Lanthanide(III) Complexes with Cyclooctatetraene Dianion. Synthetic Chemistry, Characterization, and Physical Properties[1]

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Abstract: This paper reports two series of lanthanide π-carbocyclic complexes of formula $K[Ln(C_8H_8)_2]$ and $[Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2$. Single crystal X-ray structures of the cerium member of both series have been previously determined. Analytical and spectral data strongly suggest that the other lanthanide complexes in each series are isostructural with the cerium complexes. Chemical and spectral data show that these lanthanide cyclooctatetraenyl metallocenes are highly ionic relative to the analogous actinide complexes. This trend undoubtedly results from the inability of the lanthanide 4f orbitals to contribute to covalent bonding relative to the 5f orbitals. Similar properties are found for the corresponding complex with yttrium, a metal which is not a lanthanide rare earth. Using Raman techniques the symmetrical ring–metal stretch of eight-membered ring metallocenes was measured.

Interest in the chemistry of organometallic compounds of the lanthanide transition metals has expanded rapidly within the past few years. This renaissance of interest is partly due to the preparation of "uranocene," $U(C_8H_8)_2$,[3] and subsequent isostructural complexes of thorium[4] and neptunium and plutonium.[5] Preparation of the complex $U(C_8H_8)_2$ was of particular significance because its preparation derived from the expectation that covalent stabilization may result from overlap of 5f orbitals with a symmetry-allowed combination of the highest occupied orbitals in the cyclooctatetraene dianion ligands.[6-8] Additional evidence for this view is provided by nmr[9] and chemical[6] studies.

A complete development of this organometallic chemistry now requires extension of the synthetic chemistry of the 5f elements into the 4f or lanthanide series and a comparison of these chemical, physical, and structural characteristics of the two series. Until recently, little has been known about the structural chemistry of the 14 lanthanide elements which exist predominantly in the 3+ oxidation state. Much of the earlier work emphasized only synthesis and used primarily chemical analysis of the compounds and chemical analogy for structural postulates. The first π-carbocyclic complexes of the lanthanides were the triscyclopentadienyls $Ln(C_5H_5)_3$ (where Ln is any lanthanide ion) reported by Birmingham and Wilkinson in 1954.[10] Subsequently, complexes of the type $Ln(C_5H_5)_2Cl$[11] and $Ln(C_5H_5)Cl_2$[12] were reported and characterized, as well as the preparation of the biscyclopentadienyl compounds of Eu^{II} and Yb^{II}.[13] Recent reviews on these lanthanide organometallic compounds are available.[14]

In general, all of these lanthanide complexes exhibit similar chemical and physical properties. With the exception of the dimeric $[Ln(C_5H_5)_2 \cdot X]_2$ compounds, where X = phenoxide or carboxylate,[11] all of the complexes are hydrolytically and oxidatively unstable and show pronounced ligand lability. In essence, they behave as essentially ionic compounds.[15] This predominantly ionic character suggests that the π complexes with C_8H_8 dianion would be important reference compounds for comparison with the related actinide complexes. The first such complexes of lanthanides with C_8H_8 dianion, reported by Hayes and Thomas,[16] were the 1:1 complexes with the 2+ oxidation states of Eu and Yb. Preliminary reports have already appeared on our preparations of two series of C_8H_8–lanthanide complexes of general type $[Ln(C_8H_8)_2]K$[17] and $[Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2$.[18] In the present paper we give experimental details on the preparation of these difficult to handle compounds, we consider their characterization in detail and we report their physical properties, including Raman spectra. Finally, their electronic structure and bonding as related to the actinide complexes are discussed in light of the detailed molecular structure.

Experimental Section

A description of the apparatus and techniques used in the synthesis and purification of the complexes can be found in the accompanying paper describing the detailed preparation of $U(C_8H_8)_2$.[6]

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[15] The electronic spectra of several $Ln(C_5H_5)_3$ compounds have been interpreted to indicate little covalency in ring-metal bonding: L. J. Nugent, P. G. Laubereau, G. K. Werner, and K. L. Vander Sluis, *J. Organometal. Chem.*, 27, 365 (1971).

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All reactions on the vacuum line were carried out under an inert atmosphere of commercially available argon which was used without further purification. Transfer and handling of the complexes was facilitated by the use of a Vacuum Atmospheres HE-193-2 inert atmospheres glove box having an oxygen- and moisture-free recirculating argon atmosphere.

