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A Dimeric π-Cyclooctatetraene Dianion Complex of Cerium(III). The Crystal and Molecular Structure of $[Ce(C_8H_8)Cl \cdot 2OC_4H_8]_2$

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The crystal and molecular structure of a novel dimeric cerium π complex with cyclooctatetraene dianion, $[Ce(C_8H_8)Cl \cdot 2OC_4H_8]_2$, has been determined from single-crystal, three-dimensional X-ray diffraction data collected by counter methods. There are two cerium atoms in the dimeric unit which are bridged asymmetrically by the two chloride ions with Ce–Cl bond lengths of 2.855 (2) and 2.935 (2) Å. The cyclooctatetraene dianion ring is planar with eightfold molecular symmetry and an average C–C bond length of 1.394 (4) Å. It is symmetrically bonded to the cerium atom with an average Ce–C distance of 2.710 (2) Å. The Ce–O distances are equal and average 2.583 (2) Å. The two tetrahydrofuran (THF) oxygens and the two chlorine atoms form a plane parallel to and below the COT ring to complete the inner coordination geometry. The two five-membered THF rings differ in conformation; the first is in a skew or twist form (C_2 symmetry) and the second has the envelope conformation (C_s symmetry). The dimer crystallizes from THF solutions as fluorescent, yellow-green plates with the following crystal data: monoclinic space group $P2_1/c$, cell constants $a = 11.869$ (6), $b = 12.621$ (5), $c = 13.497$ (7) Å, $\cos \beta = -0.5433$ (4), $z = 2$ (four monomers), $\rho_{obsd} = 1.69$, $\rho_{calcd} = 1.66$ g/cm^3. The structure has been refined by full-matrix, least-squares methods using 2626 independent reflections with $F^2 > 3\sigma F^2$ and a model which includes anisotropic thermal motion with fixed hydrogen positions to an unweighted R factor of 2.95%.

Introduction

The initial synthesis of the lanthanide tricyclopentadienides[2] was followed by a period of inactivity. Recently, interest in the synthesis and chemistry of organometallic compounds formed from carbocyclic π ligands and f transition series metals has undergone a renaissance. Although the chemistry of the π-carbocyclic anion complexes is now extensive, there is a distinct absence of the structural data necessary to form a solid foundation for explaining their bonding properties and spectra. The disordered structure of samarium tricyclopentadienide had been the only reported crystallographic determination on a lanthanide π-carbocyclic complex.[3] Recently, however, a structural determination of tris(indenyl)samarium has been completed.[4] Cyclooctatetraene dianion π complexes were first reported for the d transition metals.[5] Our interest in the structures of f transition series organometallic compounds has extended from the initial structural studies of the uranium cyclooctatetraene dianion complex, $U(C_8H_8)_2$,[6] and its thorium analog[7] to the recently reported cyclooctatetraene dianion (COT^{2-}) complexes of the lanthanides.[8,9]

Recent attempts by Mares, Hodgson, and Streitwieser to prepare a neutral complex containing COT^{2-} and cyclononatetraene anion resulted in a new series of lanthanide complexes containing the cyclooctatetraene dianion.[9] This series was difficult to characterize due to facile loss of THF. A single-crystal X-ray diffraction analysis was begun on the cerium member of this series and the structure determination and subsequent full elemental analysis showed that the true composition is $[Ce(C_8H_8)Cl \cdot 2THF]_2$.

Data Collection and Reduction

The synthesis of $[Ce(C_8H_8)Cl \cdot 2THF]_2$ has been reported elsewhere.[9] Crystals suitable for X-ray studies were obtained by controlled evaporation of a saturated THF solution of the complex under argon atmosphere at room temperature. The air- and water-sensitive crystals were mounted in thin-walled quartz capillaries with Kel-F fluorocarbon grease under an argon atmosphere. A series of precession photographs showed monoclinic symmetry with the following systematic absences: $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$. Space group $P2_1/c$ [C_{2h}^5] is the only choice which is consistent with these conditions.

The data crystal was a fluorescent yellow-green plate bounded by the following four pairs of planes: $11\bar{1}$, 011, $\bar{1}11$, and 100. The plane-to-plane distances are, respectively, 0.069, 0.278, 0.240, and 0.163 mm. The crystal gave ω-scan widths at half-height of 0.14, 0.08, and 0.09° for the $0\bar{1}\bar{1}$, $\bar{1}00$, and $11\bar{3}$ reflections, respectively. The crystal was mounted along the 100 direction on a Picker FACS-1 four-circle diffractometer.

