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An Ion Pair Complex Formed between Bis(cyclooctatetraenyl)cerium(III) Anion and an Ether-Coordinated Potassium Cation. The Crystal and Molecular Structure of $[K((CH_3OCH_2CH_2)_2O)][Ce(C_8H_8)_2]$

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The crystal and molecular structure of an ion pair salt between bis(cyclooctatetraenyl)cerium anion and an ether-coordinated potassium cation, $[K((CH_3OCH_2CH_2)_2O)][Ce(C_8H_8)_2]$, has been determined from three-dimensional X-ray data collected by counter methods. The molecular structure consists of a discrete $[Ce(C_8H_8)_2]^-$ anion combined in a contact ion pair with the $[K((CH_3OCH_2CH_2)_2O)]^+$ solvated cation. One side of the cation is coordinated by the complexing ether, diglyme. The opposite side is coordinated by one of the two cyclooctatetraenyl dianion rings in the structure. The Ce and K ions lie on a crystallographic mirror plane such that the entire complex has crystallographically imposed mirror symmetry. The average Ce–C bond length is 2.742 (8) Å. The cyclooctatetraene dianion rings are planar with equal aromatic C–C bond distances of 1.39 (3) Å. One ring of the complex anion is bisected by a mirror plane through two C–C bonds, and the other is bisected between two C atoms. The molecular symmetry of the $[Ce(C_8H_8)_2]^-$ anion is D_{8d}. The five independent K–C bond lengths between the K^+ ion and the $C_8H_8{}^{2-}$ ring average 3.16 (3) Å, and the two independent K–O distances from the diglyme oxygens in the ether complexed cation are 2.792 (5) and 2.741 (4) Å. The salt crystallizes from diglyme as large, bright green plates with the following crystal data: orthorhombic space group *Pnma*, cell constants $a = 16.897$ (4), $b = 14.014$ (5), $c = 9.358$ (2) Å, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.56$ g/cm³. The structure has been refined with full-matrix least-squares methods using 2789 independent reflections with $F^2 > 3\sigma(F^2)$ to a standard unweighted R factor of 5.9%.

Introduction

Our program to elucidate the structural chemistry of lanthanide and actinide organometallics began with the structure report of $U(C_8H_8)_2$ "uranocene," the biscylcooctatetraenyl dianion complex of U(IV).[2] Streitwieser and coworkers have since characterized two homologous series of lanthanide(III) complexes with cyclooctatetraene dianion,[3-5] $[Ln(C_8H_8)Cl\cdot 2C_4H_8O]_2$ and $K[Ln(C_8H_8)_2]$. The crystal and molecular structure determination of the cerium member of the monocyclooctatetraenyl chloride series[6] established the chemical composition as well as the structure of this π-carbocyclic complex. The structural result also allowed an assignment of structure for the other, homologous members of the series by comparison of their ir spectra. The second series of complexes, containing two cyclooctatetraene dianion ligands per metal, were suspected to be isostructural with $U(C_8H_8)_2$ based on striking similarities in the ir spectra of the uranium as compared to the lanthanide complexes.[3,5] To determine the molecular geometry of the $[Ln(C_8H_8)_2]^-$ anion we have completed the single-crystal structure analysis of the cerium member of the biscyclooctatetraenyl series. This structure was of interest to see if the dianion ring was again symmetrically π bonded to the metal ion in an eclipsed geometry, as in the case of $U(C_8H_8)_2$. The molecular orientation of the anions in the crystal was also of interest since this information is essential for subsequent magnetic and spectroscopic studies of oriented single crystals of complexes in this series.

As discussed previously[6] there have been only three[6-8] other structure determinations of lanthanide π-carbocyclic complexes. A preliminary communication of the fourth such structure determination of $[K((CH_3OCH_2CH_2)_2O)][Ce(C_8H_8)_2]$ has appeared,[9] and in this paper we report the details of the complete structure analysis of this complex.

Experimental Section

The synthesis of $K[Ce(C_8H_8)_2]$ has been reported previously.[3] Crystals of this compound could be obtained from slow evaporation of a saturated tetrahydrofuran (THF) solution of the complex under argon atmosphere at room temperature. As soon as the crystals were removed from the mother liquor, however, they rapidly decolored on the surface and became an amorphous powder. Since the crystals were probably losing coordinated solvent we chose to recrystallize the complex from the higher boiling, chelating ether, diglyme, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$. If a saturated solution of the complex in diglyme was prepared at the boiling point of the solvent (162°) under argon atmosphere and then allowed to cool, beautifully formed large green single crystals were obtained in sizes up to 1 × 0.5 × 0.5 mm. Several of the air- and moisture-sensitive crystals were mounted in thin-walled quartz capillaries with Kel-F fluorocarbon grease under an argon atmosphere. A series of precession photographs showed orthorhombic symmetry with the following systematic absences: $0kl$, $k + l \neq 2n$; $hk0$, $h \neq 2n$. Space group *Pnma* ($D_{2h}{}^{16}$) or its acentric counterpart $Pn2_1a$ (standard setting, $Pna2_1$ ($C_{2v}{}^9$)) are the only choices which are consistent with these conditions.

