2** is sp^2 hybridized with bond angles around bridging O(1) being 118.3, 125.6, and 101.7° (average 115.2°). In contrast, the sulfur atom is sp^3 hybridized at the bridge in **1** (bond angles around bridging S(1) are 105.6, 103.3, and 83.6°

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(2) Anal. Calcd for **2**·$2CH_3CN$ ($Fe_2S_4O_4C_{44}H_{62}N_4$): Fe, 11.75; S, 13.49. Found: Fe, 12.18; S, 13.51. Crystal data: M_r = 950.97, a = 11.580 (2) Å, b = 16.731 (6) Å, c = 12.869 (2) Å, β = 98.07(2)°, V = 2468.6 $Å^3$, monoclinic system, space group $P2_1/n$, Z = 2, D_{calcd} = 1.279 g/cm^3. Of the 4707 independent reflections (Enraf-Nonius CAD-4 diffractometer, Mo K_α, λ = 0.71069 Å, 1° $\leqslant \theta \leqslant$ 25°, Lp and empirical absorption corrections), 2242 reflections with $I > 3\sigma(I_0)$ were used and gave a final R (R_w) = 0.069 (0.077). The SDP program package was used for the calculations. The coordinate of the Fe atom was taken from a Patterson map; the other non-hydrogen atoms were located by subsequent difference Fourier syntheses and least-squares refinements.

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(average 97.5°)), and empty d orbitals may also participate in bond formation.[3] The participation of d orbitals in hybridization is shown by the lower magnetic moment of **1** ($\mu_{eff} = 2.74\ \mu_B$) compared to **2**·2CH$_3$CN ($\mu_{eff} = 7.45\ \mu_B$) caused by much stronger antiferromagnetic coupling of the two paramagnetic Fe(III) atoms through the bridge. Certainly, a different covalency, electronegativity, and atomic raidus of the bridging atom may also play a role in structural differences. The coordination geometry about Fe(III) in anion of **1** with five sulfur atoms is distorted square pyramidal,[1f] which is common for dimeric dithiolene ligated system such as $[M_2(S_2C_2(CF_3)_2)_4]^-$ (M = Fe,[1b] Co[4]), $[Fe_2(S_2C_2(CN)_2)_4]^{2-}$,[1g] $[Co_2(S_2C_6Cl_4)_4]^{2-}$,[5] or $[Fe_2(S_2C_2(CO_2Me)_2)_4]^{2-}$.[1a] The four sulfur atoms in the basal plane are from two chelating BDT^{2-} ligands. In the anion of **2**·2CH$_3$CN, the coordination unit FeO$_3$S$_2$ is in a distorted trigonal-bipyramidal geometry with O(1) and O(2) being the two apical atoms (∠O(1)–Fe–O(2) = 175.8°) and O(1′), S(1), and S(2) on the equatorial plane. Core units Fe$_2$X$_2$ of **1** and **2** are both planar rhombs but of different shapes. The bond Fe–S(1′) connecting two $[Fe(BDT)_2]^-$ fragments is longer than Fe–S(1) within a $[Fe(BDT)_2]^-$ by 0.24 Å while the corresponding Fe–O(1′) is abnormally shorter than Fe–O(1) by 0.047 Å. This difference in Fe–X$_b$ distances is reflected in the IR spectra of the compounds. The Fe–S absorption in **1** gave only one peak at 362 cm^{-1}, corresponding to terminal Fe–S vibrations. The spectrum of **2**·2CH$_3$CN is more complicated, and both Fe–S and Fe–O absorptions are multiplets. We tentatively assigned peaks at 387 and 340 cm^{-1} to Fe–S absorptions and peaks at 578 and 570 cm^{-1} to Fe–O. The Fe···Fe distances are close to each other in both compounds (Δ = 0.017 Å) regardless of the hybridization of bridging X atoms. The two phenyl rings on each Fe atom are either nearly parallel to each other (dihedral angle 10.05° in the anion of **1**) or nearly perpendicular (dihedral angle 100.2° in the anion of **2**).