The crystal orientation and unit cell constants were determined by a least-squares refinement of the orientation angles for 12 carefully centered reflections whose 2θ angles ranged from 40 to 60°.[10] The resulting cell parameters and other pertinent crystal data are summarized in Table I.

TABLE I
SUMMARY OF CRYSTAL DATA

Molecular formula: $[Ce(C_8H_8)Cl \cdot 2OC_4H_8]_2$
Molecular weight: 847.88
Linear absorption coefficient μ: 28.66 cm^{-1}
Obsd density:[a] 1.69 g/cm^3
Calcd density: 1.66 g/cm^3
Crystal dimensions: 0.34 × 0.16 × 0.07 mm
Space group: $P2_1/c$, monoclinic
Molecules/unit cell: 2 (four monomers)
Cell constants:[b] $a = 11.869$ (6), $b = 12.621$ (5), $c = 13.497$ (7) Å; $\beta = 122.91$ (3)°; $\cos \beta = -0.5433$ (4)
Cell volume: 1697.42 Å^3

[a] Accurate experimental density measurements were difficult to obtain due to rapid loss of THF from the crystals when exposed to a dry argon atmosphere. However, reasonably consistent values were obtained by rapid flotation measurements in $CHBr_3$–CCl_4. [b] Mo $K\alpha_1$ radiation, λ 0.70926 Å. Ambient temperature of 23°.

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[1] (a) National Science Foundation Trainee. (b) Alfred P. Sloan Fellow.

[2] J. M. Birmingham and G. Wilkinson, *J. Amer. Chem. Soc.*, **76**, 6210 (1954).

[3] C. H. Wong, T. Y. Lee, and Y. T. Lee, *Acta Crystallogr., Sect. B*, **25**, 2580 (1969).

[4] J. L. Atwood, J. H. Burns, and P. G. Laubereau, Abstract J10, American Crystallographic Society, Winter Meeting, Jan 1971.

[5] See, for example, M. A. Bennett, *Advan. Organometal. Chem.*, **4**, 376 (1966), and H. Breil and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **5**, 897 (1966).

[6] A. Zalkin and K. N. Raymond, *J. Amer. Chem. Soc.*, **91**, 5667 (1969).

[7] A. Avdeef, K. N. Raymond, K. O. Hodgson, and A. Zalkin, *Inorg. Chem.*, in press.

[8] F. Mares, K. Hodgson, and A. Streitwieser, Jr., *J. Organometal. Chem.* **24**, C68 (1970).

[9] F. Mares, K. Hodgson, and A. Streitwieser, *ibid.* **25**, C24 (1971).

[10] The programs used for the PDP8/I computer were those written by Busing and Levy, as modified by Picker Corp.