Data Collection

The data crystal, cleaved from a larger plate, was bounded by the following seven planes: $2\bar{1}0$, $0\bar{1}0$, 001, $00\bar{1}$, 010, $\bar{1}00$, $\bar{1}10$. The perpendicular distance to each of these planes from the intersection point of the $2\bar{1}0$, $0\bar{1}0$, and 001 planes which was defined as the crystal origin is respectively 0.0, 0.0, 0.0, 0.032, 0.016, 0.043, and 0.025 cm. The crystal gave ω-scan widths at half-height of 0.10, 0.09, and 0.08° for the 200, 020, and 002 reflections, respec-

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

(2) (a) A. Zalkin and K. N. Raymond, *J. Amer. Chem. Soc.*, **91**, 5667 (1969); (b) A. Avdeef, K. N. Raymond, K. O. Hodgson, and A. Zalkin, *Inorg. Chem.*, **11**, 1083 (1972).

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

(4) F. Maers, K. Hodgson, and A. Streitwieser, Jr., *ibid.*, **25**, C24 (1971).

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

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(9) K. N. Raymond and K. O. Hodgson, Abstract I5, American Crystallographic Society, Winter Meeting, April 1972.

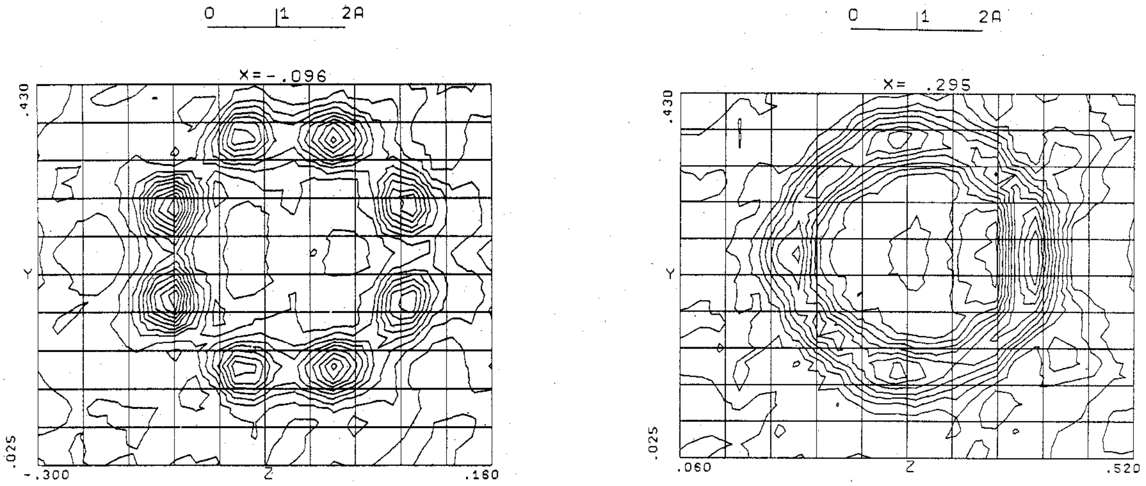

Figure 1.—Sections from the electron density map (calculated with values of F_{obsd} and phases of F_{calcd}) for cyclooctatetraene dianion rings. These sections are in the planes of the cyclooctratetraene rings. Slight deviations in the contour maps from the crystallographic mirror symmetry are an artifact of the computation procedure. Ring 1 is shown on the left and ring 2 is shown on the right. The mirror plane in both cases is horizontal at $y = {}^1/_4$ and relates the top and bottom halves of the sections.

tively. The crystal in its capillary on an *xyz* goniometer head was mounted with the $\bar{1}00$ axis nearly parallel to the ϕ axis of the Picker FACS-1 four-circle diffractometer.

The optimum crystal orientation matrix and unit cell constants were determined by least-squares refinement of the orientation and 2θ angles for 12 carefully centered reflections whose 2θ angles ranged from 40 to 50°.[10] The X-ray source and diffractometer parameters were kept identical with those used in intensity measurements.

The final refined cell parameters and other pertinent crystal data are given in Table I.

Table I

Summary of Crystal Data

Molecular formula: $[K((CH_3OCH_2CH_2)_2O)][Ce(C_8H_8)_2]$
Molecular weight: 513.64
Linear absorption coefficient μ: 48.34 cm^{-1}
Calcd density: 1.56 g/cm^3
Max crystal dimensions: 0.43 × 0.16 × 0.32 mm
Space group: Orthorhombic, *Pnma*
Molecules/unit cell: 4
Cell constants:[a] $a = 16.897\ (4)$, $b = 14.014\ (5)$, $c = 9.358\ (2)$ Å
Cell volume: 2215.92 $Å^3$

[a] At 22°.

