

Contribution from the Chemistry Department,
Oregon State University, Corvallis, Oregon 97331**Preparation, Crystal and Molecular Structure, and Properties of an Asymmetric Lanthanide Cyclooctatetraene Complex $[\text{Ln}(\text{C}_8\text{H}_8)(\text{OC}_4\text{H}_8)_2][\text{Ln}(\text{C}_8\text{H}_8)_2]$,****Where Ln = La, Ce, Nd, and Er**

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This paper reports a series of lanthanide complexes of formula $[\text{Ln}(\text{C}_8\text{H}_8)(\text{OC}_4\text{H}_8)_2][\text{Ln}(\text{C}_8\text{H}_8)_2]$ where Ln is La, Ce, Nd, and Er. The complexes were prepared by allowing metal atoms to react with cyclooctatetraene (COT) at -196°C and subsequently extracting the resulting compounds with tetrahydrofuran (THF). Reaction with Yb atoms yielded the known compound $\text{Yb}(\text{C}_8\text{H}_8)$. A single-crystal x-ray determination of the neodymium compound was done. All COT rings are present as the ten- π -electron aromatic dianion. The present structure exhibits two distinct differences from those of other lanthanide and actinide COT compounds. First, the COT^{2-} rings in the anion, $\text{Nd}(\text{COT})_2^-$, are neither equidistant from the Nd atom nor parallel. Second, the Nd atom in the cation, $\text{Nd}(\text{COT})(\text{THF})_2^+$, is asymmetrically located with respect to the central COT^{2-} ring with Nd-C distances which range from 2.68 (1) to 4.63 (3) Å. Crystal data are as follows: monoclinic space group $P2_1/c$, cell constants $a = 16.664$ (3) Å, $b = 12.778$ (3) Å, $c = 14.370$ (4) Å, $\beta = 108.90$ (2)°, $Z = 4$, $\rho_{\text{obsd}} = 1.75$ g/cm³, $\rho_{\text{calcd}} = 1.71$ g/cm³. The structure has been refined with full-matrix least-squares methods using 3351 independent and nonzero reflections. For the 1371 reflections for which $F^2 > 3\sigma(F^2)$, the standard unweighted R factor is 4.6%. Physical and chemical evidence is given which indicates that all the complexes have the structure of the Nd member.

Introduction

Interest in lanthanide organometallic chemistry has blossomed since the discovery of bis(cyclooctatetraenyl)uranium(IV) by Streitwieser and Müller-Westerhoff.¹ The development in this area has occurred through the preparation of new lanthanide organometallic compounds and through the determination of their structures. π -Carbocyclic complexes of the lanthanides have received considerable attention since the tris(cyclopentadienyls) were first reported by Wilkinson and Birmingham² in 1954. Recent work has focused on cyclooctatetraene (C_8H_8) complexes with the syntheses of the following: $\text{K}[\text{Ln}(\text{C}_8\text{H}_8)_2]$,³ $[\text{Ln}(\text{C}_8\text{H}_8)\text{Cl}\cdot 20\text{C}_4\text{H}_8]_2$,⁴ $[\text{Ln}(\text{C}_8\text{H}_8)(\text{C}_2\text{H}_5)]$,⁵ $\text{Yb}(\text{C}_8\text{H}_8)$,⁶ and $\text{Eu}(\text{C}_8\text{H}_8)$.⁶ The structural work has kept pace with the synthetic work with the molecular geometry now established for the following systems: $\text{Sm}(\text{C}_9\text{H}_7)_3$ ⁸ ($\text{C}_9\text{H}_7 = \text{indenyl}$), $\text{Nd}(\text{C}_5\text{H}_4\text{CH}_3)_3$,⁹ $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$,¹⁰ $[\text{Ce}(\text{C}_8\text{H}_8)\text{Cl}\cdot 20\text{C}_4\text{H}_8]_2$,¹¹ $\text{U}(\text{C}_8\text{H}_8)_2$,¹² octamethyluranocene,^{13a} and octaphenyluranocene.^{13b}

In all the known f transition metal cyclooctatetraene (COT) complexes, the COT behaves as a planar ten- π -electron aromatic dianion, COT^{2-} .^{14a,b} The lanthanides, with the exception of Eu and Yb, are always present as the +3 cations. The object of this work was to prepare a new class of lanthanide COT complexes with the stoichiometry $\text{Ln}_2(\text{COT})_3$ (where Ln is any lanthanide ion). This stoichiometry was observed for all the metals studied here, La, Ce, Nd, and Er with the exception of Yb which gave the known compound $\text{Yb}(\text{COT})$.⁶ Apparently the cyclooctatetraene does not oxidize Yb to Yb^{3+} which made the promise of $\text{Ce}(\text{COT})_2$ very unlikely by this technique. $\text{Ce}(\text{COT})_2$, along with $\text{Ce}_2(\text{COT})_3$, was reported by Greco^{15a} et al. while this work was in its final stages. $\text{Ce}_2(\text{COT})_3$ was prepared by them by reduction of $\text{Ce}(\text{O}-i\text{-C}_3\text{H}_7)_4$ by $(\text{C}_2\text{H}_5)_3\text{Al}$ in the presence of COT. They report, however, and we quote " $\text{Ce}_2(\text{COT})_3$ is highly sensitive to O_2 and is immediately decomposed by deaerated water or alcohols; its very low solubility in organic solvents and its microcrystalline nature frustrate attempts to characterize it through ^1H NMR spectroscopy and x-ray diffraction (single crystal investigations)". In this paper we report the metal-atom synthesis, physical and chemical properties, and the x-ray structure (for $[\text{Nd}(\text{COT})\cdot 2\text{THF}][\text{Nd}(\text{COT})_2]$) of this new class of f transition metal COT complexes. A preliminary communication of this work has appeared.^{15b}

Experimental Section

Materials. La, Ce, Nd, Er, and Yb, 99.9%, were obtained from

Michigan Chemical Corp., St. Louis, Mich., and Research Chemicals, Phoenix, Ariz. Cyclooctatetraene, generously donated by Dr. E. N. Marvel of this department, was dried over molecular sieves and used without further purification. Tetrahydrofuran (THF) (Mallinkrodt Analytical Reagent Grade) was refluxed over LiAlH_4 and stored under vacuum over LiAlH_4 for at least 2 days before it was used. It was then vacuum transferred as needed to predried flasks. KBr (Harshaw, Infrared Quality) was dried at 150°C at 10^{-4} mmHg for several days and stored in the inert atmosphere box until used. UCl_4 was purchased from Research Organic Inorganic Chemicals, Sun Valley, Calif., and used without further purification. Prepurified Grade nitrogen (Air Reduction Co.) was used as received. The maximum oxygen content is guaranteed by the supplier to be less than 8 ppm.