TABLE II

POSITIONAL[a] AND ANISOTROPIC THERMAL PARAMETERS[b] WITH STANDARD DEVIATIONS

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ce	0.22530 (2)	0.01827 (2)	0.14779 (2)	74.1 (2)	59.5 (2)	59.1 (2)	−8.9 (1)	30.8 (2)	−4.6 (2)
Cl	0.04225 (12)	−0.11024 (12)	−0.04937 (12)	95.8 (11)	76.5 (11)	88.5 (11)	8.9 (9)	25.0 (9)	−23.0 (9)
O_1	0.15699 (33)	−0.01143 (33)	0.29722 (30)	158.0 (36)	82.9 (29)	96.4 (28)	−5.5 (31)	87.4 (28)	−7.7 (28)
O_2	0.28264 (36)	−0.17235 (32)	0.23177 (32)	156.4 (42)	73.4 (30)	94.5 (31)	6.2 (29)	67.5 (31)	0.6 (26)
C_1	0.2629 (6)	0.2180 (6)	0.0957 (8)	133 (7)	76 (5)	185 (10)	−9 (5)	72 (7)	44 (6)
C_2	0.3144 (7)	0.2182 (6)	0.2170 (7)	161 (8)	73 (4)	156 (8)	−28 (5)	98 (7)	−30 (5)
C_3	0.4034 (6)	0.1586 (7)	0.3138 (6)	146 (7)	116 (6)	112 (6)	−62 (6)	73 (6)	−48 (6)
C_4	0.4770 (5)	0.0679 (7)	0.3292 (5)	96 (5)	124 (7)	86 (5)	−33 (5)	18 (4)	−5 (5)
C_5	0.4959 (5)	0.0005 (6)	0.2558 (6)	79 (4)	99 (6)	158 (7)	−4 (5)	51 (5)	−0.4 (63)
C_6	0.4446 (6)	−0.0025 (6)	0.1366 (6)	135 (6)	111 (6)	160 (8)	−33 (6)	108 (6)	−41 (7)
C_7	0.3565 (7)	0.0580 (7)	0.0392 (6)	173 (9)	148 (8)	115 (7)	−77 (7)	103 (7)	−51 (7)
C_8	0.2812 (7)	0.1482 (8)	0.0220 (6)	176 (9)	154 (9)	86 (6)	−77 (8)	54 (6)	20 (6)
C_{11}	0.1650 (6)[c]	0.0633 (6)	0.3798 (6)	190 (8)	94 (5)	110 (6)	−10 (6)	99 (6)	−21 (5)
C_{21}	0.1099 (7)	0.0100 (8)	0.4412 (6)	241 (11)	147 (8)	142 (7)	−40 (9)	145 (8)	−35 (7)
C_{31}	0.0212 (9)	−0.0746 (7)	0.3596 (8)	266 (13)	136 (8)	210 (10)	−42 (9)	187 (11)	−26 (9)
C_{41}	0.0528 (8)	−0.0873 (7)	0.2724 (7)	235 (11)	137 (8)	166 (8)	−75 (8)	147 (8)	−43 (8)
C_{12}	0.3792 (7)	−0.1922 (7)	0.3551 (6)	165 (8)	112 (7)	92 (6)	7 (6)	0.6 (56)	21 (5)
C_{22}	0.3406 (8)	−0.2957 (7)	0.3816 (7)	218 (10)	107 (7)	144 (8)	34 (7)	108 (8)	47 (7)
C_{32}	0.2493 (7)	−0.3457 (6)	0.2644 (8)	159 (8)	77 (5)	192 (10)	14 (6)	66 (8)	7 (7)
C_{42}	0.2553 (9)	−0.2737 (7)	0.1801 (7)	285 (13)	83 (6)	124 (7)	58 (7)	87 (8)	−2 (6)

[a] Fractional cell coordinates. [b] Values of β are multiplied by 10^4; the form of the thermal correction is $\exp[-(\beta_{11}h^2 + 2\beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] The subscripts on the THF carbons specify first the atom number and then the ring number.

Intensity data were collected in the θ–2θ scan mode using monochromatic Mo Kα radiation with a scintillation counter. The takeoff angle for the X-ray tube was 2.0° and the Bragg 2θ angle for the graphite monochromator crystal was 12.02°. The pulse height analyzer, centered on a Mo Kα peak, was set to admit approximately 90% of the maximum intensity at full window width. The detector was located 33 cm from the source with a 7 × 7 mm receiving aperture. A scan rate of 1°/min was used with a scan from 0.50° below the Kα_1 peak to 0.50° above the Kα_2 peak. Stationary 10-sec background counts were taken at the start and end of each scan. Copper foil attenuators were automatically inserted to maintain the count rate for a given reflection below 10,000 counts/sec. From two to six equivalent forms of intensity data were collected for the sphere $0° \leq 2\theta \leq 60°$. A total of 13,297 reflections were collected. During the experiment, the intensities of the $0\bar{1}\bar{1}$, $\bar{2}00$, and $11\bar{3}$ reflections were measured every 75 reflections as a check on the stability of the crystal and electronic equipment.

The data reduction and processing were accomplished by our program UCFACS as previously described.[11] The parameter p, introduced to avoid overweighting strong reflections, was set to 0.04. Intensities were corrected for Lorentz and polarization effects and converted to F^2. The F^2 values of the standards showed anisotropic losses of about 17, 22, and 23%, in the directions of the three standards mentioned above. A local program, CHORT, was used to correct the F^2 values for this decay. The standards were approximately mutually orthogonal. For an individual reflection it is assumed that the decomposition is an average of the decay along three directions. These three directions are the reciprocal lattice vectors of the three standard reflections. The intensity loss for each standard was interpolated from the observed standard intensities in order to determine the standard intensity at the time a given reflection was measured. The final correction for a reflection was then the weighted average of intensity corrections for the three standards. If F^2 is the observed intensity and F_o^2 is the value that would have been determined prior to intensity loss, we may define a correction factor $k = F^2/F_o^2$. We assume that $k = p_1k_1 + p_2k_2 + p_3k_3$, where k_1 to k_3 are the correction factors observed for the standard reflections at the time F^2 was measured. The values p_i are defined by

$$p_i = s\frac{|\vec{r}\cdot\vec{r}_i|}{|\vec{r}||\vec{r}_i|}$$

Here $\vec{r}$ is the reciprocal lattice vector of the reflection being corrected, $\vec{r}_i$ is the reciprocal lattice vector of the ith standard, and s is defined such that $p_1 + p_2 + p_3 = 1$. As a check, the corrections calculated in this way were found to work well in those cases where the same reflection was measured more than once.