Materials. In all syntheses and further characterizations, reagent grade solvents were used after having been carefully purified to remove water and oxygen. Tetrahydrofuran (THF) was dried by transferring under vacuum onto $LiAlH_4$ and stirring for 1–2 days. After degassing by repeated freezing–evacuating–thawing cycles, the THF was vacuum transferred into reactors or flasks for storage under argon atmosphere. Toluene and benzene were dried and degassed in a similar manner. Linde 4A molecular sieves, activated by heating with a cool flame under high vacuum, were used to dry $CHCl_3$, CCl_4, $CHBr_3$, Nujol for ir, and deuterated solvents for nmr. Lanthanide trichlorides were obtained in high purity from Research Organic/Inorganic, Sunnyvale, Calif. The trichlorides of Ce, Pr, Nd, Sm, and Tb were found to be completely anhydrous and were used without further purification. However, the ir spectra of the trichlorides of Y, La, and Gd showed varying amounts of water and were dehydrated prior to use by the method described by Reed, Hopkins, and Audrieth.[19]

Elemental Analysis. Metal analyses of the lanthanides were accomplished using direct or back complexometric titration procedures with disodium EDTA.

Direct Titration.[20] Approximately 50 mg of the lanthanide complex was weighed in the inert atmosphere of a glove box using a Cahn M-10 electrobalance. The weighed solid was removed and quickly hydrolyzed with 5–10 ml of distilled water. After addition of 1 ml of concentrated HCl, the solution was diluted to about 90 ml, 10 mg of ascorbic acid was added, and the solution was buffered to pH 8–8.5 with triethanolamine. Eriochrome-T-black (Erio-T) indicator solution was prepared by dissolving 0.2 g of solid Erio-T in 15 ml of triethanolamine and 5 ml of absolute ethanol. Enough indicator was added to give the solution a deep pink color, and the stirred mixture was then titrated with ~0.01 *M* Na_2EDTA solution to an end-point change of pink to blue. The end point was taken as the point at which the color change was permanent for at least 1 min.

Back Titration.[21,22] The sample was hydrolyzed as above and a measured excess of ~0.01 *M* Na_2EDTA solution was added followed by 10–20 mg of citric acid. The solution was then buffered to pH 8–8.5 with NH_4Cl–NH_4OH and the total volume was brought to 100 ml. About 0.3 g of solid NH_4Cl was added and the pH was adjusted to 8–9. Erio-T, in a solid form mixed with NaCl, was added until a deep blue color was obtained. The solution was titrated with standardized ~0.1 *M* $ZnSO_4$ until the sharp end-point change of blue or violet to pink occurred. End-point determination gave better results with the back titration procedure.

Synthetic Procedures. Preparation of $K[Ce(C_8H_8)_2]$ and Analogous Complexes of Y, La, Pr, Nd, Sm, Tb, and Gd. A solution of K_2COT was prepared in a manner similar to that described by Katz,[23] by adding 10.0 g (0.092 mol) of C_8H_8 to a stirred dispersion of 4.9 g (0.126 mol) of metallic potassium in 100 ml of THF at −10°. After reacting for 1 hr between −5 and −15°, the solution was characterized by the dark brown color of C_8H_8 dianion and the disappearance of the potassium. A suspension of 10.29 g (0.042 mol) of anhydrous $CeCl_3$ in 50 ml of dry degassed THF was rapidly added through the side arm under argon flush to the stirred solution of $K_2C_8H_8$. The reaction mixture immediately turned green–brown and was allowed to warm slowly to room temperature while stirring under the positive argon pressure. The reaction mixture was degassed and the THF was vacuum transferred off to yield 15 g of crude material which was purified by extracting in a specially designed Soxhlet extractor[6] with THF. After two extractions, 8.49 g of pure light green amorphous solid was obtained (yield 51.2%). For the other lanthanides, yields ranged from 36 to 78%. Analyses are summarized in Table I.