Synthetic Procedures. The compounds in this study were all synthesized by reaction of metal atoms with COT. Several recent reviews of the technique are available.^{16,17}

The reactions were carried out in the reaction vessel shown in Figure 1. The vessel was constructed from a Pyrex 2-L round-bottom flask and a 3-in. glass pipe flange. It is equipped with three ports and a removable top plate. The 1-in. port is used for constant pumping on the system during the deposition. One $3/8$ -in. port is used to pump out volatile compounds after cocondensation is complete and the second $3/8$ -in. port, not shown in the drawing, is fitted with a high-vacuum gauge and a dry nitrogen inlet. Port connections are made using Cajon ultra-torr fittings. The top plate is vacuum fitted to the flange using an aluminum collar and O-rings. A $1/8$ -in. copper tube, through which the organic substrate is introduced, and two water-cooled copper electrodes are in the top plate. Adequate dispersion of the organic substrate is obtained by placing a tee and numerous holes in the $1/8$ -in. line. The metal atoms are generated by resistively heating a Sylvania Type BC 10064X30 tungsten basket or an aluminum oxide coated molybdenum boat, Sylvania MS003.

Following cocondensation of the reactants, the flask was allowed to warm to room temperature, and the volatile materials were pumped out under vacuum. The vessel was filled with nitrogen and, taking extreme precautions to exclude air by carefully capping all ports, was transferred to either a Forma Scientific Model No. 3818 stainless steel inert atmosphere box fitted with a No. 3851 evacuable interchange assembly and an oxygen and moisture free recirculating nitrogen atmosphere or a Vacuum Atmospheres Model He-493-2 drybox equipped with a recirculating train.

Typical Preparation of $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$. Fifteen milliliters (130 mmol) of COT and 1.0–2.0 g (7–14 mmol) of metal were cocondensed at -196°C for 30–60 min. The pressure inside the reaction vessel during cocondensation was kept below 4×10^{-4} mmHg. Higher pressures led to the polymerization of COT as the predominant reaction. Reaction was observed to take place on the vessel walls at -196°C as evidenced by the immediate formation of a gold colored substance with La, Ce, and Er, a bright green substance with Nd, and a purple substance with Yb. The vessel was warmed to room temperature and the excess COT removed leaving nonvolatile,

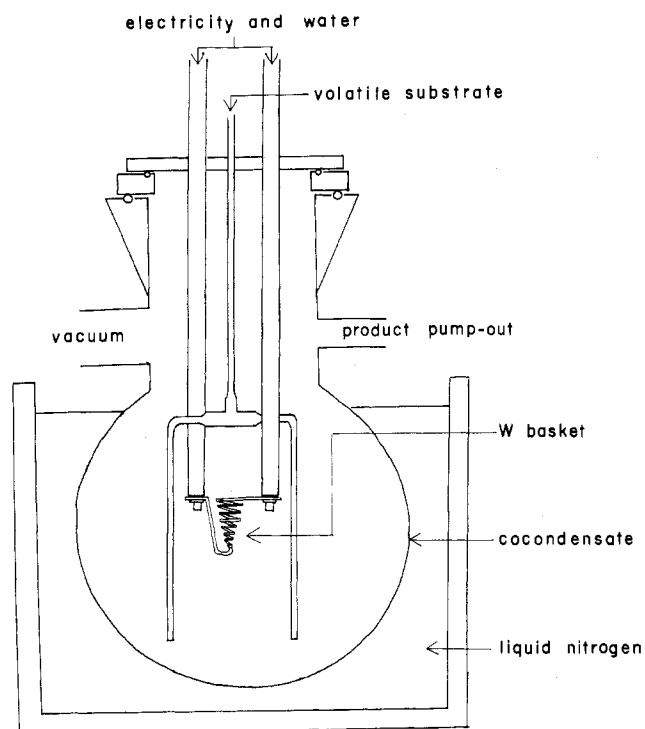


Figure 1. A schematic drawing of the metal atom reaction vessel.

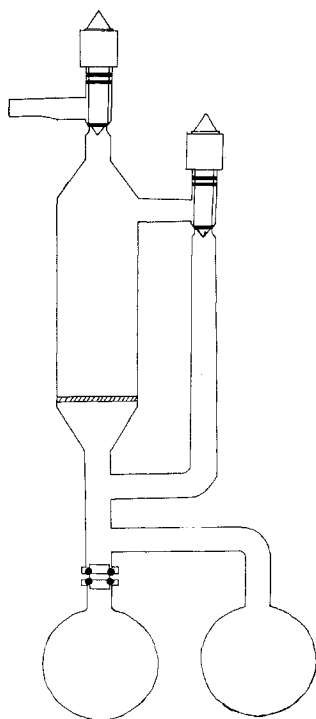


Figure 2. A schematic drawing of the Soxhlet extractor used for the purification and crystallization of $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$ compounds.

extremely air- and moisture-sensitive solids.

The vessel was transferred to the inert atmosphere box and the solid was placed in a Soxhlet extractor designed for continuous extraction through a sintered-glass filter.

The extractor is shown in Figure 2. The basic design of the extractor is that used by Streitwieser and co-workers¹⁴ for the purification of $\text{U}(\text{COT})_2$. Two major modifications have been made. First, the solvent flask is connected to the body of the extractor via a Fischer-Porter Solv-seal Teflon joint. This joint allows easy removal of the flask without having to break the extractor. Second, the

Table I. Metal Analyses of Cyclooctatetraene Lanthanide Complexes

Complex	% Ln	
	Found	Calcd
$[\text{La}_2(\text{C}_8\text{H}_8)_3] \cdot 2\text{C}_4\text{H}_8\text{O}$	39.24	37.83
$[\text{Ce}_2(\text{C}_8\text{H}_8)_3]$	47.25	47.28
$[\text{Nd}_2(\text{C}_8\text{H}_8)_3] \cdot 2\text{C}_4\text{H}_8\text{O}$	39.33	38.72
$[\text{Er}_2(\text{C}_8\text{H}_8)_3] \cdot 2\text{C}_4\text{H}_8\text{O}$	42.58	42.28
$\text{Yb}(\text{C}_8\text{H}_8)$	64.08	62.43

extractor has two J. Young Acton Type POR/10mm/RA valves purchased from Chemvac Associates, Columbus, S.C. These valves have Teflon O-ring seals and seats which allow a grease-free system.

After transfer of the solid, the extractor was removed from the drybox and evacuated; 75 mL of tetrahydrofuran (THF) was distilled into the extractor from the vacuum line and the extractor was sealed. The atmosphere within the extractor consisted of solvent vapor only. This allows operating temperatures below the normal boiling point of the solvent, an important feature if thermal stability is a problem. This also eliminates problems caused by maintaining a positive pressure on the system.

The first two or three extractions, containing dark yellow impurities, were poured into the side arm. These impurities were assumed to be polymeric material. Following these extractions, the solution passing the filter was nearly colorless. Gold crystals of $[\text{La}(\text{COT})(\text{THF})_2][\text{La}(\text{COT})_2]$ or $[\text{Ce}(\text{COT})(\text{THF})_2][\text{Ce}(\text{COT})_2]$ and green crystals of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$ grew during the 7–10-day extraction. Longer extraction times were required, 14–21 days, to grow the reddish brown $[\text{Er}(\text{COT})(\text{THF})_2][\text{Er}(\text{COT})_2]$ crystals. The $\text{Yb}(\text{COT})$ was extracted in 3 days using pyridine.