The calculated absorption coefficient, μ, is 28.7 cm^{-1}. The maximum and minimum thicknesses, t, for the crystal give a range of μt from 0.20 to 0.97. A numerical absorption correction was therefore applied, and the applied corrections ranged from 1.33 to 2.53. After this correction the data were averaged to give 2626 independent reflections with $F^2 > 3\sigma(F^2)$. These were used in the final refinement. The agreement factor on F^2 for averaging is 6.3% which compares well with the final least-squares agreement factor on F of 3.6%.

Solution and Refinement of the Structure

The structure was solved by the application of heavy-atom techniques.[12] Full-matrix, least-squares refinements on F were used in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, w, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Ce, O, Cl, and C were taken from the values tabulated by Cromer and Mann[13] and those for neutral hydrogen from Stewart, Davidson, and Simpson.[14] Correction for anomalous dispersion effects of the cerium and chlorine atoms using both $\Delta f'$ and $\Delta f''$ were included in the calculation of the F's.

The positions of the cerium and chlorine atoms were located from a three-dimensional Patterson map. Isotropic least-squares refinement of these two heavy-atom positions followed by a difference Fourier synthesis on F located the COT ring carbon and the two THF oxygen atoms. Three additional least-squares cycles and another difference Fourier located all remaining nonhydrogen atoms. The hydrogen atom positions were calculated by assuming the appropriate tetrahedral (for the THF rings) or planar (for the COT) geometry and C–H bond lengths of 1.0 Å. In the final anisotropic refinement, the hydrogen atom contributions to the structure factors were calculated from these fixed positions and the temperature factors for all hydrogens were set to 5.0 Å^2. The final agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (weighted R factor) $= [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ were 2.95 and 3.59%, respectively. The final error in an observation of unit weight is 0.85. The final difference Fourier showed no peaks greater than 6% of the height of a C atom peak which were not due to residual peaks around the Ce atom.[15]

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(11) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971).

(12) In addition to local systems programs for the CDC 6400 computer, modifications of the following programs were used: Ibers' NUCLS, a group least-squares version of the Busing–Levy ORFLS program; Zalkin's FORDAP Fourier program; ORFFE, a function and error program by Busing and Levy; Johnson's ORTEP thermal ellipsoid plot program; and Hamilton's GONO absorption program.

(13) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) A listing of structure factors will appear immediately following this article in the microfilm edition of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

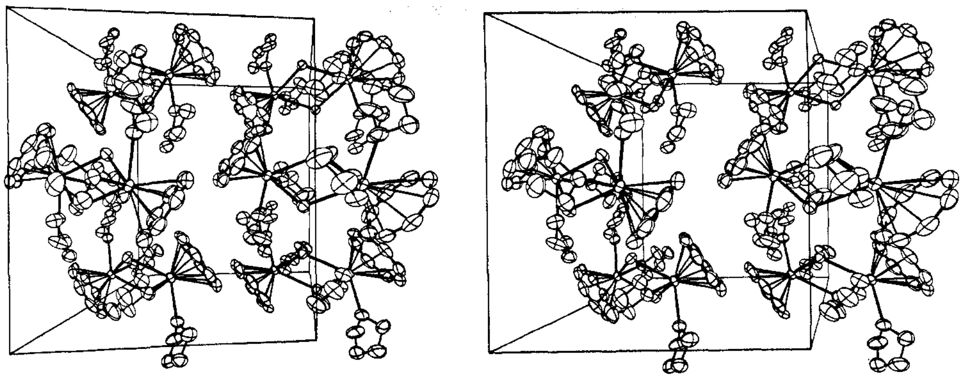

Figure 1.—A stereoscopic packing diagram of $[Ce(C_8H_8)Cl \cdot 2OC_4H_8]_2$ viewed normal to the xy plane. One unit cell is outlined. The origin is at the back lower left, the horizontal axis is **a**, and the vertical axis is **b**. The dimeric units at 001, 010, 011, and 111 have been omitted.