Preparation of $[Ce(C_8H_8)Cl\cdot 2C_4H_8O]_2$ and Analogous Complexes of Pr, Nd, and Sm. A solution of $C_8H_8^{2-}$ was prepared as described above by adding 3.87 g (0.037 mol) of C_8H_8 to a stirred dispersion of 2.98 g (0.075 mol) of metallic potassium in 100 ml of THF at −10°. After the potassium had completely reacted (about 1 hr) at −5 to −15° a suspension of 9.18 g (0.037 mol) of anhydrous $CeCl_3$ in 50 ml of dry degassed THF was added with stirring at −10°. The reaction mixture turned yellow-green and was allowed to warm slowly to room temperature while stirring under argon atmosphere. The reaction mixture was degassed and the solvent was vacuum transferred off to yield 16 g of crude material which contained a large amount of $K[Ce(C_8H_8)_2]$ in addition to the desired product. The two compounds were separated by Soxhlet extraction of the crude material using 80 ml of THF. The $K[Ce(C_8H_8)_2]$ is more soluble in THF than the chloride and was removed by repeated washing with pure solvent. This procedure yielded 5.6 g of crystalline yellow-green solid material, yield 37.5%. It was later observed that pure $[Ce(C_8H_8)Cl\cdot 2C_4H_8O]_2$ could be synthesized in better than 80% yield by reverse addition of 1 equiv of $K_2(C_8H_8)$ to 1 equiv of $CeCl_3$ with work-up in the same manner. Analyses are reported in Table II.

Table I. Color and Analyses of Biscyclooctatetraene Lanthanide Complexes

Complex	Color	% Ln Found	% Ln Calcd
$K[Y(C_8H_8)_2]$	Yellow	~20[a,b]	26.44
$K[La(C_8H_8)_2]$	Green	36.74[a]	35.96
$K[Ce(C_8H_8)_2]$	Pale green	36.61	36.16
$K[Pr(C_8H_8)_2]$	Yellow gold	36.09	36.29
$K[Nd(C_8H_8)_2]$	Pale green	36.80	36.31
$K[Sm(C_8H_8)_2]$	Brown	38.39	37.80
$K[Gd(C_8H_8)_2]$	Yellow	37.39	38.86
$K[Tb(C_8H_8)_2]$	Yellow brown	39.50	39.11

[a] These analyses are poor because of the difficulty of determining the end point of the compleximetric titration. [b] Sample contained no Cl by $AgNO_3$ test.

Table II. Characterization of the Lanthanide Cyclooctatetraene Chlorides

Complex	Color	% Ln Found	% Ln Calcd
$[Ce(C_8H_8)Cl\cdot 2C_4H_8O]_2$	Yellow green	33.16	33.05
$[Pr(C_8H_8)Ce\cdot 2C_4H_8O]_2$	Pale green	*a*	33.18
$[Nd(C_8H_8)Ce\cdot 2C_4H_8O]_2$	Bright green	33.83	33.69
$[Sm(C_8H_8)Ce\cdot 2C_4H_8O]_2$	Purple	*a*	34.63

[a] Metal analyses on these complexes were variable due to rapid loss of THF in the desolvating atmosphere of the inert atmosphere box. See discussion of analysis.

Reaction of $K[Ce(C_8H_8)_2]$ with UCl_4. Under inert atmosphere, 44.8 mg (0.12 mmol) of UCl_4 was dissolved in 10 ml of dry degassed THF. To this bright green solution was added 45.5 mg (0.12 mmol) of solid $K[Ce(C_8H_8)_2]$. A deep green color formed immediately and brightened somewhat on standing. The visible spectrum of the solution was measured and showed that $U(C_8H_8)_2$ was produced in 89% yield.

Reaction of $K[Ce(C_8H_8)_2]$ with $CeCl_3$. Under inert atmosphere 5.78 mg (0.015 mmol) of $K[Ce(C_8H_8)_2]$ was dissolved in 25 ml of dry degassed THF. To 15 ml of this pale green solution was added 5.51 mg (0.022 mmol) of solid $CeCl_3$ with stirring. As the $CeCl_3$ went into solution the green color of the $K[Ce(C_8H_8)_2]$ disappeared and was replaced by the distinctive yellow-green color of $[Ce(C_8H_8)Cl\cdot 2C_4H_8O]$. The visible spectrum of this solution at 691 nm showed no detectable $K[Ce(C_8H_8)_2]$ remaining, but a new peak at 477 nm corresponded to the absorption of $[Ce(C_8H_8)Cl\cdot 2C_4H_8O]$ which was produced quantitatively in the reaction.