^{1}H NMR spectra[6] in solvents of different polarity revealed the dissociation of dimer D into monomer M on solvation of **1** and **2** and that the dissociations are of different degrees:

$$\underset{\text{D}}{[Fe_2(XSC_6H_4)_4]^{2-}} \xrightleftharpoons{\text{solvent}} \underset{\text{M, } n = 1 \text{ or } 2}{2[Fe(XSC_6H_4)_2(sol)_n]^-}$$

Compound **1** has similar chemical shifts in DMSO–d_6 (32.7, 29.8 ppm) and in DMF-d_7 (34.1, 28.8 ppm), indicating the presence of the same monomer species $[Fe(S_2C_6H_4)_2(sol)_n]^-$ (n^9 = 1 or 2); a slight difference in chemical shifts is induced by solvent coordination. The spectrum in the less polar solvent CD$_3$CN is exceedingly different from those in the other two and is a complicated multiplet from more than at least six different protons. The signals moved very much to the central field at 10–18 ppm and were induced by strong antiferromagnetic coupling of the two metal centers, and the isotropic shift $(\Delta H/H_0)_{iso}$ should be smaller than that for the paramagnetic monomer. Compound **2** gave different spectra in all three solvents. The spectra in the two extremities of DMSO-d_6 and CD$_3$CN indicated the presence of dissociated monomer M (−48.0 −36.0, 23.9 ppm) and undissociated dimer D (−40, −22, 18.5 ppm), respectively. In the solvent DMF-d_7 of polarity intermediate between those of DMSO-d_6 and CD$_3$CN, an equilibrium of D:M ∼ 8:1 is observed. Ease of dissociation is expected for compound **1** as one of the Fe–S$_b$ bonds is much weaker than the other (Δ(Fe–S$_b$) = 0.14 Å) while both Fe–O$_b$ distances in **2** are of similar strength (Δ(Fe–O$_b$) = 0.047 Å). In addition, the square-pyramidal geometry of the Fe atom in **1** affords a greater vacancy near the Fe atom and favors the entry of a solvent molecule. Dissociation from dimer into monomer has been observed for $[Fe_2(S_2C_2(CO_2Me)_2)_4]^{2-}$ [1a] and $[Mn_2(S_2C_6H_4)_4]^{2-}$.[7]

Cyclic voltammetric studies[8] also confirmed the existence of solvated monomer M in DMSO and undissociated dimer D in CH$_3$CN. Both compounds **1** and **2** showed only one reversible redox couple in DMSO at $E_{1/2} = -0.97$ and -0.92 V, respectively, in the range of ∼0 to −2.0 V for the reaction

$$[Fe(XSC_6H_4)_2(DMSO)_n]^- \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Fe(XSC_6H_4)_2(DMSO)_n]^{2-}$$

In CH$_3$CN, both compounds gave two single-electron reduction waves:[8] **1**, $E_{1p,c} = -0.94$ V, $E_{2p,c} = -1.75$ V; **2**, $E_{1p,c} = -0.94$ V, $E_{2p,c} = -1.59$ V. These corresponded to reaction couples $[Fe_2(XSC_6H_4)_4]^{2-/3-}$ and $[Fe_2(XSC_6H_4)_4]^{3-/4-}$, respectively. Except for the process of $[Fe_2(BDT)_4]^{2-/3-}$, which is quasi-reversible ($i_{p,a}/i_{p,c} \cong 0.7$), all of the reduction processes are irreversible either chemically or electrochemically. ESR spectra also gave evidence of dissociation in solution.[9] The work is now in progress.

Quadrupole splitting ΔE_Q[10] of **1** (2.95 mm/s) at 77 K is much larger than that of **2**·2CH$_3$CN (1.18 mm/s), indicating that the Fe atom in the former is in an intermediate-spin state ($S = {}^3/_2$) and in the latter is in a high-spin state ($S = {}^5/_2$).[11] Large ΔE_Q values are often observed for Fe^{3+} with $S = {}^3/_2$ spin state[12] due to a lesser degree of symmetry for the sum of d orbitals of Fe atoms compared to that with $S = {}^5/_2$ whose charge distribution around Fe(III) atom is spherically symmetrical, and ΔE_Q can only be induced by ligands. Magnetic susceptibility measurements revealed the presence of antiferromagnetic coupling between the two Fe(III) atoms in both compounds as μ_{Fe} values of 1.93 (**1**) and 5.28 (**2**·2CH$_3$CN) μ_B are both smaller than $\mu_{Fe} = 3.87\ \mu_B$ for $S = {}^3/_2$ and 5.92 μ_B for $S = {}^5/_2$ respectively, calculated with spin only. The lower magnetic moment of **1** is confirmed by the higher quadrupole splitting and the smaller chemical shift[13] of ^{1}H NMR in comparison with those of compound **2**.

Acknowledgment. This work was supported by the NNSF and the SFCAS. We appreciate very much the experimental assistance of L. J. Ho, J. H. Cai, Q. L. Sun, and A. Z. Cong.

Registry No. **1**, 110572-92-4; **2**, 113036-50-3; **2**·2CH$_3$CN, 113085-32-8; $[Fe_2(BDT)_4]^{3-}$, 113036-45-6; $[Fe_2(BDT)_4]^{4-}$, 113036-47-8; $[Fe_2(MP)_4]^{3-}$, 113036-46-7; $[Fe_2(MP)_4]^{4-}$, 113036-48-9.