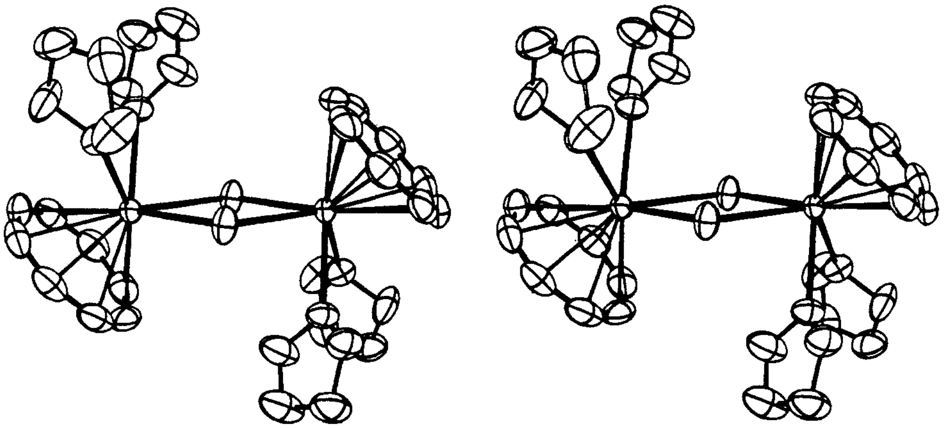

Figure 2.—A stereoscopic diagram of the $[Ce(C_8H_8)Cl \cdot 2OC_4H_8]_2$ complex. Thermal ellipsoids are drawn at the 40% probability contour. The numbering sequence in the COT ring on the right is counterclockwise, such that C_8 is uppermost and C_1 is before C_8. THF ring 1 is in the right foreground. Carbon atom numbering for both THF rings is clockwise and sequential and begins at the oxygen atom.

The positional parameters from the final least squares are given in Table II. Tables III and IV list the thermal parameters and the rms amplitudes of vibration along the principal axes of the thermal ellipsoids for all nonhydrogen atoms.

TABLE III

CALCULATED POSITIONS FOR CYCLOOCTATETRAENE AND TETRAHYDROFURAN HYDROGEN ATOMS[a]

Atom	x	y	z	Atom	x	y	z
H_1	0.1984	0.2813	0.0539	H_{15}	−0.0741	−0.0554	0.3231
H_2	0.2760	0.2780	0.2391	H_{16}	−0.0398	−0.1429	0.4056
H_3	0.4182	0.1867	0.3899	H_{17}	−0.0282	−0.0746	0.1928
H_4	0.5306	0.0438	0.4136	H_{18}	0.0866	−0.1613	0.2759
H_5	0.5603	−0.0581	0.3002	H_{21}	0.3772	−0.1343	0.4036
H_6	0.4809	−0.0642	0.1159	H_{22}	0.4707	−0.1970	0.3687
H_7	0.3477	0.0306	−0.0341	H_{23}	0.2934	−0.2836	0.4241
H_8	0.2292	0.1675	−0.0650	H_{24}	0.4211	−0.3406	0.4320
H_{11}	0.1131	0.1284	0.3383	H_{25}	0.1532	−0.3496	0.2436
H_{12}	0.2618	0.0842	0.4374	H_{26}	0.2777	−0.4188	0.2594
H_{13}	0.0573	0.0616	0.4574	H_{27}	0.1700	−0.2733	0.1019
H_{14}	0.1840	−0.0199	0.5188	H_{28}	0.3307	−0.2958	0.1714

[a] Calculated positions. Tetrahedral (THF) or trigonal (COT^{2-}) geometries are assumed for the carbon atoms. A C–H bond length of 1.0 Å and an isotropic thermal parameter of 5.0 Å^2 were assumed.

Description and Discussion of the Structure

The crystal structure consists of discrete dimers which show no unusually short intermolecular nonbonded distances. There are two dimers per unit cell and they occupy the symmetry-related positions 0, 0, 0 and 0, $^1/_2$, $^1/_2$ with $\bar{1}$ crystallographic site symmetry. A stereoscopic view of the unit cell packing as viewed normal to the xy plane is shown in Figure 1.