Spectral Analyses. The visible, uv, and near-ir spectra were recorded on Cary 14 or Perkin-Elmer 202 spectrometers. In order to obtain reproducible results from solutions which were stable for extended periods of time, it was imperative to either heat under vacuum all of the glassware used in the preparation and spectral

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(23) T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784 (1960).

studies or to allow the glassware to stand in the dry inert atmosphere of the glove box for at least 24 hr. The THF solutions of the complexes were prepared in the inert atmosphere box and transferred into cells fitted to a stopcock with a vacuum seal above the cell. On the vacuum line the solutions in the cells were frozen with liquid nitrogen and the cells were permanently sealed. Solutions handled in this way have shown no decrease in absorbance and no signs of decomposition for periods of more than 2 years.

Infrared spectra were obtained from Nujol mulls prepared in the glove box from predried and degassed Nujol. When sandwiched between NaCl plates, the mulls could be handled in the air for at least 2–3 hr without appreciable decomposition.

Raman spectra were recorded on powdered samples sealed in glass melting point capillaries with a Cary 83 laser Raman spectrometer.

Proton magnetic resonance spectra of diamagnetic compounds were recorded on a Varian T-60 spectrometer with external TMS as the reference. Sample tubes were prepared in the glove box by filtering a saturated THF solution of the desired complex into a standard sample tube and capping with a pressure cap which had been lightly coated with silicone grease. Progressive oxidation to C_8H_8 could be followed by removing the cap briefly, shaking, and again recording the spectrum. Oxidation of the $K[Ln(C_8H_8)_2]$ complexes in this fashion resulted in formation of a small amount of precipitate in the sample tube which did not, however, appear to interfere with the observation of the growth of the C_8H_8 signal. Proton magnetic resonance spectra of the paramagnetic complexes were measured on a Varian HR-100 spectrometer modified for variable frequency modulation.[9a] Sealed sample tubes were employed using THF-d_8 as the solvent. The shifts were referenced to the high-field line of residual protons of THF.

Magnetic Susceptibility Measurements. The magnetic susceptibilities were measured at ambient temperature using a standard Gouy balance. Tubes of 2-mm id were calibrated using $HgCo(NCS)_4$ as a standard and were then filled with the complex and constricted under vacuum above the sample. The weight of the tube was taken in and out of the magnetic field and the susceptibilities were calculated in the standard manner.[24] This technique allowed permanent sealing of the susceptibility tubes without affecting their weight or calibration.

Results and Discussion

Physical Properties of the Complexes. The biscyclooctatetraene complexes of Y, La, Ce, Sm, Pr, Nd, Gd, and Tb have similar physical properties. All of the compounds have characteristic colors (see Table I) ranging from brown for the Sm complex to pale green for the Nd complex. The complexes also exhibit similar thermal behavior which is different under vacuum and under argon atmosphere. The complexes decompose when heated above 160° in high vacuum and there is no evidence of sublimation at 1×10^{-4} Torr. Under sealed argon at 1 atm, however, the complexes are thermally stable and all but one show no sign of decomposition up to 360°. $K[Tb(C_8H_8)_2]$ does decompose slowly at this temperature. Thermal stability and even volatility of organometallic compounds cannot be taken as indicative of covalent ring–metal interaction. The triscyclopentadienyl lanthanides can be sublimed but appear to be almost wholly ionic.[15] Furthermore, cyclooctatetraenedipotassium is surely an ionic compound represented as $C_8H_8^{2-} \cdot 2K^+$, yet this compound sublimes under vacuum.[25]

The complexes are generally insoluble in $CHCl_3$, CCl_4, and hexane, exhibit low solubility in benzene and toluene, and are moderately soluble in THF and dioxane. The solubilities were determined in the inert atmosphere box using dry degassed solvents at about 27°.

The mono-C_8H_8 lanthanide chloride dimers (Table II) exhibit physical properties markedly similar to the bis-C_8H_8 complexes. When heated under vacuum (*ca.* 10^{-3} Torr) they begin to lose THF of solvation at about 50° and above 80° slowly lose all coordinated solvent after heating for 24 hr. During this time there is some darkening of the chloride complexes indicating slow thermal decomposition. For the cerium chloride complex, the total weight loss observed was 39.24% compared to a theoretical weight loss of 34.02% if only two molecules of THF were lost. The complexes cannot be sublimed at 10^{-3} Torr and begin to decompose as the temperature is raised above 100°. In sealed tubes under argon atmosphere the chloride complexes begin to lose solvent at 115° and gradually darken but do not melt as the temperature is raised to 345°.