Supplementary Material Available: Listings of positional and thermal parameters, bond distances and angles, and least-squares planes and unit cell and packing diagrams for **1** and **2**·2CH$_3$CN (8 pages). Ordering

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(9) Preliminary results of ESR studies (*g* at 77 K for **1**: 4.47, 2.03 (DMF); 3.62 (DMSO) *g* for **2**: 4.24 (DMF); 4.47 (DMSO)) showed completely different spectra for both **1** and **2** in the solid state and in solution (DMSO or DMF), supporting the presence of monomer $[Fe(XSC_6H_4)_2(sol)_n]^-$ (M1, X = S; M2, X = O) in the latter and indicating different spin states too: $S = {}^3/_2$ ground state for M1 with 5-coordinate Fe^{3+}, $n = 1$; $S = {}^5/_2$ for M2 with 6-coordinate Fe^{3+}, $n = 2$.[7]

(10) IS (mm/s) and QS (ΔE_Q, mm/s) for **1** and **2**·2CH$_3$CN at 77 K are 0.314 and 2.95 and 0.407 and 1.18, respectively, measured with a ^{57}Co source in a Pd matrix by using a constant acceleration spectrometer. The velocity scale was calibrated with the known peak positions in the spectrum of α-Fe foil.

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(14) To whom correspondence should be addressed at the Fujian Institute of Research on the Structure of Matter.

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Fujian Institute of Research on the Structure of Matter and Fuzhou Laboratory of Structural Chemistry
Chinese Academy of Sciences
Fuzhou, Fujian, China

B. S. Kang*[14]
L. H. Weng
D. X. Wu
F. Wang
Z. Guo
L. R. Huang
Z. Y. Huang
H. Q. Liu

Received October 7, 1987

Synthesis, Structure, and Reactivity of Tricoordinate Cerium(III) Aryloxides. The First Structurally Characterized Monomeric $Ln(OR)_3$ Complexes

Sir:

Compounds of the type $Ln(OR)_3$ (Ln = lanthanide metal, R = alkyl or aryl) generally exist as oligomers, both in solution and in the solid state[1]—a natural consequence of the preference for high coordination numbers by the lanthanide metal ions. The only previously reported monomeric complexes belonging to the above group are $Ln[2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O]_3$.[2] While the monomeric nature of these compounds in solution was established by cryoscopic measurements, their solid-state structures remained unknown. Interestingly, the corresponding Sc analogue[2] exhibits a near-planar MO_3 skeleton in sharp contrast to the pyramidal MN_3 skeletons for $Ln[N(SiMe_3)_2]_3$ compounds[3]—the only previously reported, structurally characterized, tricoordinate complexes of the lanthanide metals. Herein, we report the synthesis, structural elucidation, and reactivity of a series of Ce(III) aryloxides, $Ce[2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}XC_6H_2O]_3$ (X = H (**1a**), Me (**1b**), *t*-Bu (**1c**)). The noteworthy features of these complexes are as follows. (a) The crystal structure of **1a** constitutes the first structural characterization of a *monomeric* $Ln(OR)_3$ complex. Such well-defined aryloxide compounds are potentially useful as precursors to the corresponding oxides through the low-temperature sol-gel process.[4] (b) The above complexes are only the second general class of tricoordinate lanthanide metal compounds (vide supra). (c) **1a** exhibits a pyramidal structure *unlike* the near-planar Sc analogue and *like* the $Ln[N(SiMe_3)_2]_3$ compounds. (d) The ability of Ce(III) to adopt an apical position makes it accessible to a variety of incoming ligands, including the "soft" *t*-BuNC and tetrahydrothiophene, leading to the formation of $LCe(OR)_3$ species. (e) With slender ligands, 2:1 adducts, $L_2Ce(OR)_3$, were also formed. A crystal structure of the $(t\text{-}BuNC)_2Ce(OR)_3$ complex revealed a novel distorted trigonal bipyramid geometry with a cis disposition of the *t*-BuNC ligands.

The aryloxides **1a–e** were synthesized by the reaction of $Ce[N(SiMe_3)_2]_3$[5] with the appropriate phenol in pentane. The compounds were characterized by NMR, IR, and elemental analysis (C, H, N). All were volatile (sublimed at 180–190 °C, 10^{-5} Torr), yellow-green crystalline solids and were soluble in hydrocarbon solvents.