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION OF ALL NONHYDROGEN ATOMS ALONG PRINCIPAL AXES, 10^3 Å

Atom	Axis 1	Axis 2	Axis 3	Atom	Axis 1	Axis 2	Axis 3
Ce	184.0 (4)	209.3 (4)	224.9 (4)	C_7	207 (4)	257 (5)	287 (4)
Cl	203 (2)	219 (2)	317 (2)	C_8	217 (8)	281 (7)	316 (7)
O_1	201 (8)	263 (7)	393 (11)	C_{11}	219 (8)	308 (9)	389 (10)
O_2	219 (8)	270 (8)	333 (9)	C_{21}	244 (9)	316 (11)	411 (10)
C_1	201 (8)	262 (8)	357 (9)	C_{31}	237 (8)	280 (10)	409 (10)
C_2	189 (7)	285 (8)	339 (9)	C_{41}	240 (5)	245 (5)	284 (4)
C_3	196 (5)	282 (8)	344 (8)	C_{12}	204 (7)	304 (9)	399 (9)
C_4	208 (6)	257 (9)	358 (9)	C_{22}	234 (9)	307 (8)	360 (10)
C_5	213 (8)	234 (8)	398 (10)	C_{32}	242 (9)	289 (8)	391 (10)
C_6	197 (8)	246 (8)	427 (10)	C_{42}	220 (9)	284 (8)	424 (10)

A stereoscopic drawing of the dimer is shown in Figure 2. The molecular structure consists of two cerium atoms which are asymmetrically bridged by the two chloride ions with Ce–Cl bond lenghths of 2.855 (2) and 2.935 (2) Å. The cyclooctatetraene dianion is planar and is symmetrically π bonded to the cerium atom. The individual Ce–C and C–C bond lengths are each within four standard deviations of their averages (determined from the individual standard deviations from the variance–covariance matrix), which are 2.710 (2) and 1.395 (4) Å, respectively.

The coordination of the cerium atom in this structure may be described as cubic. The COT^{2-} anion occupies one face of this cube and the opposite face has the two chloride ions and two THF oxygen atoms on adjacent corners. This geometrical formalism would imply eight-coordination. However, the COT^{2-} anion has five π-electron pairs available for coordination. If these and the dative bonds from the chlorine and oxygen atoms are included, the formal coordination number is 9. The two chloride and two oxygen atoms each lie within 0.2 Å of their weighted least squares plane (Table V). The Cl–Cl distance in the dimer, 3.461 (3) Å, is significantly shorter than the van der Waals contact distance of 3.6 Å. This close nonbonded contact is required for formation of the bridge. The corresponding Ce–Ce nonbonded distance is 4.642 (3) Å. In a cube, the angle formed by the center of the cube and two adjacent corners is 70.5°. The corresponding Cl–Ce–Cl′ angle, 73.41 (5)°, is only somewhat larger than this. The thermal motion of the cerium atom is nearly isotropic. In contrast, the chlorine atoms are distinctly anisotropic and show a preferential vibration which is perpendicular to the plane formed by the cerium and chlorine atoms.

TABLE V

WEIGHTED LEAST-SQUARES PLANES

Plane of cyclooctatetraene ring[a]		Plane of O and Cl atoms[a]		Plane of C atoms in THF 1[a]		Plane of C atoms in THF 2[a]	
C_1	0.0094 (59)	Cl	−0.072 (2)	C_{11}	−0.024 (7)	C_{12}	−0.030 (8)
C_2	−0.0106 (62)	Cl′	0.072 (2)	C_{21}	0.077 (9)	C_{22}	0.037 (8)
C_3	0.0048 (59)	O_1	−0.219 (4)	C_{31}	−0.098 (10)	C_{32}	−0.037 (7)
C_4	−0.0045 (60)	O_2	0.271 (4)	C_{41}	0.062 (9)	C_{42}	0.028 (8)
C_5	0.0050 (56)						
C_6	−0.0030 (57)						
C_7	−0.0004 (60)						
C_8	−0.0034 (62)						
A[b]	0.960		0.987		0.719		0.104
B	0.718		0.698		−0.722		−0.582
C	−0.425		0.568		0.183		−0.500
D	0.367		0.154		0.145		0.333

[a] Distances in ångströms of individual atoms from weighted least squares. [b] Equations for least-squares planes in monoclinic coordinates of the form $Ax + By + Cz - D = 0$.

This report is the third structure determination to date for cyclooctatetraene dianion π complexes of f transition metals.[5–7] It is the first such report for a lanthanide. In the previous structures reported which contain a π-bonded COT^{2-} anion, the ring has localized eightfold molecular symmetry in each case and normal aromatic C–C bond distances. All of the eight COT carbon atoms in the present structure lie within 0.01 Å of the least-squares plane (Table V). The average C–C bond length is 1.394 (4) Å. This bond length and the planarity of the ring demonstrate the aromatic nature of the cyclooctatetraene dianion in this structure. Another severe test of the aromatic nature of the ring is a comparison of the two averages for alternate bonds. These alternate bond lengths must be equal in an aromatic hydrocarbon ring. The averages 1.388 (5) and 1.400 (5) Å are equal to within experimental error. The mean C–C–C interior angle in the COT ring is 135.0 (2)°, which is the interior angle of a regular octahedron. As expected, the relatively large anisotropic thermal motion of the COT carbon atoms (Figure 3) shows a preferential oscillation about the molecular eightfold symmetry axis. The mean rms amplitude of vibration along the major axis is 0.369 (3) Å for the carbon thermal ellipsoids. This approximately represents the average thermal motion along the circumference of the COT ring.