Analytical Results. Since commercial analyses of these air-sensitive complexes were unsatisfactory, the following complexometric titration procedures, which involve modifications of methods in the literature,[21,22] were used. The Na_2EDTA was prepared as a $\sim$0.01 *M* aqueous solution and was stored in glassware pretreated with a hot alkaline solution of EDTA to remove trace ion impurities which can change the normality of the stored solution. Erio-T indicator, either in solution or as a solid diluted with NaCl, is a suitable indicator.

There are two techniques which can be used satisfactorily for complexometric metal determination of the lanthanides. The direct titration with Na_2EDTA is simpler to use, but in the case of the lanthanides, the metal ions react somewhat slowly with the complexing agent and end-point determination is difficult. To overcome this difficulty, a back titration with standardized $ZnSO_4$ can be used.

Since the complexes are extremely air sensitive, they were weighed on a Cahn electrobalance in an inert atmosphere glove box. To obtain a soluble decomposed product it is important to hydrolyze the complex with distilled water or dilute HCl rather than to allow it to oxidize to the lanthanide oxide. The remainder of the titration is straightforward and is detailed in the Experimental Section.

Both techniques previously mentioned were used to analyze the lanthanide C_8H_8 dianion complexes. As noted, however, the back titration with $ZnSO_4$ proved to be the more useful method since the end points were sharper. When using the back-titration method, pH control was found to be critical. The average results (Tables I and II) show good agreement for most of the complexes. Analysis of possible sources of titration error indicates that these titrations should be accurate to about 0.5%.

The difficulties in obtaining satisfactory analyses for the Sm and Pr bridged chloride complexes deserve comment. If one begins with material freshly extracted with THF and weighs the material in the inert atmosphere box, decoloration is observed on the surface within a few seconds after exposure to the argon atmosphere, probably due to the loss of the THF of solvation; hence, even the best analyses of these complexes are 1–2% high. If we attempt to remove all solvent by pumping under high vacuum, heating is required for removal of all traces of solvent. In this process some thermal decomposition occurs resulting in loss of additional organic material, and again analyses are 1–2% above the values calculated for the unsolvated com-

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(24) B. N. Figgis and J. Lewis, in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 6.

(25) D. F. Starks, unpublished observations.

Table III. Infrared Spectra of the K[Ln(C_8H_8)$_2$][a,b] Complexes from 1300 cm^{-1}

Ce	Pr	Nd	Sm	Tb	Y	La	Gd	$C_8H_8^{2-}$ [c]
1280 (w)								
1070 (w)					1048 (s)	1040 (m)		
1000 (w)								
875 (m)	890 (s)	890 (s)	890 (s)	880 (s)	892 (s)	885 (s)	896 (s)	880 (s)
790 (w)		810 (s)	775 (s)	770 (w)	880 (s)	800 (w, sh)	780 (m)	
		795 (s)						
		770 (m)						
730 (w)	735 (s)	730 (ms)	740 (m)	730 (m)	740 (s)	742 (w, sh)	742 (s)	
720 (w)	720 (m)	715 (m)	720 (m)		706 (m, sh)			
670 (s)	675 (vs)	670 (s)	680 (s)	675 (s)	684 (s)	676 (vs)	678 (s)	684 (s)
					662 (s)			

[a] As Nujol mulls. [b] vs = very strong and sharp, s = strong, m = medium, w = weak, wb = weak and broad, sh = shoulder. [c] H. P. Fritz and H. Keller, *Chem. Ber.*, **95**, 158 (1962).

plexes. Nevertheless, the remaining physical, structural, and spectra data clearly substantiate the identity of these complexes. They also definitely contain chloride as shown by Volhard determination, but the quantitative results are subject to the same errors as described above. The presence of THF is demonstrated in the nmr spectrum after oxidation of the complexes and by their ir spectra.

For undoubtedly similar reasons it was not possible to obtain satisfactory and reproducible C,H combustion analyses; for example, with [Ce(C_8H_8)Cl·2C_4H_8O]$_2$, a combustion analysis on the complex assumed to contain two molecules of THF gave the following analysis. *Anal.* Calcd: C, 45.33; H, 5.70. Found: C, 42.63; H, 5.42. After heating a sample of the complex at 80° for 12 hours the following results were obtained. *Anal.* Calcd: C, 34.35; H, 2.88. Found: C, 35.86; H, 3.74. Because of these difficulties in obtaining pure stoichiometric solvated complexes, further combustion analyses were not attempted. The total compositions of the complexes have been established by a single crystal X-ray diffraction analysis.[26] The presence of potassium in the biscyclooctatetraene lanthanide salts was shown qualitatively by precipitation with NaBPh$_4$.