Intensity data were collected in the θ–2θ scan mode using monochromatic Mo Kα radiation and a scintillation counter. The Bragg 2θ angle for the graphite monochrometer crystal was 12.02° and X-ray tube takeoff angle was 2.0°. The pulse height analyzer, centered on a Mo Kα peak, was set to admit about 90% of the maximum intensity at full window width. The detector was located 33 cm from the source with a receiving aperture of 7 × 7 mm. The 2θ scans were from 0.5° below the Kα_1 peak to 0.5° above the Kα_2 peak with a scan rate of 1.0°/min. Stationary 10-sec background counts were taken at the start and end of each scan and copper foil attenuators were automatically inserted to maintain the count rate for a given reflection below 10^2 counts/sec.

Throughout the experiment, the intensities of the three standard reflections, 800, 040, and 002, were measured every 75 reflections as a check on the stability of the crystal and the instrument. The 11,412 reflections collected included almost two complete forms of intensity data ($\pm h$, $+k$, $+l$) within a sphere $0 \leq 2\theta \leq 70°$.

The data reduction and processing were accomplished by our program UCFACS as previously described.[11] The parameter p, introduced in the expression for $\sigma(F^2)$ 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 in intensity of only 1, 3, and 1%, respectively, for the three standards mentioned above. Our decay correction program, CHORT,[12] was used to correct the F^2 values for this minimal decay. As a check, a comparison of standard F^2's taken at the beginning and end of data collection always agreed within 1% after the decay correction.

The calculated absorption coefficient, μ, is 48.34 cm^{-1}. The maximum and minimum thicknesses, t, for the crystal gave a range of μt from 0.77 to 1.55. An absorption correction was applied using a Gaussian numerical integration program.[12] The transmission factors ranged from 0.26 to 0.43. After this correction the data were averaged to give the 2789 independent reflections with $F^2 > 3\sigma(F^2)$ which were used in the final refinement.

Solution and Refinement of the Structure

The structure was solved by the application of heavy-atom techniques. 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 $4F_o^2/\sigma(F_o^2)$. The atomic scattering factors for neutral Ce, K, O, and C were taken from the values tabulated by Cromer and Mann[13] and those for neutral hydrogen from Stewart, Davidson, and Simpson.[14] The calculations included both $\Delta f'$ and $\Delta f''$ corrections for anomalous dispersion effects of the cerium and potassium atoms.[15]

The positions of the cerium and potassium atoms were determined from a three-dimensional Patterson map. Isotropic least-squares refinement of these two heavy-atom positions assuming the centric space group, followed by a difference Fourier, located the diglyme oxygen and carbons and four crystallographically independent carbons of one of the cyclooctatetraene dianion (COT^{2-}) rings. This ring was oriented such that the mirror plane bisected two of its opposite C–C bonds and thus generated the other four atoms in the ring by the mirror operation. After three cycles of least-squares refinement another difference Fourier was calculated. Four broad peaks were located for the second COT ring which again had the mirror plane bisecting two of the C–C bonds in the COT ring. Isotropic refinement of this model reduced the R factor to only 11% and the carbon atoms of ring 2 displayed abnormally high (>12 $Å^2$)

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[10] Programs used for the PDP 8/I computer were those written by Busing and Levy, as modified by Picker Corp.

[11] E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1485 (1971).

[12] In addition to local programs for the 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; Johnson's ORTEP thermal ellipsoid plot program; AGNOST, an absorption correction program written by P. Coppens, L. Leiserowitz, and D. Rabinovich and modified by W. Haton, J. Edmonds, J. Ibers, and D. Cahen.

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

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

[15] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

TABLE II

POSITIONAL[a] AND ANISOTROPIC[b] THERMAL PARAMETERS

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ce	0.01078(3)	1/4	0.12093(4)	21.1(1)	45.7(2)	82.8(4)		-14.0(2)	
K	0.17927(11)	1/4	0.52383(14)	28.5(7)	46.6(8)	98.1(15)		-9.9(7)	
O_1	0.2368(4)	1/4	0.8034(5)	23(2)	52(3)	111(5)		0(2)	
O_2	0.1979(3)	0.0805(3)	0.6662(4)	45(2)	53(2)	110(4)	-3(2)	-5(2)	9(3)
C_{11}	0.0100(4)	0.2042(5)	-0.1643(6)	33(2)	68(3)	92(4)	2(2)	1(3)	-15(3)
C_{12}	-0.0345(5)	0.1288(4)	-0.0942(5)	37(3)	42(3)	117(6)	5(2)	-19(3)	-13(3)
C_{13}	-0.0970(4)	0.1288(4)	0.0022(5)	37(3)	49(3)	126(6)	-12(2)	-25(3)	14(4)
C_{14}	-0.1422(4)	0.2000(5)	0.0710(5)	24(2)	81(4)	108(5)	-11(3)	-10(3)	16(4)
C_{21}	0.1690(8)	1/4	0.1815(11)	25(4)	236(19)	97(10)		-2(4)	
C_{22}	0.1442(8)	0.1595(9)	0.2121(9)	86(7)	160(10)	163(10)	92(7)	-75(7)	-91(9)
C_{23}	0.0853(11)	0.1238(5)	0.2977(13)	155(12)	38(3)	233(14)	-7(5)	-147(11)	12(6)
C_{24}	0.0280(9)	0.1637(11)	0.3857(10)	77(7)	159(11)	152(10)	-75(8)	-66(6)	99(10)
C_{25}	0.0076(6)	1/4	0.4191(11)	20(3)	121(12)	135(11)		6(4)	
C_{d1}	0.2827(4)	0.1653(4)	0.8225(5)	30(2)	57(3)	115(5)	11(2)	-6(3)	-3(4)
C_{d2}	0.2278(4)	0.0824(4)	0.8079(5)	43(3)	51(3)	99(5)	10(2)	-4(3)	7(3)
C_{d3}	0.1481(6)	0.0029(4)	0.6418(5)	57(4)	43(3)	129(6)	1(3)	-6(4)	-1(4)