After extraction, the THF was poured into the side arm. Small amounts of THF were distilled back from the side arm and the crystals were washed. The washings were again poured into the side arm. The crystals were washed at least twice in this manner. The combined solutions in the side arm were reduced to near dryness under vacuum. In a typical run with 1.0 g of metal, approximately 0.5 g of product compound was isolated.

Analyses. Because these complexes are extremely air and moisture sensitive, commercial analyses were unsatisfactory. Streitwieser et al.¹⁴ have observed the same difficulty with their bis(cyclooctatetraene) lanthanide complexes.

Metal analyses were accomplished using back-complexometric titration procedures with disodium ethylenediaminetetraacetate (Na_2EDTA).¹⁸ Approximately 100 mg of sample was weighed in a sealed tube on a Mettler Type H16 balance. Two milliliters of distilled water was added to the weighed sample. The hydrolysis products were dissolved in dilute HNO_3 and diluted to 100 mL; 20-mL aliquots were treated with excess 0.01 M Na_2EDTA , 10 mL, and buffered to pH 8.4–8.7 with $\text{NH}_4\text{Cl}-\text{NH}_4\text{OH}$. Two drops of 1% Eriochrome black-T in 2,2',2''-nitrilotriethanol was added as the indicator. The solution was titrated with 0.01 M ZnCl_2 until the blue had completely changed to pink. Results are presented in Table I.

The gold cerium compound was observed to rapidly lose THF of solvation in the drybox and turn to a bright green. Therefore prior to analysis the cerium compound was pumped on under high vacuum at 160 °C for 1 h. This effectively removed all the THF of solvation and yielded a bright green solid which analyzed to be $\text{Ce}_2(\text{C}_8\text{H}_8)_3$. A ^1H NMR of a CCl_4 extract of the hydrolysis product of this compound showed no residual THF. The YbC_8H_8 compound was heated to 250 °C for 2 h prior to analysis to ensure removal of all excess pyridine.

Physical Measurements. Infrared spectra were recorded as KBr pellets or Nujol mulls on a Perkin-Elmer 621 grating spectrophotometer and calibrated vs. polystyrene. Maxima are believed to be accurate to $\pm 2\text{ cm}^{-1}$.

The Raman spectrum of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$ was recorded on a sample sealed in a glass tube with a Cary 82 spectrophotometer using the 6471-Å exciting line of a Spectra Physics Model 164 krypton ion laser operating at 100 mW.

Magnetic susceptibilities were measured at ambient temperature on samples sealed in glass tubes using an automatic Faraday susceptibility apparatus designed and built by Dr. John Gardner of the Physics Department of this University.

Structure of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$. X-Ray Data Collection and Reduction. Several crystals were sealed in 0.3-mm glass capillaries

Table II. Summary of Crystal Data

Molecular formula: $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$
 Mol wt: 745.13
 Linear absorption coefficient, μ : 33.19 cm^{-1}
 Obsd density:^a 1.75 g/cm^3
 Calcd density: 1.71 g/cm^3
 Crystal dimensions: $0.3 \times 0.08 \times 0.08$ mm
 Space group: $P2_1/c$, monoclinic
 Molecules/unit cell: 4
 Cell constants:^b $a = 16.664$ (3), $b = 12.778$ (3), $c = 14.347$ (4) Å;
 $\beta = 108.90$ (2) $^\circ$; $\cos \beta = 0.32393$
 Cell volume: 2894.74 Å³

^a Experimental density measurements were obtained by flotation measurements in $\text{CCl}_4\text{-CBr}_4$. ^b Mo $K\alpha_1$ radiation, λ 0.70926 Å. Ambient temperature of 21 $^\circ\text{C}$.

under a nitrogen atmosphere. In order to hold the crystals in place, the inside walls had been coated with a thin layer of Dow Corning Silicone High Vacuum Lubricant. The capillaries were outgassed at 80–100 $^\circ\text{C}$ at 10^{-4} mmHg for 15 h before they were taken to the inert atmosphere box.

The crystal chosen for study was a bright green rod which was mounted on a Syntex $P\bar{1}$ computer-controlled four-circle diffractometer.¹⁹ A 3 h exposure orientation photograph was taken using graphite-monochromatized Mo $K\alpha$ radiation. The unit cell parameters were initially determined using the reflections from the photograph. A preliminary set of reflections was measured to determine the space group. These reflections showed monoclinic symmetry with the following systematic absences: $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$. Space group $P2_1/c$, No. 14, is the only choice which is consistent with these conditions. This was subsequently verified by the complete crystal structure determination.

The final unit cell constants and orientation matrix were determined by a least-squares refinement of 15 reflections whose 2θ angles ranged from 12 to 22 $^\circ$. The resulting cell parameters and other pertinent data are presented in Table II.

Intensity data were collected using a θ - 2θ scan mode and a scintillation counter. The 2θ scans for each reflection were from 1 $^\circ$ below the $K\alpha_1$ peak to 1 $^\circ$ above the $K\alpha_2$ peak with a scan rate of 1 $^\circ$ /min. The background counting time was equal to the scan time for each reflection. All independent reflections in the sphere $0 < 2\theta \leq 42.5^\circ$ and about 150 reflections in the sphere $42.5 \leq 2\theta \leq 45^\circ$ were collected. During the experiment, the intensities of the 012, $\bar{1}02$, and 714 reflections were measured every 50 reflections as a check on the stability of the crystal and the instrument. Of the total of 4203 reflections collected, 3541 were independent and 3351 were both independent and nonzero.

Unfortunately, after the data had been collected, but before absorption correction data could be taken, the crystal fell from its position in the capillary and orientation data were therefore impossible to collect. The maximum absorption correction is calculated to be 2.08 while the minimum correction is 1.21. However, because the crystal was mounted with the long axis parallel to the ϕ axis few reflections would require the maximum correction.

STUDIT, a program which averages intensities with identical and point-group-equivalent indices, and INCOR, a program which applies the Lorentz and polarization factors, were used in the data reduction. Coefficients for a sharpened Patterson function and E coefficients were calculated using PASHCO. The above calculations were done locally on a CDC 3300 computer.

Solution and Refinement of the Structure. The solution and refinement calculations were done on a CDC 7600 computer at the University of California, Berkeley. The programs used are part of the x-ray crystallographic library maintained by Dr. Allan Zalkin.