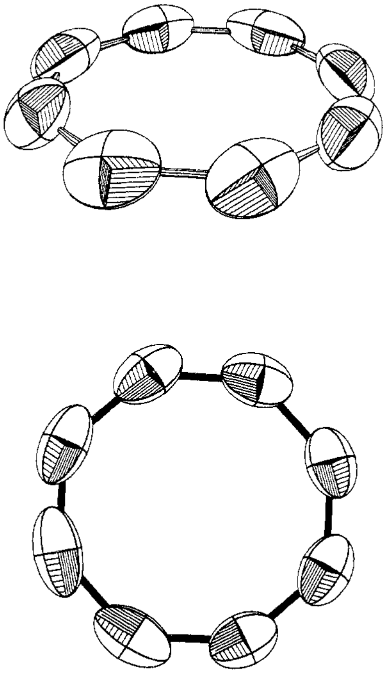

Figure 3.—The cyclooctatetraene dianion ring carbons viewed perpendicular to the plane of the ring are shown in the lower view. In the upper view the plane is rotated 65°. The numbering sequence increases sequentially in a clockwise direction from the upper right carbon atom, C_1, in both rings.

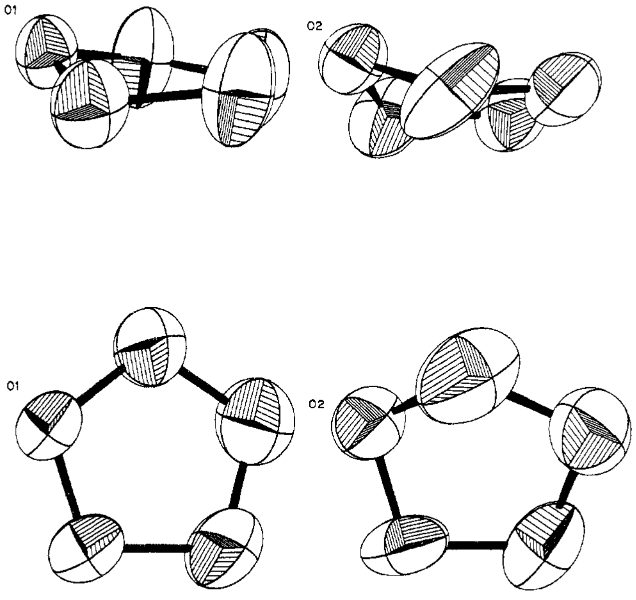

Figure 4.—Perspective drawings of the two tetrahydrofuran molecules. The THF ring carbon atoms are numbered sequentially, beginning with C_{11} or C_{12} and proceeding in a counterclockwise direction from the oxygen atom. The first number in the subscripts names the carbon atom and the second number specifies the ring. The left-hand side of the figure shows two views of ring 1 and the right-hand side shows corresponding views of ring 2.

The two Ce–O coordinate bonds formed by the tetrahydrofuran molecules are equal and average 2.583 (2) Å. The average C–C bond length in the THF rings is 1.47 Å. This is shorter than the expected value. The large thermal motion of the carbon atoms results in observed C–C bonds which are systematically short. The average C–O bond length is 1.43 Å. Two views of THF ring 1 are shown in Figure 4 (left side). In this conformation the molecule assumes a twist configuration with approximate C_2 molecular symmetry in which the twofold axis passes through the oxygen atom and bisects the C_{12}–C_{13} bond. Ring 2, shown in Figure 4 (right side), has all four carbon atoms approximately in a plane with the oxygen raised above the plane by an angle of 38°. This envelope conformation has C_s molecular symmetry. The thermal motion of the carbon atoms in both conformers is approximately perpendicular to the plane of the C–C or C–O bonds to these atoms. The rms amplitudes of vibration for the THF rings are listed in Table IV. A summary of selected intramolecular bond distances and angles for the inner coordination sphere of the cerium atoms, the COT dianion ring, and the two THF molecules is tabulated in Tables VI–VIII.

