Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Lanthanide complexes with cyclooctatetraene di-anion

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

(Received July 23rd, 1970)

A series of actinide complexes of cyclooctatetraene have recently been synthesized[1,2,3] for which X-ray analysis[4] proves a D_{8h} di-π-cyclooctatetraene actinide sandwich structure. The direct involvement of actinide 5*f* atomic orbitals has been proposed to contribute significantly to the electronic structure of these complexes[1]. In the present communication we report results of similar experiments with the lanthanide rare earths for which a comparable involvement of 4*f* atomic orbitals should be less likely.

The complexes of cerium, praseodymium, neodymium, terbium and samarium were prepared in a manner analogous to the actinide series. A suspension of anhydrous lanthanide trichloride in tetrahydrofuran (THF) was added to a dark brown tetrahydrofuran solution of 1.5 equivalent of dipotassium cyclooctatetraene and 0.5 equivalent of cyclooctatetraene (COT). After vigorous stirring overnight, the solvent was evaporated and the remaining solid was extracted with THF in a specially constructed Soxhlet extractor. Compounds of different colors were isolated as amorphous materials which were then washed several times with THF and re-extracted. After several repetitions, the pure complexes were obtained in yields of 50–80%. Under these conditions $EuCl_3$ and $YbCl_3$ did not give complexes, probably because of their reduction to the relatively stable +2 oxidation state with concomitant oxidation of COT dianion to the radical anion. All of the complexes gave satisfactory analyses for $Ln(COT)_2K$. Although we did not obtain complexes of this formula with europium and ytterbium, the 1/1 complexes, Eu(COT) and Yb(COT), have been reported by Hayes and Thomas[5] and are actually the first known complexes between COT and lanthanide elements.

The complexes decompose without melting at about 160° and cannot be sublimed. They are virtually insoluble in all common organic solvents (hexane, toluene, benzene, ether, dioxane and acetonitrile) but are soluble in THF. The complexes ignite on exposure to air. Controlled air oxidation gives COT in almost quantitative yield. The complexes react readily with protic solvents such as amines, alcohols, and water. The methanolysis rate increases in the series studied from cerium to samarium and yields a mixture of COT and cyclooctatrienes.

Each complex gives a broad peak in the visible or ultraviolet region with the λ_{max} shifting from longer to shorter wavelength along the series from cerium to terbium (Table 1). The infrared spectra taken in nujol were especially revealing. All of the

TABLE 1

UV SPECTRA AND MAGNETIC MOMENTS OF THE LANTHANIDE COMPLEXES

Complex $[(COT)_2Ln]^-K^+$	λ_{max} (mμ)	ϵ_{max}	Magnetic moment (μ)
Ln = Ce	691	782	1.88
Pr	502	290	2.84
Nd	486	145	2.98
Sm	396	1371	1.42
Tb	–	–	9.86

complexes give an IR spectrum in the 600–1200 cm^{-1} region identical with that of uranocene (Fig.1). This comparison strongly suggests that the lanthanide complexes also possess D_{8h} sandwich structure, $[Ln(COT)_2]^-K^+$. In such a structure the high solubility in THF is undoubtedly a consequence of solvation of the potassium cation. The magnetic moments summarized in Table 1 show that all of the complexes prepared are paramagnetic.

The chemical and physical data presented so far give little information about the ionic or covalent character of the metal–ligand bonding in these lanthanide complexes. However, the fact that the addition of the cerium complex to a solution of uranium tetrachloride in THF gave an immediate reaction producing an 89% yield of uranocene strongly suggests that the bonding in the lanthanide complexes is substantially ionic.

ACKNOWLEDGEMENT

This structure was supported in part by grant No. 13369 of the National Science Foundation and by a generous sample of cyclooctatetraene donated by the BASF Company.

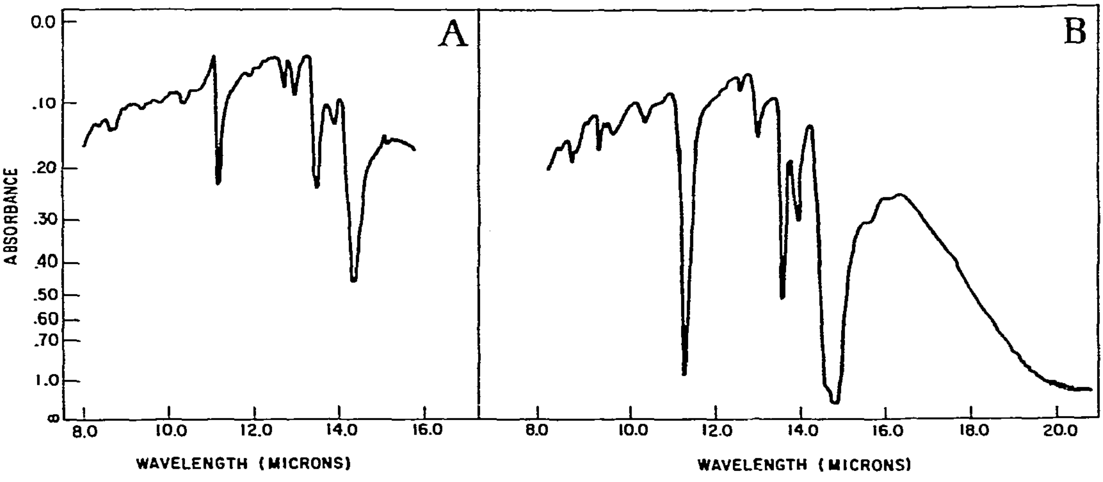

Fig.1. IR Spectra of (A) uranocene and (B) potassium salt of di-π-cyclooctatetraenepraseodymium.

REFERENCES

1 A. Streitwieser, Jr. and U. Mueller-Westerhoff, *J. Amer. Chem. Soc.*, 90 (1968) 7364.
2 A. Streitwieser, Jr. and N. Yoshida, *J. Amer. Chem. Soc.*, 91 (1969) 7528.
3 D.G. Karraker, G.A. Stone, R.E. Jones and N. Edelstein, *J. Amer. Chem. Soc.*, in press.
4 A. Zalkin and K.N. Raymond, *J. Amer. Chem. Soc.*, 91 (1969) 5667.
5 R.G. Hayes and J.L. Thomas, *J. Amer. Chem. Soc.*, 91 (1969) 6876.