[a] Fractional cell coordinates. [b] Values of β are multiplied by 10^4; the form of the thermal correction is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$.

TABLE III

POSITIONS FOR CYCLOOCTATETRAENE AND DIGLYME HYDROGEN ATOMS

Cyclooctatetraene[a]				Diglyme[b]			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
H_{11}	0.0522	0.1769	−0.2300	H_1	0.3244	0.1619	0.7462
H_{12}	−0.0149	0.0631	−0.1221	H_2	0.3085	0.1656	0.9182
H_{13}	−0.1153	0.0618	0.0306	H_3	0.2575	0.0213	0.8288
H_{14}	−0.1847	0.1725	0.1370	H_4	0.1835	0.0884	0.8790
H_{21}	0.2178	0.2500	0.1229	H_5	0.1032	0.0043	0.7096
H_{22}	0.1725	0.1076	0.1660	H_6	0.1293	0.0033	0.5415
H_{23}	0.0818	0.0556	0.2989	H_7	0.1796	−0.0583	0.6584
H_{24}	0.0002	0.1137	0.4331				
H_{25}	−0.0379	0.2500	0.4853				

[a] Calculated positions. Trigonal planar geometries are assumed for the carbon atoms. A C–H bond length of 1.0 Å and an isotropic thermal parameter of 6.0 Å^2 were assumed. [b] Positions for methylene hydrogens H_1–H_4 calculated assuming tetrahedral carbon atom geometries and the same bond length and thermal parameter as for the COT^{2-} methyl hydrogen positions; H_5–H_7 were obtained by idealizing the geometry of three observed peak positions as discussed in the text.

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	148.3 (6)	212.7 (5)	213.3 (6)	C_{21}	189 (14)	208 (10)	485 (20)
K	185 (2)	215 (2)	224 (2)	C_{22}	165 (10)	205 (8)	536 (16)
O_1	183 (8)	222 (5)	227 (7)	C_{23}	174 (8)	196 (9)	545 (18)
O_2	211 (4)	233 (5)	261 (6)	C_{24}	177 (8)	206 (10)	514 (18)
C_{11}	193 (5)	219 (8)	266 (7)	C_{25}	166 (13)	247 (10)	348 (17)
C_{12}	190 (6)	201 (7)	267 (7)	C_{d1}	186 (8)	224 (6)	257 (7)
C_{13}	181 (7)	206 (7)	288 (8)	C_{d2}	195 (6)	222 (7)	264 (9)
C_{14}	174 (8)	214 (6)	297 (7)	C_{d3}	208 (7)	238 (6)	288 (10)

isotropic thermal parameters. Anisotropic refinement of this model showed rms amplitude of vibration around the ring circumference for the carbons which were greater than 0.6 Å, and the C–C distances were unrealistic.

To solve this problem a Fourier synthesis on F_{obsd} with phases from F_{calcd} was computed for one section in the plane of the COT ring (Figure 1). From this map it can be seen that there is some continuous distribution of electron density around the ring with evidence for higher density or localization at the locations on the mirror plane ($y = 0.25$), and at three positions off the plane. Three cycles of anisotropic refinement of this model lowered the weighted R factor to 7.39%.

In an effort to improve the model and to establish the nature of the thermal motion or disorder we treated the abnormal ring as five independent atoms each of which had an occupancy α. Superimposed on this was a torus of electron density which was scaled as $1 - \alpha$. The occupancy factor, α, of one of the ring carbons was varied and the value refined to 0.92. Since no significant improvement accompanied this model, the COT ring was described simply as five crystallographically independent atoms, two on the mirror plane and three off. It should be emphasized that, in contrast, ring 1 is localized as shown by the Fourier section in Figure 1. The alternative choice of space group $Pn2_1a$ was rejected after trial refinements in which the carbon atoms of ring 2 were slightly shifted from the imposed geometry of the mirror plane.