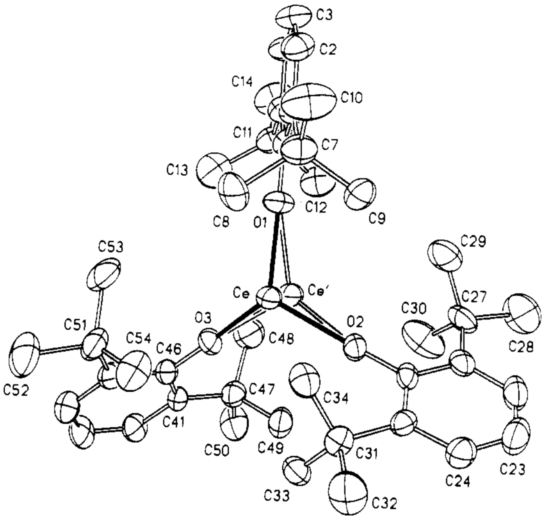

Figure 1. Thermal ellipsoid (40% probability) diagram for **1a**.[6] Important bond distances (Å) and angles (deg): Ce⋯Ce′, 1.075 (2); Ce–O(1), 2.140 (5); Ce–O(2), 2.174 (4); Ce–O(3), 2.135 (5); Ce′–O(1), 2.180 (5); Ce′–O(2), 2.112 (4); Ce′–O(3), 2.127 (5); O(1)–Ce–O(2), 114.9 (2); O(1)–Ce–O(3), 115.5 (2); O(2)–Ce–O(3), 110.2 (2); O(1)–Ce′–O(2), 115.9 (2); O(1)–Ce′–O(3), 114.2 (2); O(2)–Ce′–O(3), 114.2 (2); Ce–O(1)–C(6), 165.7 (4); Ce–O(2)–C(26), 161.7 (4); Ce–O(3)–C(46), 165.0 (5); Ce′–O(1)–C(6), 163.2 (5); Ce′–O(2)–C(26), 166.8 (4); Ce′–O(3)–C(46), 165.5 (5).

The structure of **1a** was determined by single-crystal X-ray diffraction and is shown in Figure 1.[6] The compound is monomeric with the oxygens arranged in a trigonal pyramid about Ce, which is disordered between two such sites. The oxygens and ipso carbons are coplanar to within 0.026 Å.[7] **1a** is significantly more pyramidal than any other known tricoordinate lanthanide complex, as measured by the distance of the metal from the plane of the ligating atoms (0.54 Å average for **1a** versus 0.44, 0.34, and 0.42 Å, respectively, for $M[N(SiMe_3)_2]_3$ (M = Sc,[8] Nd,[3b] Eu[8]) and 0.13 Å for $Sc[2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O]_3$[2]). The pyramidal structure may, however, be the result of crystal-packing forces since it has been reported that $Eu[N(SiMe_3)_2]_3$, which is also pyramidal in the solid state, has a solution dipole moment of zero.[8] This suggests that the metal can move freely perpendicular to the ligand plane and that its position is a function of the ligand environment—a property that may be responsible for what little coordination chemistry has been reported for other tricoordinate lanthanide metal complexes.[2,9]

The tendency of **1a** to form adducts with Lewis bases was probed by NMR spectral titrations. For example, the addition of tetrahydrofuran (THF) to a C_6D_6 solution of **1a** resulted in

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(6) Crystal data for $C_{42}H_{63}O_3Ce$: monoclinic, $P2_1/c$, a = 11.345 (2) Å, b = 31.918 (6) Å, c = 11.808 (2) Å, β = 104.92 (1)°, V = 4131 (1) Å^3, Z = 4, D(calcd) = 1.216 g cm^{-3}, μ(Mo Kα) = 11.4 cm^{-1}, T = 295 K. A capillary-mounted yellow-green crystal (0.35 × 0.35 × 0.40 mm) was obtained by slow evaporation of a heptane solution. Of 5865 reflections collected (maximum 2θ = 45°, no data beyond) and corrected for adsorption, 2743 independent, observed ($3\sigma F_o$) reflections were used to solve (heavy atom) and refine the structure. Two Ce atom locations exist along a psuedothreefold rotational axis; their refined occupancies are Ce (0.58) and Ce′ (0.42). At convergence (all non-hydogen atoms anisotropic, all hydrogen atoms idealized such that d_{C-H} = 0.960 Å and U_H = 1.2U for attached carbon) $R(F)$ = 6.33%, $R(wF)$ = 6.57%, GOF = 1.23, Δ/σ = 0.07, $\Delta(\rho)$ = 0.42 e Å^{-3}, and N_o/N_v = 7.7. All computations used the SHELXTL (version 5.1) library (Nicolet Corp., Madison, WI).

(7) Deviations from the least-squares plane formed by the six atoms were as follows (Å): O1, 0.021; O2, –0.026; O3, –0.001; C6, –0.012; C26, 0.017; C46, 0.002.

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