Structure of the Complexes. The structures of the two cerium complexes have been established by X-ray crystal analysis.[26,27] In the structure of [Ce(C_8H_8)Cl·2C_4H_8O]$_2$ the two cerium atoms in the dimeric unit are bridged asymmetrically by the chlorines. The C_8H_8 ring is a planar octagon with aromatic C–C bond lengths. The two THF oxygens and the two chlorines complete the inner coordination geometry.

Crystals of [Ce(C_8H_8)$_2$]K obtained from diglyme solution contain 1 mol of coordinated solvent. The single crystal structure as determined by X-ray diffraction[27] is that of a (Ce(C_8H_8)$_2$]$^-$ anion and an ether-coordinated cation combined in a contact ion pair. The chelating ether coordinates only one side of the K$^+$ ion. The opposite side is coordinated symmetrically to one of the two independent COT dianion rings. These rings are planar with equal aromatic C–C distances. The [Ce(C_8H_8)$_2$]$^-$ structure is similar to that of uranocene, U(C_8H_8)$_2$.[28,29] The C–C bond distances are essentially the same in both compounds.

With the X-ray crystal structures established for the two Ce complexes, spectroscopic and chemical similarities establish that the other lanthanides are isostructurally related.

Infrared Spectra. In the 600–1000-cm^{-1} region, the infrared spectra are similar for all of the K[Ln(C_8H_8)$_2$] complexes (Table III). This similarity suggests that these complexes are all related in structure to that established for the cerium compound. This conclusion is further supported by the close similarity to the spectrum of U(C_8H_8)$_2$. A comparison of the spectra of U(C_8H_8)$_2$ and K[Pr(C_8H_8)$_2$] may be found in ref 17.

The D_{8h} symmetry of an isolated $C_8H_8^{2-}$ ligand gives rise to only four ir active fundamental modes. Excluding C–H stretching and C–C stretching, the most prominent features of the ir spectra of the K[Ln(C_8H_8)$_2$] compounds can be assigned to the C–H (||) and C–H (⊥) bending fundamentals. Additional bands appearing in the ir presumably arise from a combination of factors such as changing effective site symmetry of the ligand and ir active skeletal (molecular) fundamentals.

An isostructural relationship for the [Ln(C_8H_8)Cl·2C_4H_8O]$_2$ compounds is also suggested by the similarity of the ir spectrum of [Ce(C_8H_8)Cl·2C_4H_8O]$_2$ to those of the other [Ln(C_8H_8)Cl·2C_4H_8O]$_2$ compounds (Table IV and Figure 1). The tightly coordinated THF of these bridged chloride compounds generally appears in the ir spectrum as shown by the relative decay of the 1010-cm^{-1} band (C–O stretch) upon prolonged heating under high vacuum.

Table IV. [Ln(C_8H_8)Cl·2C_4H_8O]$_2$ Infrared Spectra[a] (cm^{-1})

Ce	Pr	Nd	Sm
1070 (w)	1060 (w)	1060 (w)	1065 (vw)
1010 (s)	1010 (s)	1010 (s)	1010 (s)
965 (w)	960 (w)		962 (vw)
918 (w, sh)	923 (w, sh)	923 (w, sh)	924 (vw)
885 (s)	880 (s, split)	880 (s, split)	880 (s, split)
792 (w)	798 (w)	801 (w)	795 (w)
736 (w)	745 (m)	745 (m)	745 (m)
715 (w, sh)	716 (w, sh)	716 (w, sh)	716 (w, sh)
703 (sh)	705 (sh)	705 (sh)	705 (sh)
694 (vs)	696 (vs)	696 (vs)	697 (vs)

[a] vs = very strong and sharp, s = strong, m = medium, w = weak, vw = very weak, sh = sharp.

Raman. Raman spectra of powder samples of K[Ce(C_8H_8)$_2$] and U(C_8H_8)$_2$ are quite similar as expected from their structural similarities. Prominent features occur in the region 200 and 750 cm^{-1} with a weaker

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Table V. Raman Spectra for a Series of Homologous Complexes (cm^{-1})[a]

$Fe(C_5H_5)_2$[b]	$Cr(C_6H_6)_2^+$[c]	$C_7H_7^+$[d]	$U(C_8H_8)_2$	$K[Ce(C_8H_8)_2]$	Mode
301 (s)	279 (p, vs)		215 (s)	200 (s)	Sym ring–metal stretch
390 (s)	333 (d, m)				Sym ring tilt
			380 (w)	370 (m)	
892 (w) 600 (w)	420	433			Ring distortion
1105 (s)	972 (p, s)	868	750 (m)	750 (m)	Sym ring breathing

[a] p = polarized, d = depolarized, vs = very strong and sharp, s = strong, m = medium, w = weak. [b] See reference 30. [c] See reference 31. [d] See reference 32.