The hydrogen atom positions for the two COT rings and the methylene carbons on the diglyme were calculated by assuming tetrahedral (for the methylene carbons) or planar (for the COT) geometry and C–H bond lengths of 1.0 Å.[2]

A difference Fourier synthesis on F which included all nonhydrogen atoms and fixed contributions from the calculated ring and methylene hydrogen atoms was calculated after three cycles of least-squares refinement. The data with $(\sin\theta)/\lambda$ greater than 0.4 were rejected. The three largest peaks in the Fourier map which were not ripple around the Ce atom were all about 0.9–1.0 Å from the methyl carbon atom of the diglyme and had approximately tetrahedral geometry around the methyl carbon. A group of three hydrogen atoms with imposed tetrahedral symmetry was fitted to these three observed peak positions.

In the final anisotropic refinement, the structure factor contributions for the ring, methylene, and methyl hydrogen atoms were included. A fixed, isotropic thermal parameter for each hydrogen atom of 6.0 Å was assumed. Inspection of the most intense reflections revealed evidence of secondary extinction so the extinction parameter was also varied.[16]

The model converged to give the final agreement factors

$$R_1 = [\sum||F_o| - F_c||]/\sum|F_o| = 0.059$$

$$R_2 = [(\sum w(|F_o| - |F_c|)^2)/\sum wF_o^2]^{1/2} = 0.067$$

The final error in an observation of unit weight is 1.59.

A final difference Fourier showed no peaks greater than 0.59 e/Å^3 which were not within 1 Å of the cerium atom position. The largest of the remaining peaks were distributed between the carbon atoms of COT ring 2. The positional and anisotropic thermal parameters from the final least-squares cycle and their associated standard deviations are listed in Table II. The calculated hydrogen positions are given in Table III and the root-mean-square amplitude of vibration of all nonhydrogen atoms are given in Table IV.[17]

Description of Structure and Discussion

The molecular structure consists of a contact ion pair formed by the $[Ce(C_8H_8)_2]^-$ anion and the diglyme-coordinated potassium cation, as shown in Figure 2. The anion consists of a central cerium atom lying on the mirror plane which is symmetrically π bonded to the two $C_8H_8^{2-}$ rings. The Ce–C bond lengths are equal within experimental error and average 2.742 (8) Å. The mean M–C–M angle for adjacent carbons in the dianion ring is 30.2 (10)°. Carbon–metal–carbon angles, where the two carbon atoms are separated by three ring atoms and are on opposite sides of the ring, average 81.7 (9)°. As discussed in the Experimental Section, the best model for the geometry of the cyclooctatetraene dianion rings was one in which the mirror plane bisects two C–C bonds in ring 1 and passes two carbon atoms in ring 2. This imposes crystallographic mirror symmetry upon the $[Ce(C_8H_8)_2]^-$ anion. The molecular geometry, however, is very close to D_{8d}. The bond lengths and angles for the cerium inner coordination sphere are summarized in Table V.

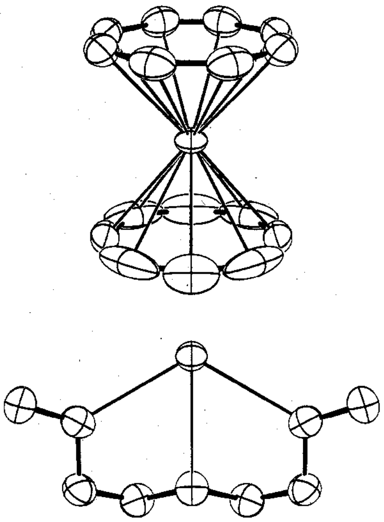

Figure 2.—A perspective view of the contact ion pair, $[K(diglyme)][Ce(C_8H_8)_2]$. Thermal ellipsoids are drawn at the 50% probability contour scale.

TABLE V

BOND LENGTHS AND ANGLES FOR THE $[Ce(C_8H_8)_2]^-$ ANION

Atoms	Distance, Å	Group	Angle, deg
Ce–C_{11}	2.745 (5)	Mean C_i–Ce–C_{i+1}	30.2 (10)[b]
Ce–C_{12}	2.743 (5)		
Ce–C_{13}	2.727 (6)	Mean C_i–Ce–C_{i+4}	81.7 (9)[c]
Ce–C_{14}	2.718 (6)		
Ce–C_{21}	2.733 (13)		
Ce–C_{22}	2.723 (8)		
Ce–C_{23}	2.729 (7)		
Ce–C_{24}	2.772 (6)		
Ce–C_{25}	2.791 (11)		
Mean Ce–C	2.742 (8)[a]		

[a] Standard deviations for the mean values reported in this and subsequent tables were estimated from the variance using the equations $\sigma^2 = (\Sigma_{i=1}^{n}(x_i - \bar{x})^2)/(n - 1)$ and $\sigma(\bar{x}) = \sigma/(\sqrt{n}$ where σ is the standard deviation of an individual observation and $\sigma(\bar{x})$ is the standard deviation of the mean. [b] Atoms i and $i + 1$ are adjacent in the cyclooctatetraene rings. [c] Atoms i and $i + 4$ are separated by three carbon atoms in the ring; half this value is the angle between the molecular axis and the ring carbon atoms.