The positions of the Nd atoms were determined directly from an E map using the phases calculated by MULTAN for the 300 largest E coefficients from PASHCO. These positions were checked against a three-dimensional Patterson map and were consistent with the major peaks. Anisotropic least-squares refinement on the neodymium atoms using LSLONG, followed by difference Fourier synthesis on F using FORDAP, located the positions of the two THF oxygen atoms and 22 COT carbon atoms. Three additional least-squares cycles with the neodymium atoms assigned anisotropic thermal parameters and the other atoms assigned isotropic thermal parameters followed by another difference Fourier located the positions of the remaining carbon atoms. Four least-squares cycles with all nonhydrogen atoms assigned an-

Table III. Final Positional Parameters and Isotropic Thermal Factors with Esd's^a

Atom	x	y	z	B_{iso} , Å ²
Nd(1)	0.51941 (8)	0.24249 (12)	0.10846 (10)	
Nd(2)	0.82817 (9)	0.31416 (12)	0.14978 (11)	
O(1)	0.8456 (10)	0.4663 (13)	0.2742 (11)	4.3 (4)
O(2)	0.8132 (9)	0.4841 (12)	0.0511 (12)	3.8 (4)
C(1)	0.3591 (16)	0.1887 (25)	0.0134 (19)	5.5 (6)
C(2)	0.3678 (20)	0.1530 (24)	0.1048 (25)	6.8 (8)
C(3)	0.4052 (18)	0.1909 (27)	0.1962 (22)	6.3 (7)
C(4)	0.4349 (18)	0.2878 (23)	0.2356 (21)	5.4 (7)
C(5)	0.4524 (21)	0.3856 (27)	0.2006 (25)	7.1 (8)
C(6)	0.4438 (19)	0.4237 (24)	0.1074 (24)	6.4 (8)
C(7)	0.4103 (21)	0.3874 (26)	0.0096 (24)	7.0 (8)
C(8)	0.3726 (16)	0.2849 (20)	-0.0316 (19)	4.8 (6)
C(9)	0.6061 (16)	0.1088 (21)	0.0220 (20)	4.5 (6)
C(10)	0.6175 (15)	0.0660 (18)	0.1142 (18)	3.6 (5)
C(11)	0.6492 (15)	0.1059 (19)	0.2087 (17)	3.5 (5)
C(12)	0.6786 (13)	0.2038 (18)	0.2527 (16)	3.0 (5)
C(13)	0.6810 (13)	0.3082 (20)	0.2148 (16)	3.1 (5)
C(14)	0.6632 (13)	0.3557 (17)	0.1175 (16)	2.7 (5)
C(15)	0.6429 (14)	0.3126 (20)	0.0255 (16)	3.3 (5)
C(16)	0.6160 (15)	0.2100 (19)	-0.0166 (17)	4.1 (6)
C(17)	0.9410 (17)	0.2964 (21)	0.0510 (19)	4.9 (6)
C(18)	0.8770 (18)	0.2215 (22)	0.0134 (20)	5.8 (7)
C(19)	0.8353 (19)	0.1416 (23)	0.0487 (22)	5.8 (7)
C(20)	0.8416 (21)	0.1058 (24)	0.1438 (27)	6.6 (8)
C(21)	0.8944 (20)	0.1359 (25)	0.2413 (24)	6.7 (8)
C(22)	0.9580 (17)	0.2168 (22)	0.2818 (19)	5.4 (7)
C(23)	0.9945 (19)	0.2938 (23)	0.2398 (22)	5.8 (7)
C(24)	0.9912 (19)	0.3268 (23)	0.1458 (23)	6.2 (7)
C(25)	0.7814 (19)	0.5499 (24)	0.2684 (21)	6.1 (7)
C(26)	0.8289 (19)	0.6389 (23)	0.3334 (22)	6.1 (7)
C(27)	0.9036 (17)	0.5798 (22)	0.4106 (20)	5.3 (7)
C(28)	0.9264 (16)	0.4908 (19)	0.3528 (19)	4.4 (6)
C(29)	0.8796 (20)	0.5674 (25)	0.0763 (22)	6.9 (8)
C(30)	0.8474 (18)	0.6510 (23)	0.0010 (21)	6.2 (8)
C(31)	0.7976 (20)	0.5950 (25)	-0.0896 (22)	6.0 (7)
C(32)	0.7712 (15)	0.4890 (18)	-0.0553 (17)	3.4 (5)

^a Estimated standard deviation of the last digit(s) is in parentheses.

Table IV. Final Anisotropic Temperature Factors (Å²)^a

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Nd(1)	2.57 (6)	3.18 (8)	3.89 (7)	0.34 (7)	1.14 (5)	0.27 (7)
Nd(2)	2.92 (6)	3.54 (8)	3.54 (7)	1.05 (6)	1.17 (6)	0.37 (7)

^a Anisotropic temperature factors are of the form $\exp[-1/4(a^{*2} B_{11}h^2 + b^{*2}B_{22}k^2 + c^{*2}B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl)]$.

isotropic thermal parameters gave two carbon atoms, C(1) and C(29), nonpositive thermal parameters. Rather than pursue the anisotropic calculation further we returned to the least-squares calculation with the Nd atoms assigned anisotropic thermal parameters and the carbon and oxygen atoms assigned isotropic thermal parameters. No attempt was made to locate the hydrogen atoms.

Full-matrix least-squares refinements of F were used in which the function minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, w , is $1/\sigma^2(F_o)^2$. The scattering factors for Nd³⁺ and neutral O and C were taken from the values tabulated by Cromer and Mann.²⁰ Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ were taken from the values tabulated in ref 21. The final agreement factors $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and R_2 (weighted R factor) = $[\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ were 4.6 and 3.7%, respectively. The standard deviation of an observation of unit weight is 0.900.

The positional parameters and isotropic thermal parameters from the final least-squares refinement together with their estimated standard deviations are given in Table III. The anisotropic thermal parameters for the two neodymium atoms are given in Table IV.

Bond distances and angles were calculated using DISMAT. The planarity of the COT rings and the dihedral angles between the planes were calculated using LSPLAN.

Figure 3 was drawn using ORTEPB1, a local version of C. K. Johnson's ORTEP plotting program.

Table V. Bond Lengths and Angles in Cyclooctatetraene Rings

Bond	Length, Å	Group	Angle, deg
C(1)-C(2)	1.35 (4)	C(8)-C(1)-C(2)	138 (3)
C(2)-C(3)	1.35 (4)	C(1)-C(2)-C(3)	134 (3)
C(3)-C(4)	1.38 (4)	C(2)-C(3)-C(4)	135 (3)
C(4)-C(5)	1.41 (4)	C(3)-C(4)-C(5)	137 (3)
C(5)-C(6)	1.39 (4)	C(4)-C(5)-C(6)	133 (3)
C(6)-C(7)	1.41 (4)	C(5)-C(6)-C(7)	137 (3)
C(7)-C(8)	1.49 (4)	C(6)-C(7)-C(8)	132 (3)
C(8)-C(1)	1.44 (4)	C(7)-C(8)-C(1)	133 (3)
Av	1.40 (2)	Av	135 (1)
C(9)-C(10)	1.39 (3)	C(16)-C(9)-C(10)	136 (2)
C(10)-C(11)	1.39 (3)	C(9)-C(10)-C(11)	133 (2)
C(11)-C(12)	1.41 (3)	C(10)-C(11)-C(12)	137 (2)
C(12)-C(13)	1.44 (3)	C(11)-C(12)-C(13)	134 (2)
C(13)-C(14)	1.46 (3)	C(12)-C(13)-C(14)	136 (2)
C(14)-C(15)	1.37 (3)	C(13)-C(14)-C(15)	132 (2)
C(15)-C(16)	1.45 (3)	C(14)-C(15)-C(16)	135 (2)
C(16)-C(9)	1.44 (3)	C(15)-C(16)-C(9)	135 (2)
Av	1.42 (1)	Av	135 (1)
C(17)-C(18)	1.40 (3)	C(24)-C(17)-C(18)	135 (3)
C(18)-C(19)	1.42 (3)	C(17)-C(18)-C(19)	139 (3)
C(19)-C(20)	1.41 (4)	C(18)-C(19)-C(20)	133 (3)
C(20)-C(21)	1.44 (4)	C(19)-C(20)-C(21)	133 (3)
C(21)-C(22)	1.46 (4)	C(20)-C(21)-C(22)	135 (3)
C(22)-C(23)	1.39 (4)	C(21)-C(22)-C(23)	134 (3)
C(23)-C(24)	1.40 (4)	C(22)-C(23)-C(24)	138 (3)
C(24)-C(17)	1.40 (4)	C(23)-C(24)-C(17)	133 (3)
Av	1.41 (1)	Av	135 (1)