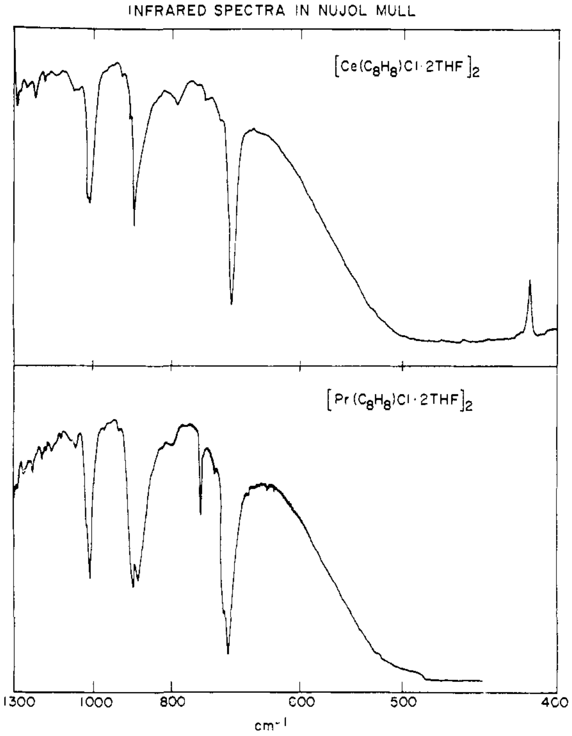

Figure 1. Infrared spectra in Nujol mull of two mono-C_8H_8 lanthanide chloride dimers.

band at 370 cm^{-1}. Comparison of these spectra with Raman assignments of $Fe(C_5H_5)_2$,[30] $Cr(C_6H_6)_2^+$,[31] and $C_7H_7^+$[32] justify the tentative assignment of the 200-cm^{-1} band of $K[Ce(C_8H_8)_2]$ and the 215-cm^{-1} band of $U(C_8H_8)_2$ as the symmetrical ring–metal stretch and the 750-cm^{-1} band of both complexes as the symmetrical ring breathing mode (Table V). Assignment of the weaker 370-cm^{-1} band is more difficult; a possible assignment may be the symmetrical ring tilt. These assignments are based on relative intensities and frequency trends. Measurement of the polarization ratios of these bands has not yet been possible because of the relatively low solubilities of $[Ce(C_8H_8)_2]K$ and $U(C_8H_8)_2$.

The Raman studies give information about the relative strengths of the M–C bonds in the actinide as compared to the lanthanide complexes. The symmetrical ring–metal stretch has A_{1g} symmetry. Since the metal does not move in this normal mode, one does not have to consider the reduced mass of the metal in order to compare directly the M–C stretching force constants. The A_{1g} mode of $U(C_8H_8)_2$ occurs at 15 cm^{-1} higher frequency than the corresponding mode for $K[Ce(C_8H_8)_2]$; the higher force constant implies stronger bonding.

Raman spectra of the other $K[Ln(C_8H_8)_2]$ and $[Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2$ compounds have not yet been recorded due to absorption near the laser exciting frequency; further work is still in progress. At the time of our studies the Raman spectrum of the $C_8H_8^{2-}$ moiety had not been reported; however, our conclusions above have recently been confirmed in a report on the Raman spectrum of $(C_8H_8)_2Th$.[33]

Proton Magnetic Resonance. Proton magnetic resonance studies of the $K[Ln(C_8H_8)_2]$ complexes involving Ln(III) ions with closed configurations gave results as expected for diamagnetic complexes. The pmr spectra of $K[Y(C_8H_8)_2]$ and $K[La(C_8H_8)_2]$ showed sharp singlets in THF at 5.75 and 5.90 ppm, respectively, downfield from external TMS. These results are consistent with metallocene-type structures, each complex involving 16 equivalent protons. Note that the proton resonance of the ligand rings is similar to that of free cyclooctatetraene dianion.