TABLE VI

BOND LENGTHS AND ANGLES FOR THE POTASSIUM–DIGLYME COMPLEX

Atoms	Distance, Å	Diglyme[a] atoms	Molecule distance
K–C_{21}	3.208 (10)	O_1–C_1	1.429 (7)
K–C_{22}	3.236 (7)	C_1–C_2	1.493 (9)
K–C_{23}	3.183 (8)	C_2–O_2	1.420 (6)
K–C_{24}	3.110 (9)	O_2–C_3	1.394 (8)
K–C_{25}	3.062 (12)		
		Group	Angle, deg
Mean K–C	3.160 (32)	C_1'–O_1–C_1	112.3 (5)
K–O_1	2.792 (5)	O_1–C_1–C_2	107.3 (5)
K–O_2	2.741 (4)	C_1–C_2–O_2	108.7 (4)
		C_2–O_2–C_3	112.4 (4)

[a] Oxygen atom O_1 is on the mirror plane and C_3 is the diglyme methyl carbon atom.

One surprising feature of the molecular structure is the coordination of the potassium ion. The potassium ion also lies on the crystallographic mirror plane. Only one side of the potassium ion is coordinated by the diglyme; the remaining side is symmetrically coordinated to COT^{2-} ring 2 with an average K–C bond length of 3.16 (3) Å. In the diglyme complex the two independent K–O distances, 2.792 (5) Å from the oxygen on the mirror plane and 2.74 (4) Å for the other oxygen, are approximately equal. The diglyme molecule has normal bond distances and angles which are summarized along with the bond distances for the potassium inner coordination sphere in Table VI.

The two cyclooctatetraene dianion rings are both planar and have average C–C bond lengths of 1.388 (28) and 1.356 (21) Å for ring 1 and ring 2, respectively.

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[16] W. H. Zachariasen, *Acta. Crystallogr.*, **16**, 1139 (1963).

[17] A listing of structure factors will appear following these pages in the microfilm edition of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to code number INORG-72-3030. Remit check or money order of $3.00 for photocopy or $2.00 for microfiche.

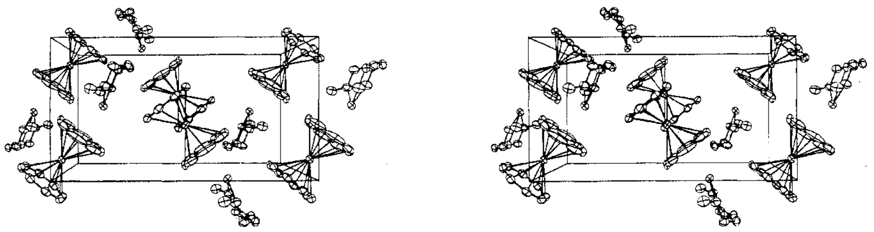

Figure 3.—A stereoscopic packing diagram of $[K(diglyme)][Ce(C_8H_8)_2]$. The entire unit cell is shown. The horizontal axis is *a* and the vertical is *c*. The origin of the cell is the lower left front corner.

TABLE VII
BOND LENGTHS (Å) AND ANGLES (DEG) FOR THE CYCLOOCTATETRAENE DIANIONS

Ring 1		Ring 2	
Bond	Distance	Bond	Distance
C_{11}–C_{11}' [a]	1.284 (14)	C_{21}–C_{22}	1.366 (17)
C_{11}–C_{12}	1.453 (10)	C_{22}–C_{23}	1.372 (20)
C_{12}–C_{13}	1.390 (10)	C_{23}–C_{24}	1.389 (20)
C_{13}–C_{14}	1.413 (9)	C_{24}–C_{25}	1.296 (20)
C_{14}–C_{14}'	1.400 (13)	Av C–C	1.356 (21)
Av C–C	1.388 (28)		
Group	Angle	Group	Angle
C_{11}'–C_{11}–C_{12}	136.6 (5)	C_{22}'–C_{21}–C_{22}	136.3 (7)
C_{11}–C_{12}–C_{13}	133.4 (6)	C_{21}–C_{22}–C_{23}	133.2 (9)
C_{12}–C_{13}–C_{14}	135.0 (5)	C_{22}–C_{23}–C_{24}	134.8 (8)
C_{13}–C_{14}–C_{14}'	135.0 (7)	C_{23}–C_{24}–C_{25}	134.8 (9)
Av C–C–C	135.0 (6)	C_{24}'–C_{25}–C_{24}	138.0 (8)
			135.4 (8)

[a] Prime indicates mirror related atom.