Discussion

Structure of [Nd(COT)(THF)₂][Nd(COT)₂]. The molecular structure consists of an ion pair composed of an [Nd(COT)₂]⁻ anion and a [Nd(COT)(THF)₂]⁺ cation as shown in Figure 3. The anion is composed of Nd(1) and COT rings 1 and 2. The carbon atoms in ring 1 are numbered 1-8, while those in ring 2 are numbered 9-16. The cation is composed of Nd(2), COT ring 3, and two THF rings. The carbon atoms in ring 3 are numbered 17-24. The atoms in the first THF ring are numbered O(1) and C(25)-C(28), while the atoms in the second THF ring are numbered O(2) and C(29)-C(32).

In all of the known cyclooctatetraene complexes of f transition metals for which the structure has been determined [K(diglyme)][Ce(COT)₂],¹⁰ [Ce(COT)Cl·2THF]₂,¹¹ and U(COT)₂¹² (as well as the octamethyl-^{13a} and octaphenyl-uranocene^{13b}) the cyclooctatetraene behaves as a COT²⁻ anion. The ring is observed to have eightfold symmetry with normal aromatic C-C bond distances. The three cyclooctatetraene rings in the present structure show the same aromatic character. For example, the average C-C bond lengths in rings 1, 2, and 3 are 1.40 (2), 1.42 (1), and 1.41 (1) Å, respectively, Table V. These distances are within experimental error of the 1.39 Å average C-C bond length found in the above structures. The C-C-C interior angle of a planar octagon is 135°. The observed average angles in rings 1, 2, and 3 are all 1.35 (1)°. Finally the planar nature of the COT²⁻ dianion is clearly shown by reference to Table VI, in which the carbons in rings 1, 2, and 3 are seen to average 0.02, 0.04, and 0.02 Å from their respective least-squares planes.

There are a number of unusual features observed in this structure which have not been observed for other f transition metal cyclooctatetraene complexes. All the previously known structures which contain an M(COT)₂ unit show either D_{8h} or D_{8d} symmetry for this unit.¹⁰⁻¹³ The symmetry of the anion Nd(COT)₂⁻ unit in the present structure is C_s. The reduction in symmetry comes from nonequivalent metal-plane bond lengths and the nonparallelism of the planes of the rings. Ring 1 and ring 2 are symmetrically bonded to Nd(1) with an average Nd-C distance of 2.68 (1) Å for ring 1 and 2.79 (1) Å for ring 2 (Table VII). The planes of rings 1 and 2 intersect at an angle of 7.28°. This tilt causes the C(n)-C(n+8) distances to range from 3.71 (3) to 4.26 (4) Å (see Table VIII).

Table VI. Least-Squares Planes of Cyclooctatetraene Rings

Ring 1		Ring 2		Ring 3	
Atom	Distance ^a	Atom	Distance ^a	Atom	Distance ^a
C(1)	0.01	C(9)	-0.01	C(17)	-0.02
C(2)	-0.04	C(10)	-0.05	C(18)	0.01
C(3)	0.06	C(11)	0.01	C(19)	0.01
C(4)	-0.02	C(12)	0.07	C(20)	0.00
C(5)	-0.02	C(13)	-0.02	C(21)	-0.03
C(6)	0.02	C(14)	-0.07	C(22)	0.01
C(7)	0.01	C(15)	-0.05	C(23)	0.03
C(8)	-0.01	C(16)	0.03	C(24)	-0.02
Parameters from Equation of Planes ^b					
<i>A</i>	15.733	<i>A</i>	16.285	<i>A</i>	-12.578
<i>B</i>	-4.153	<i>B</i>	-2.591	<i>B</i>	8.372
<i>C</i>	-3.66	<i>C</i>	-3.711	<i>C</i>	3.919
<i>D</i>	4.81	<i>D</i>	9.516	<i>D</i>	-9.139
Angles between Planes, ^c Deg					
1-2	7.28	1-3	-22.47	2-3	-29.69

^a Distances in angstroms of individual atoms from least-squares plane. ^b Equation for least-squares plane in monoclinic coordinates of the form $Ax + By + Cz - D = 0$. ^c Negative values for angles involving plane 3 are a result of the form of the direction cosines of the normals to the planes.

Table VII. Neodymium-Carbon Distances

Ring 1	Distance, Å	Ring 2	Distance, Å
Nd(1)-C(1)	2.67 (3)	Nd(1)-C(9)	2.78 (2)
Nd(1)-C(2)	2.76 (3)	Nd(1)-C(10)	2.77 (2)
Nd(1)-C(3)	2.68 (3)	Nd(1)-C(11)	2.79 (2)
Nd(1)-C(4)	2.70 (3)	Nd(1)-C(12)	2.83 (2)
Nd(1)-C(5)	2.70 (3)	Nd(1)-C(13)	2.76 (2)
Nd(1)-C(6)	2.63 (3)	Nd(1)-C(14)	2.76 (2)
Nd(1)-C(7)	2.66 (3)	Nd(1)-C(15)	2.83 (2)
Nd(1)-C(8)	2.67 (3)	Nd(1)-C(16)	2.80 (2)
Av	2.68 (1)	Av	2.79 (1)
Ring 3	Distance, Å	Ring 2	Distance, Å
Nd(2)-C(17)	2.71 (3)	Nd(2)-C(14)	2.69 (2)
Nd(2)-C(18)	2.63 (3)	Nd(2)-C(13)	2.89 (2)
Nd(2)-C(19)	2.66 (3)	Nd(2)-C(15)	3.02 (2)
Nd(2)-C(20)	2.67 (3)	Nd(2)-C(12)	3.57 (2)
Nd(2)-C(21)	2.68 (3)	Nd(2)-C(16)	3.81 (3)
Nd(2)-C(22)	2.68 (3)	Nd(2)-C(11)	4.28 (3)
Nd(2)-C(23)	2.66 (3)	Nd(2)-C(9)	4.44 (3)
Nd(2)-C(24)	2.74 (3)	Nd(2)-C(10)	4.63 (3)
Av	2.68 (1)		

Table VIII. C(n)-C(n+8) Distances (Å) between Cyclooctatetraene Rings 1 and 2

C(1)-C(9)	4.20 (4)	C(5)-C(13)	3.87 (3)
C(2)-C(10)	4.26 (4)	C(6)-C(14)	3.71 (3)
C(3)-C(11)	4.15 (4)	C(7)-C(15)	3.92 (4)
C(4)-C(12)	4.13 (4)	C(8)-C(16)	4.10 (4)

The carbon atoms in the M(COT)₂ unit are in a nearly eclipsed configuration.