The conformation of five-membered rings has been extensively studied by spectroscopic techniques. The unusual ease of interconverting certain of the conformations in these rings appears to be a rotation of the puckering about the ring. This was the first system in which the term "pseudorotation" was applied.[16] For tetrahydrofuran there are two predominant conformations. The first of these is the envelope, with C_s symmetry, and the second is a twist form, with C_2 symmetry. The relative energies and interconversion barriers have been studied by microwave[17,18] and far-infrared[19,20] techniques. The skew or twist conformer is found to be lowest in energy but by an amount which is less than 0.1 kcal/mol. Both types of conformations have been found in previous structure reports of THF coordination compounds,[21,22] although no comment was made regarding the conformations in either case. The two crystallographically independent rings of this structure display both of these conformations.

Table VI

Bond Lengths and Angles for the Cerium Inner Coordination Sphere

Atoms	Distances, Å	Group	Angle, deg
Ce-Ce	4.642 (3)	Cl-Ce-Cl′	73.41 (5)
Ce-Cl	2.855 (2)	O_1-Ce-O_2	69.01 (13)
Ce-Cl′	2.935 (2)	O_1-Ce-Cl	104.07 (10)
Cl-Cl′	3.461 (3)	O_2-Ce-Cl	76.47 (9)
Ce-C_1	2.718 (7)		
Ce-C_2	2.699 (7)		
Ce-C_3	2.735 (6)		
Ce-C_4	2.714 (5)		
Ce-C_5	2.721 (5)		
Ce-C_6	2.701 (5)		
Ce-C_7	2.703 (6)		
Ce-C_8	2.690 (6)		
Ce-O_1	2.577 (3)		
Ce-O_2	2.588 (4)		

Av Bond Lengths

Atoms	Distances, Å
Ce-C	2.710 (2)
Ce-O	2.583 (2)

Table VII

Bond Lengths and Angles for the Cyclooctatetraene Dianion

Bond	Length, Å	Group	Angle, deg
C_1–C_2	1.403 (11)	C_8–C_1–C_2	132.7 (7)
C_2–C_3	1.375 (10)	C_1–C_2–C_3	136.9 (7)
C_3–C_4	1.386 (11)	C_2–C_3–C_4	133.7 (6)
C_4–C_5	1.413 (10)	C_3–C_4–C_5	136.0 (6)
C_5–C_6	1.378 (10)	C_4–C_5–C_6	134.3 (7)
C_6–C_7	1.382 (11)	C_5–C_6–C_7	136.2 (7)
C_7–C_8	1.387 (12)	C_6–C_7–C_8	134.3 (6)
C_8–C_1	1.430 (12)	C_7–C_8–C_1	135.8 (7)

Av of two sets of alternate C–C bonds, Å	Av C–C bond Lengths, Å
1.388 (5) 1.400 (5)	1.394 (4)

Av C–C–C interior angle, deg
135.0 (2)

Table VIII

Bond Lengths and Angles for the Tetrahydrofuran Molecules

Bond	Length, Å	Length, Å[a]	Group	Angle, deg
O_1–C_{11}	1.423 (7)	1.535 (7)	C_{41}–O_1–C_{11}	107.7 (4)
C_{11}–C_{21}	1.468 (9)	1.599 (9)	O_1–C_{11}–C_{21}	106.2 (6)
C_{21}–C_{31}	1.484 (11)	1.627 (10)	C_{11}–C_{21}–C_{31}	105.3 (5)
C_{31}–C_{41}	1.426 (9)	1.599 (9)	C_{21}–C_{31}–C_{41}	107.1 (6)
C_{41}–O_1	1.452 (7)	1.577 (7)	C_{31}–C_{41}–O_1	108.0 (6)
Av C–C	1.459 (6)		Av C–C–C	106.2 (6)
O_2–C_{12}	1.440 (7)	1.573 (7)	C_{42}–O_2–C_{12}	103.8 (6)
C_{12}–C_{22}	1.491 (11)	1.624 (10)	O_2–C_{12}–C_{22}	106.0 (6)
C_{22}–C_{32}	1.488 (11)	1.603 (10)	C_{12}–C_{22}–C_{32}	104.9 (6)
C_{32}–C_{42}	1.488 (11)	1.612 (10)	C_{22}–C_{32}–C_{42}	104.2 (6)
C_{42}–O_2	1.408 (9)	1.544 (8)	C_{32}–C_{42}–O_1	105.6 (6)
Av C–C	1.489 (6)		Av C–C–C	105.0 (3)

[a] Corrected for independent thermal motion; W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17,** 142 (1964).

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