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Preliminary communication

Monocyclooctatetraenelanthanide chlorides, a new class of cyclooctatetraene complexes

F. MARES, K.O. HODGSON and A. STREITWIESER, JR.
Department of Chemistry, University of California, Berkeley, California 94720 (U.S.A.)

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Two types of cyclooctatetraene dianion complexes of the lanthanides have been described recently. Reaction of cyclooctatetraene [COT] with metallic europium or ytterbium in liquid ammonia gives the mono-COT complex, $(\mathrm{Ln}\cdot\mathrm{COT})_x$[1]. With the lighter lanthanides, the anhydrous trichlorides in THF react with two equivalents of dipotassium cyclooctatetraenide to give the complexes, $[\mathrm{Ln(COT)_2}]\mathrm{K}$[2]. These complexes appear to have a sandwich structure on the basis of the similarity of their IR spectra to that of uranocene, $\mathrm{U(COT)_2}$[3], for which the D_{8h} sandwich structure has been established by X-ray analysis[4]. We now report a third type of complex between the lanthanides and COT dianion isolated as the unexpected product of the attempted synthesis of neutral bis-10-π-electron complexes of Ln^{3+} ions with COT dianion and cyclononatetraenyl anion[5].

After many synthetic attempts only compounds of the empirical composition $\mathrm{Ln(COT)Cl\cdot 2THF}$ could be isolated, always accompanied by moderate to large amounts of the di-π-cyclooctatetraenelanthanide potassium salts previously reported[2]. The syntheses of the complexes of praseodymium, neodymium, samarium, and cerium were accomplished by adding a suspension of the anhydrous lanthanide trichloride in dry degassed THF to a stirred red brown solution containing 1 equivalent each of cyclooctatetraene dianion potassium salt ($\mathrm{K_2COT}$) and cyclononatetraenide potassium salt (KCNT) at −20°. After vigorous stirring overnight, the solvent was evaporated and the product mixture was separated by extraction in a specially constructed vacuum Soxhlet extractor. Complete separation of the two complexes was facilitated by the much higher solubility of the potassium salts in THF. After several washings with THF, pure brightly colored complexes were obtained in yields of 30–60%. These same complexes were also synthesized by reacting the lanthanide trichloride with one equivalent of COT dianion in THF at −15° giving high yields of the mono-COT complexes.

The physical properties of the present series are similar to those of the di-π-cyclooctatetraene lanthanide complexes[2]. Under high vacuum, they rapidly lose THF above 60° and cannot be sublimed without appreciable decomposition. All are slightly soluble in THF but are completely insoluble in other common organic solvents. The complexes undergo vigorous spontaneous air oxidation and are hydrolytically unstable with the rates of hydrolysis comparable to the di-COT compounds.

Each of the complexes gave lanthanide analysis by titrimetric methods consistent with the formula, Ln(COT)Cl · 2THF or the formula Ln(COT)Cl for the complexes whose THF had been removed by heating to 70° under high vacuum. The several Volhardt chloride and C,H combustion analyses run were also consistent. Controlled oxidation with oxygen at −15° yielded a mixture of COT and THF as demonstrated by NMR analysis of the product mixture. The visible spectra (Table 1) of the complexes show characteristic broad absorptions with ϵ about 10^2 in the visible region. The IR spectra reveal only one additional distinctive peak at 1010 cm^{-1} in comparison with the IR spectra of the $[Ln(COT)_2]K$ complexes. This peak can be attributed to the C–H bending of the coordinated THF molecules. The simplicity of the IR spectra suggests a symmetric molecular structure. The near IR spectra of all of the complexes occur in the same region as the corresponding lanthanide ions. Magnetic moments (Table 1), measured on a Gouy balance at ambient temperature, show that all of the complexes are paramagnetic with moments close to those of the corresponding free ions.