The coordination sphere about Nd(2) is also unique for f transition metal cyclooctatetraene complexes. It consists of ring 3, symmetrically bonded to Nd(2) with an average Nd-C distance of 2.68 (1) Å, together with the two THF oxygen atoms, average Nd-O distance of 2.57 (2) Å, and part of ring 2. In particular, C(14) from ring 2 is definitely in the coordination sphere of Nd(2) and C(13) and C(15) may well be. The Nd(2)-C(14) distance is 2.69 (2) Å while those of Nd(2)-C(13) and Nd(2)-C(15) are 2.89 (2) and 3.02 (2) Å, respectively. The asymmetric coordination of Nd(2) to ring 2 is probably a consequence of the Nd(2) filling its coordination sphere. The coordination number for Nd(2) may be counted as 5 from the COT²⁻ dianion (five π-electron pairs—see Hodgson and Raymond¹¹) and 2 from THF oxygens yielding 7. In contrast, by the same counting method Nd(1)

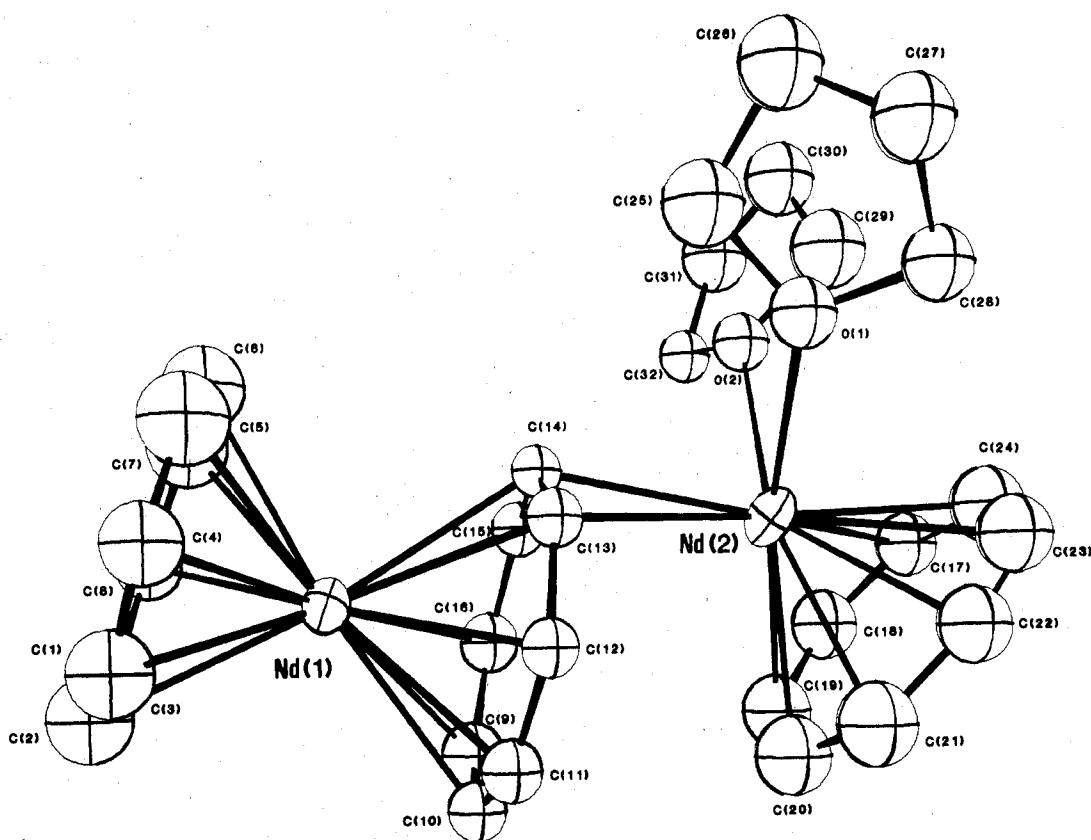


Figure 3. An ORTEP drawing of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$ approximately along the c axis.

is 10-coordinate. Therefore, Nd(2) is augmenting its coordination number from 7 to 10 by coordinating with carbons 13, 14, and 15 from ring 2. Although this coordination does not break the planarity of ring 2 it must be responsible for the Nd(1)-C bond distance increase for ring 2 of more than 0.1 Å. Both ring 1 and ring 3 are well within the estimated Nd-C bond distance of 2.69 Å while the ring 2 Nd-C distance is 2.79 (1) Å. This estimate was calculated by the method used by Raymond and co-workers.^{10,12} They accurately estimated the Th-C and Ce-C bond lengths in $\text{Th}(\text{COT})_2$ and $[\text{K}(\text{diglyme})][\text{Ce}(\text{COT})_2]$ by adding the difference between ionic radii of the metals and U^{4+} to the average U-C bond length in $\text{U}(\text{COT})_2$. The difference between Nd^{3+} , 1.09 Å, and U^{4+} , 1.05 Å, is 0.04 Å.²² Since the average U-C bond length in $\text{U}(\text{COT})_2$ is 2.65 Å¹² this gives an estimated Nd-C bond length of 2.69 Å.

The expansion of the coordination sphere to individual carbons in π -carbocyclic complexes has been observed for lanthanide cyclopentadienide compounds. For example, the crystal structure of neodymium tris(methylcyclopentadienide) shows both η^1 Nd-C and η^5 Nd-C interactions.⁹ The η^1 Nd-C bond lengths, 2.990 and 2.978 Å, are about 0.2 Å greater than the average of the η^5 bonds. Both $\text{Sc}(\text{C}_5\text{H}_5)_3$ and $\text{Sm}(\text{C}_5\text{H}_5)_3$ ⁷ also show η^5 and η^1 metal cyclopentadienide coordination. One of the more unusual examples is that of μ -di(η^5 : η^1 -cyclopentadienyl)thorium(IV) for which the η^1 bond lengths are 0.28 Å shorter than the η^5 bond lengths.²⁴

The question arises whether Nd(2) is π or σ bonded to C(14). The bond distance, 2.69 (2) Å, suggests π bonding. This distance is 0.2–0.4 Å longer than expected for a Nd-C σ bond based on the assumption that the difference between a Nd-C and a U-C σ bond is small. U-C σ bonds range from 2.33 to 2.50 Å.²⁵ The observed distance is that expected for a normal π bond between Nd^{3+} and a COT^{2-} ring (vide supra). Clearly, however, the Nd(2)-C(14) interaction cannot be a normal π bond, because no other Nd(2)-ring 2 distances are