Bond lengths and angles for the two rings are summarized in Table VII. Ring 1 has maximum root-mean-square amplitudes of vibration which average 0.28 Å, but the corresponding values for ring 2 are almost two times as large. This value of the rms amplitude of vibration for ring 2 is much larger than has been observed in other structures containing COT^{2-}.[2,6,18] The short average bond distance for ring 2 is apparently a result of the large vibrational motion around the circumference of the dianion ring. It is impossible to distinguish between the possibilities of a static rotational disorder or unually high thermal motion. In any case it is clear that ring 2 is primarily located in a staggered configuration with respect to ring 1, but it is much less rigidly fixed in space. A weighted least-square plane (Table VIII) through the dianion rings has all of the atoms within 0.0005 Å of the plane for ring 1 and 0.007 Å for ring 2, with a standard deviation of about 0.005 and 0.009 Å, respectively. The planar rings in both compounds have the regular interior octagonal angle of 135°. The planarity of the rings and their bond distances and angles confirm the aromatic nature of the ten π-electron dianion rings in this structure.

TABLE VIII
WEIGHTED LEAST-SQUARES PLANES FOR PLANE OF CYCLOOCTATETRAENE DIANION

Ring 1		Ring 2	
Atom	Distance[a]	Atom	Distance[a]
C_{11}	−0.0002 (60)	C_{21}	0.006 (11)
C_{12}	0.0005 (55)	C_{22}	−0.003 (7)
C_{13}	−0.0004 (51)	C_{23}	−0.001 (8)
C_{14}	0.0002 (54)	C_{24}	0.005 (8)
		C_{25}	−0.007 (11)
Parameters from Equation of Plane[b]			
A	10.98	*A*	10.72
B	0.109	*B*	−0.407
C	7.11	*C*	7.23
D	−1.04	*D*	3.02

[a] Distances in Ångströms of individual atoms from weighted least-squares plane. [b] Equation for least-squares plane in orthorhombic coordinates of the form $Ax + By + Cz - D = 0$.

The crystal structure consists of four anion–cation ion pairs per unit cell. A stereoscopic packing diagram of the molecule is shown in Figure 3 as viewed normal to the *xz* plane. The cerium atoms lie on the mirror planes at $y = 0.25$ and $y = 0.75$. The molecules stack in sheets along these two planes as seen in the packing diagram. Within each planar array there are two different kinds of symmetry-related ion pairs. In a manner identical with the packing in the $U(C_8H_8)_2$ structure,[2] the two ion pairs have their symmetry axes approximately 90° apart and form a herringbone pattern along the mirror plane. The packing arrangement between such sheets can be clearly seen in the left of the diagram. If a vector from the cerium ion to the potassium ion of the same contact ion pair is imagined, it will be seen that such vectors point in opposite directions and make an angle of about 40° with the *c* axis. This kind of packing arrangement gains stability from a quadrupolar interaction in which the dipoles of one ion pair are directed in an opposite sense to the dipoles of the ion pair separated by $^1/_2$ in *y*. For the molecule whose cerium atom is approximately at $^1/_2$, $^1/_4$, $^3/_8$, it can be seen that the hydrogen atom of the ordered ring points almost directly at the cerium atom of the molecule with a cerium coordinate of $^1/_2$, $^3/_4$, $^5/_8$. The nonbonded cerium–hydrogen distances, however, are all greater than 3.5 Å and the closest intermolecular contacts occur between hydrogens of ring 1 and of the anion at $^1/_2$, $^1/_4$, $^3/_8$ and the hydrogens of ring 2 of the molecule at $^1/_2$, $^3/_4$, $^5/_8$. The shortest such distance is 2.99 Å. Thus there appears to be no significant intermolecular contacts which affect the molecular packing and the predominant effect may be the electrostatic one.

The general features of the bonding in this cerium salt are substantially the same as have been observed in the other π-carbocyclic structures with COT^{2-}. As discussed in the structure reports on $U(C_8H_8)_2$ and $Th(C_8H_8)_2$,[2] accurate predictions of M–C bond lengths in these homologous complexes can be made simply from changes in ionic radii. The Ce–C bond length in the structure reported in this paper can be estimated by taking the difference in ionic radii of Ce(III), 1.15 Å, and U(IV), 1.05 Å,[19] and adding this to the mean U–C bond length of $U(C_8H_8)_2$, 2.647 (4) Å. The

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predicted Ce–C bond length of 2.75 Å compares very well with the observed value of 2.742 (8) Å.

The one distinct difference of this structure from the ones previously reported which contain COT^{2-} is the large thermal motion of the COT^{2-} ring 2 coordinated to both the Ce and K ions. In this case the dianion is sandwiched between two positive charges and might be expected to be somewhat less tightly coordinated to the cerium. However, the equal average Ce–C bond lengths for rings 1 and 2 evidence that this is not the case.

In summary, the molecular symmetry of [Ce(C$_8$H$_8$)]$^{2-}$ anion is D_{8d}. Although the rings are staggered instead of eclipsed, the coordination geometry is substantially identical with that for the actinide compounds, U(C$_8$H$_8$)$_2$ and Th(C$_8$H$_8$)$_2$.[2] In both the [Ce(C$_8$H$_8$)$_2$]$^-$ and U(C$_8$H$_4$(CH$_3$)$_4$)$_2$[20] complexes the characterization of rotameric configurations different from the eclipsed geometry demonstrates that the barrier to rotation is very low and that the most stable geometry in the solid state may be largely determined by intermolecular rather than intramolecular interactions.