TABLE 1

VISIBLE SPECTRA AND MAGNETIC PROPERTIES OF THE LANTHANIDE CYCLOOCTATETRAENE COMPLEXES

Ln(COT)Cl · 2THF Ln	λ_{max} (nm)	ϵ_{max}	Magnetic moment μ (B.M.) per Ln
Ce	477	419	1.79
Pr[a]	–	–	3.39
Nd	578	58	3.37
	605	93	
	623	51	
Sm	542	243	1.36

[a] Pr shows no absorption in the visible region.

A single crystal X-ray diffraction analysis[6] established the structure of the Ce complex to be a dimer with a planar COT ring associated with each Ce. The two cerium atoms are asymmetrically bridged by two chlorine atoms. Two THF molecules associated with each cerium complete the coordination sphere. The structure shown in Fig.1 was refined with cerium and chlorine anisotropic and all other atoms isotropic. A complete anisotropic refinement is now in progress and will be published elsewhere. The similarity of the IR spectra indicate that the other complexes have analogous structures. All of the observed physical and chemical properties again suggest that the bonding in these structures is highly ionic. These complexes also exhibit markedly similar physical properties to the cyclooctatetraene complexes of europium(II) and ytterbium(II) which also apparently have strong solvent interactions[2].

The present work demonstrates that the monocyclononatetraenyl anion does not easily form sandwich complexes analogous to $(COT)^{2-}$ and further studies are being carried out to determine if $(COT)^{2-}$ is unique in its ability to form these types of complexes with the actinides and lanthanides or if further modification in reaction conditions and reagents will allow eventual isolation of the neutral mixed complexes.

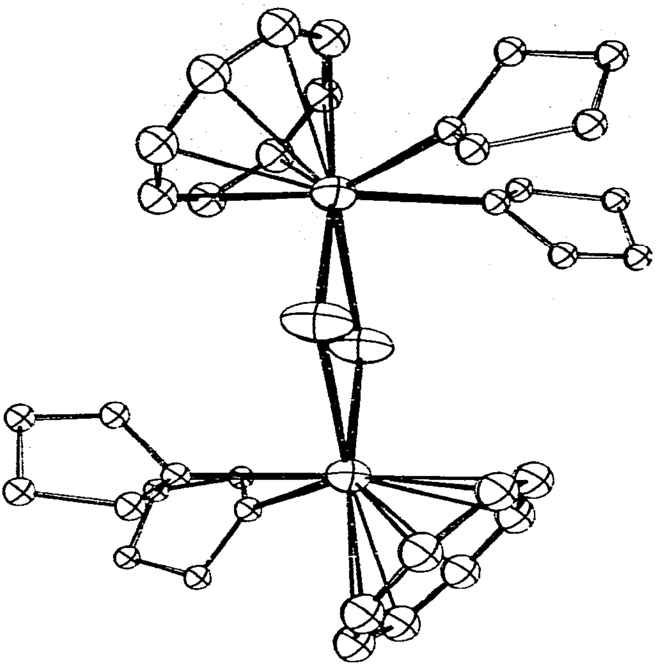

Fig.1. Structure of $[Ce(C_8H_8)(C_4H_8O)_2Cl]_2$. The COT rings are planar with C–C distances of 1.40 Å. The two Ce–Cl bond lengths are 2.85 and 2.94 Å. We are indebted to Professor Kenneth Raymond for this figure and for permission to publish.

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REFERENCES

1 R.G. Hayes and J.L. Thomas, *J. Amer. Chem. Soc.*, 91 (1969) 6876.
2 F. Mares, K.O. Hodgson and A. Streitwieser, Jr., *J. Organometal. Chem.*, 24 (1970) C68.
3 A. Streitwieser, Jr. and U. Mulier-Westerhoff, *J. Amer. Chem. Soc.*, 90 (1968) 7364.
4 A. Zalkin and K.N. Raymond, *J. Amer. Chem. Soc.*, 91 (1969) 5667.
5 E.A. Lancette and R.E. Benson, *J. Amer. Chem. Soc.*, 87 (1965) 1941.
6 K.O. Hodgson and K.N. Raymond, to be published.