Table IX. Bond Lengths (Å) and Angles (deg) for Tetrahydrofuran Rings

O(1)-C(25)	1.49 (3)	C(29)-C(30)	1.49 (4)
C(25)-C(26)	1.52 (4)	C(30)-C(31)	1.48 (4)
C(26)-C(27)	1.56 (4)	C(31)-C(32)	1.55 (4)
C(27)-C(28)	1.53 (3)	C(32)-O(2)	1.46 (3)
C(28)-O(1)	1.48 (3)	Nd(2)-O(1)	2.59 (2)
O(2)-C(29)	1.49 (3)	Nd(2)-O(2)	2.56 (2)
C(28)-O(1)-C(25)	110 (2)	O(2)-C(29)-C(30)	106 (2)
O(1)-C(25)-C(26)	106 (2)	C(29)-C(30)-C(31)	105 (2)
C(25)-C(26)-C(27)	102 (2)	C(30)-C(31)-C(32)	106 (2)
C(26)-C(27)-C(28)	104 (2)	C(31)-C(32)-O(2)	106 (2)
C(27)-C(28)-O(1)	104 (2)	O(1)-Nd(2)-O(2)	73.4 (5)
C(32)-O(2)-C(29)	107 (2)		

of comparable length. The next closest distance found is Nd(2)-C(13), 2.89 (2) Å.

It is also interesting that rings 1 and 2 are tilted so that the C(14)-C(6) distance is the shortest ring to ring distance, 3.71 (3) Å (see Table VIII). In $\text{Th}(\text{C}_8\text{H}_8)_2$ the ring to ring distance is 4.007 Å. Because Th^{4+} has the same ionic radius as Nd^{3+} , 1.09 Å, we expect the normal ring to ring distance for the $\text{Nd}(\text{COT})_2^-$ unit to be 4.007 Å. It appears that the Nd(2) to C(14) coordination has caused the ring to ring distances in the $\text{Nd}(\text{COT})_2^-$ unit to close to their shortest value across C(6)-C(14). At present the reason for the tilt in this direction is not understood.

The bond lengths and angles for the THF rings, Table IX, are in good agreement with those found in $[\text{Ce}(\text{COT})\text{Cl}\cdot 2\text{THF}]_2$.¹¹ The oxygen atom of each THF is coordinated to Nd(2). The Nd(2)-O(1) and Nd(2)-O(2) distances are 2.59 (2) and 2.56 (2) Å, respectively. The O(1)-Nd(2)-O(2) angle is 73.4 (5)° and the O(1)-O(2) distance is 3.08 Å.

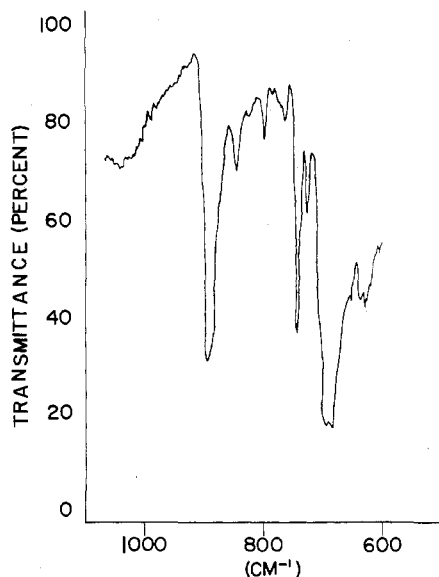
The intramolecular Nd(1)-Nd(2) distance is 5.07 Å.

The crystal structure consists of four anion-cation pairs per unit cell. The anions lie very close to the glide planes at $y = 0.25$ and $y = 0.75$ with $y(\text{Nd}(1)) = 0.243, 0.757, 0.743,$ and

Table X. $[\text{Ln}(\text{COT}) \cdot 2\text{C}_4\text{H}_8\text{O}][\text{Ln}(\text{COT})_2]$ Infrared Spectra (cm^{-1}) (KBr pellet)^f

La	Ce ^c	Ce ^a	Nd	Nd ^a	Er	Yb ^{b,c}	KNd(COT) ₂ ^d	K ₂ (COT) ^e
1019 s	1012 m		1010 s		1007 s			
894 s	893 s	890 s	893 s	894 s	894 s	888 s	890 s	880 s
861 s	859 m	855 m	862 s		855 s			
832 m		800 m	832 m		830 m			
		765 m	780 m	798 m	775 m		810 s	
				771 m			795 s	
736 m	739 m	740 s	741 m	744 s	742 m		770 m	
	724 m	728 m					730 ms	
709 sh			710 sh		723 m		715 m	
688 vs	681 vs	690 vs	688 vs	685 vs	670 vs	678 s	670 s	684 s

^a Solvation THF absent $\text{Ln}_2(\text{COT})_3$. ^b The Yb compound is $\text{Yb}(\text{COT})$. ^c Taken in Nujol mull. ^d Reference 14. ^e Reference 26.
^f Key: vs = very strong and sharp, s = strong, m = medium, w = weak.

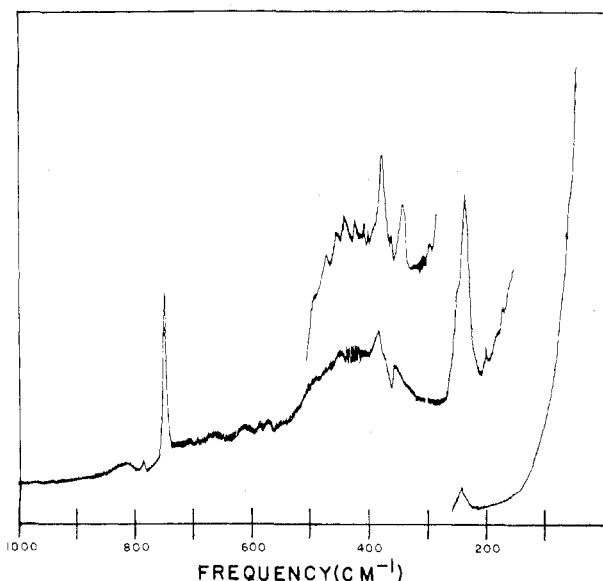
Figure 4. Infrared spectrum of $\text{Ce}_2(\text{COT})_3$.

0.257 and very close to the (200) plane with $x(\text{Nd}(1)) = 0.519$, 0.481, 0.481, and 0.519, with the ring-Nd(1)-ring axis in the x direction. The cations are located on the ends of the anion extending almost to the (100) plane. This packing arrangement gives an overall layer lattice type structure.

Infrared Spectra. The infrared spectra of $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$ and $\text{Ln}_2(\text{COT})_3$ are presented and compared with similar compounds in Table X. The infrared spectrum of $\text{Ce}_2(\text{COT})_3$ is shown in Figure 4. The close similarity of the infrared spectra of the $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$ complexes clearly establishes them to be isostructural with the established structure of the neodymium complex.