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Electron Spin Resonance Studies of Ni(diars)$_2$Cl$_2$$^+$

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Electron spin resonance studies have been carried out on the spin-doublet complexes [Ni(diars)$_2$Cl$_2$]Y (Y$^-$ = Cl$^-$, ClO$_4$$^-$). The esr parameters measured on samples diluted in a diamagnetic host crystal [Co(diars)$_2$Cl$_2$]ClO$_4$ are as follows: $g_{\parallel} = 2.008$, $g_{\perp} = 2.142$; $A_\sigma{}^{As} = -8.5$, $A_\pi{}^{As} = -6.9$, $A_z{}^{As} = -32$, $A_x{}^{Cl} = -32$, $A_y{}^{Cl} = -50$, $A_z{}^{Cl} = -29$ G. From these studies it is suggested that the energy-level ordering of 3d orbitals in Ni(diars)$_2$Cl$_2$$^+$ is $a_g(x^2 - y^2) < b_{2g}(xz) \approx b_{3g}(yz) < a_g(z^2) < b_{1g}(xy)$, and that in the ground state the unpaired electron occupies the $a_g(z^2)$ molecular orbital which is strongly delocalized over the metal and all six ligand donor atoms. In a concentrated powder of [Ni(diars)$_2$Cl$_2$]Cl, a rhombic g tensor is observed ($g_1 = 2.054$, $g_2 = 2.091$, $g_3 = 2.142$). Admixture of Ni 3d$_{xz}$ in the $a_g(z^2)$ molecular orbital as a result of a change in axial (Ni–Cl) interaction in the concentrated powder is suggested as the probable explanation of this observation.

Introduction

The electronic structure of the six-coordinate paramagnetic species [Ni(diars)$_2$X$_2$]Y (diars = *o*-phenylenebisdimethylarsine; X$^-$ = Cl$^-$, Br$^-$, SCN$^-$; Y$^-$ = Cl$^-$, Br$^-$, SCN$^-$, ClO$_4$$^-$) has been the subject of two recent electron spin resonance studies. Rogers and Manoharan,[1] on the basis of the observed halide superhyperfine splittings, proposed that the unpaired electron is in the metal d$_{z^2}$ orbital. However, we had pointed out in an earlier communication[2] that a $^2A_g(d_{z^2})$ ground state is not consistent with the highly anisotropic three-g-value powder spectrum exhibited by [Ni(diars)$_2$Cl$_2$]Cl. As an alternative we proposed a model in which the unpaired electron is delocalized primarily over the ligands in an orbital of xy symmetry.

Comparison of our powder data and the solution results of Rogers and Manoharan[1] suggests that the g values of the Ni(diars)$_2$X$_2$$^+$ system are extremely sensitive to environmental effects. Thus we have investigated single-crystal and dilute-powder esr spectra of the Ni(diars)$_2$Cl$_2$$^+$ cation in several hosts. In this paper we report an analysis of the new esr data and discuss the probable electronic ground state of the [Ni(diars)$_2$X$_2$]Y complexes.

Experimental Section

Preparation of Compounds.—[Ni(diars)$_2$Cl$_2$]Cl,[3] [Co(diars)$_2$Cl$_2$]Cl,[4] [Ni(diars)$_2$Cl$_2$]ClO$_4$,[3] [Co(diars)$_2$Cl$_2$]ClO$_4$,[4] and [Rh(diars)$_2$Cl$_2$]Cl[5] were prepared according to literature methods. Crystals for esr spectra were grown from ethanol solution. These crystals contained 1–3% Ni(diars)$_2$Cl$_2$$^+$ doped into the two cobalt salts. Powders were prepared by grinding crystals of [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl and [Ni(diars)$_2$Cl$_2$]Cl in [Rh(diars)$_2$Cl$_2$]Cl which contained approximately 75, 50, 25, 10, and 3 mol % Ni.

Instrumental Procedure.—Esr spectra were taken using both a Varian V-4502 X-band spectrometer with a V-4532 dual sample cavity and a Varian V-4500 K-band spectrometer. In the X-band experiments the field was calibrated using a standard solid sample of DPPH. In the K-band experiments an Alpha Model 675 nmr gaussmeter was used for field calibration. All low-temperature experiments were done using a Varian V-4540 variable temperature apparatus.

Single-Crystal Measurements.—Single-crystal measurements on the X-band spectrometer were made using a Magna Devices M-10 rotating sample holder. Spectra were taken on doped crystals of [Ni(diars)$_2$Cl$_2$]Cl in [Co(diars)$_2$Cl$_2$]Cl and [Ni(diars)$_2$Cl$_2$]ClO$_4$ in [Co(diars)$_2$Cl$_2$]ClO$_4$. The crystal structures of both

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