The localized D_{8h} symmetry of an isolated COT^{2-} ligand gives rise to only four IR-active fundamental modes. These are the C-H and C-C stretching and the C-H(\parallel) and C-H(\perp) bending modes. Only the latter two occur in the 600–1000- cm^{-1} region and the strong bands located in the 890- and 685- cm^{-1} regions are assigned to these modes.^{14,26} The strong 1010- cm^{-1} band completely disappears when the THF of solvation is pumped off and is therefore assigned to a C-O stretching fundamental of the THF ring. Additional bands appearing in the spectra presumably arise from changes in effective site symmetry of the COT^{2-} ligand infrared active molecular fundamentals.

Raman Spectra. The Raman spectrum of a polycrystalline sample of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$ consists of two strong bands at 750 and 242 cm^{-1} and a complex region from 340 to 500 cm^{-1} , with somewhat more intense resonances at 351 and 385 cm^{-1} as shown in Figure 5. The 750- cm^{-1} band

Figure 5. Raman spectrum of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$.

is assigned to the symmetric breathing mode of the COT^{2-} rings and is identical with the 750- cm^{-1} band observed for $\text{U}(\text{COT})_2$ and $\text{K}[\text{Ce}(\text{COT})_2]$.¹⁴ The 242- cm^{-1} band is substantially higher in frequency than the lowest frequency bands observed for $\text{U}(\text{COT})_2$, 215 cm^{-1} , and $\text{K}[\text{Ce}(\text{COT})_2]$, 200 cm^{-1} .¹⁴ In addition the 350–500- cm^{-1} region is considerably more complex than that observed for the above two compounds. We suggest the above differences are due to the molecular asymmetry of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$. This asymmetry induces a mixing of the symmetric and antisymmetric ring-metal stretching modes. This mixing increases the frequency of the symmetric mode because the antisymmetric mode lies above the symmetric mode. For example, in the classic sandwich molecule, ferrocene, the symmetric ring-metal stretch is observed at 303 cm^{-1} while the antisymmetric ring-metal stretch is observed at 478 cm^{-1} .²⁷ This mixing also makes the higher frequency asymmetric Nd-ring stretch Raman active which contributes to the complexity of the 350–500- cm^{-1} region. This region is further complicated by $\text{C}_8\text{H}_8^{2-}$ and THF ring bending and Nd-O stretching modes.

No Raman spectra of any of the other complexes were observed because of fluorescence.

Nuclear Magnetic Resonance. Repeated attempts to observe the proton magnetic resonance spectrum of $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$ for La and Nd proved fruitless. This was attributed to the low solubility which was estimated to be no greater than a maximum of 0.5 mmol/L.

Magnetic Susceptibility Measurements. The magnetic susceptibilities were measured at ambient temperature using

Table XI. Magnetic Moments of $\text{Ln}_2(\text{C}_8\text{H}_8)_3 \cdot 2\text{C}_4\text{H}_8\text{O}$

Ln	Magnetic moment	
	μ, μ_B	
Ce	1.86	
Nd	3.20	
Er	9.31	

an automated Gouy balance designed and built by Dr. John Gardner. Magnetic susceptibility results are shown in Table XI. The moments correspond closely to those of the +3 free ions indicating that the electron configuration of the metals in these complexes is similar to that of the free ions.

Chemical Properties and Reactions. The most prominent property of the COT compounds is their extreme sensitivity to air and moisture. Trace quantities of oxygen and H_2O cause decomposition. On exposure to air they spontaneously inflame, often leaving only an Ln_2O_3 colored powder.

All the $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$ complexes readily lose their THF of solvation. The cerium complex in particular was observed to lose solvation THF on standing in the inert atmosphere of the drybox turning from gold to green. The thermal stability of the resulting $\text{Ln}_2(\text{COT})_3$ complexes was varied. The Nd complex was observed to begin decomposing at approximately 85 °C while the cerium complex remained stable to 250 °C. The stoichiometry of the La and Nd complexes was initially established by controlled hydrolysis of weighed samples. Degassed water was transferred on the vacuum line into frozen weighed samples of $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$ at liquid nitrogen temperature. Very careful warming of the mixture affords complete hydrolysis and produces an insoluble powder, presumably $\text{Ln}(\text{OH})_3$, and a yellow organic layer. (If the mixture is allowed to warm too rapidly a red solid is formed and hydrolysis is incomplete.) The yellow organic layer was extracted into a standard benzene- CCl_4 solution and dried with MgSO_4 , and a ^1H NMR spectrum was obtained. The spectrum showed a broad singlet at δ 2.4 and a complex multiplet at about δ 5.9 with area ratio of 4:6 indicative of cyclooctatrienes. THF was also observed. Comparison of the integrated intensities with the standard yielded a metal:COT molar ratio of nearly 2:3 and a metal:THF molar ratio of 1:1.

In contrast to the quantitative hydrolysis results the controlled oxidation of the complexes did not result in complete oxidation to cyclooctatetraene. Weighed amounts of the La or Nd $[\text{Ln}_2(\text{COT})_3(\text{THF})_2]$ complexes were oxidized by bubbling dry O_2 or air through a stirred suspension of the compound in a standard benzene CCl_4 solution at -15 °C. The suspended solid turned red and was removed from the solution by filtration. The ^1H NMR of the resulting solution showed only a strong singlet at δ 5.8 indicative of COT. Comparison of integrated intensities showed that only 40% of the dianion was converted to COT.

These oxidation results are in sharp contrast to those of either $\text{KLn}(\text{COT})_2$ or $\text{U}(\text{COT})_2$ carried out in the same manner.¹⁴ With the latter compounds quantitative oxidation of the dianion to COT was achieved. The insoluble nature of the remaining red material in this study suggests it to be polymeric. Apparently the complexes in this study undergo polymerization more readily once oxidation is initiated. This may be a consequence of the unusual coordination of the central COT^{2-} .

A final reaction involved treatment of solid $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$ for La or Nd with a solution of UCl_4 in THF which produced $\text{U}(\text{COT})_2$ characterized by its visible spectrum. Unlike the reactions of $\text{KLn}(\text{COT})_2$ with UCl_4 ,^{14b}

reaction was not instantaneous but rather took 20–30 min to complete. This difference in reactivity is attributed to the low solubility of $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$ and does not suggest that they are more stable than $\text{KLn}(\text{COT})_2$. It does indicate that, like the $\text{KLn}(\text{COT})_2$ complexes, these complexes are highly ionic in character.

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Registry No. $[\text{La}_2(\text{C}_8\text{H}_8)_3] \cdot 2\text{C}_4\text{H}_8\text{O}$, 65101-96-4; $[\text{Ce}_2(\text{C}_8\text{H}_8)_3]$, 60605-80-3; $[\text{Nd}_2(\text{C}_8\text{H}_8)_3] \cdot 2\text{C}_4\text{H}_8\text{O}$, 59458-55-8; $[\text{Er}_2(\text{C}_8\text{H}_8)_3] \cdot 2\text{C}_4\text{H}_8\text{O}$, 65101-97-5; $\text{Yb}(\text{C}_8\text{H}_8)$, 65036-19-3.

Supplementary Material Available: A listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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