Air oxidation of these samples resulted in progressive decay of the above singlets with concomitant appearance of a singlet at δ 5.67 ppm relative to external TMS (δ 5.90 ppm relative to internal TMS), indicating that the cyclooctatetraene dianion moiety had been oxidized to cyclooctatetraene. The compounds involving ions with a partly filled 4f shell showed spectral behavior characteristics of paramagnetic complexes: solvent peaks were broadened, and sample singlets were observed either upfield or downfield from TMS (Table VI).

Table VI. Nmr Spectra of $K[Ln(C_8H_8)_2]$ Complexes in THF-d_8

	Ln		
	Nd	Sm	Tb
Observed[a] line position	10.0	−11.4	−117.5

[a] Shifts in ppm referenced to the high-field line of THF and measured at ambient temperature of 34°.

Temperature-dependent pmr studies are currently in progress to facilitate interpretation of these paramagnetic shifts.[34]

Visible Spectra. Each of the di-π-cyclooctatetraene lanthanide complexes exhibits a broad absorption in the visible region of the electronic spectrum. The po-

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sition of the maxima in THF along with molar extinction coefficients for these complexes are listed in Table **VII**.

Table VII. Visible Spectra and Magnetic Moments of $K[Ln(C_8H_8)_2]$[a]

Ln	λ_{max}, nm	ϵ_{max}	Magnetic moment μ, BM	Magnetic moment of free ion
Y	*b*			
La	*b*			
Ce	691	782	1.88	2.46[c]
Pr	502	290	2.84	3.47[d]
Nd	486	145	2.98	3.52[d]
Sm	396	1371	1.42	1.58[d]
Gd	490	30		
Tb	413 448 480		9.86	9.6[d]

[a] In THF. [b] Broad absorption extending into the visible region without a distinct λ_{max}. Note that THF absorbs below 310 nm. [c] Observed in $Ce(C_5H_5)_3$. [d] Observed in $Ln(SO_4)_3 \cdot 8H_2O$; ref 35.

This region of the spectrum is striking in that it bears no resemblance to the same spectral region for the corresponding lanthanide(III) aquo ions which are characterized in this region by sharp absorptions with low intensity (ϵ about 1–10).[35] The molar extinction coefficients of the $C_8H_8^{2-}$ complexes are 10 to 100 times more intense than the f–f transitions of the aquo ions and are much broader. This difference suggests that the visible spectra of the complexes are not wholly f–f in character.

The triscyclopentadienide lanthanide complexes do not show broad, intense bands in the visible region with one exception; all of the complexes except $Yb(C_5H_5)_3$ have colors and spectra that correspond closely to the aquo ions in solution[10,13] and clearly originate in metal f–f transitions. The intensely green $Yb(C_5H_5)_3$ complex, however displays two broad absorptions in the red and violet which are obviously different in character from the other 13 lanthanide triscyclopentadienides.[36] Calderazzo, Pappalardo, and Losi[36] have suggested that this broad absorption may be due to either 4f → 5d transitions, charge transfer from ligand to metal, or to intraligand transitions. They were, however, unable to distinguish unambiguously among these mechanisms. Ultraviolet transitions of the type 4f → 5d have been observed for ionic lanthanide perchlorates in solution where the lanthanide is capable of forming a relatively accessible quadrivalent state (Ce, Pr, and Tb). Jorgensen and Brinen have also observed absorptions in the uv for the lanthanides which give accessible dipositive ions (Eu and Yb).[37] These absorptions were attributed to ligand to metal charge transfer, since by going to ligands more reducing than water the bands shift toward the visible regions. In similar studies on lanthanide complexes Barnes[38] has correlated the reducing power of ligands as well as solvating molecules with shifts in the uv absorption spectra of the lanthanide complexes. He also observed that the position of a charge transfer band in the lanthanide spectra is ordered by increasing ease of electron removal from the ligand.

The visible spectra of the biscyclooctatetraene lanthanide complexes can be interpreted readily with such a charge-transfer assignment. As already mentioned, the high intensity and broadness of the bands rule out f–f transitions. The band maxima also exhibit a trend across the periodic table which correlates with the gas phase ionization potentials of the metals. If we assume that the ability of M^{3+} to gain an electron is correlated inversely with the ionization potential of M, then one would observe a trend of increasing energy from Ce to Sm (the ionization potentials decrease) followed by a decrease in energy from Sm to Tb. This order corresponds exactly to the trend observed for the complexes (Table VII), at least for the lower lanthanides. For the higher lanthanides the situation is apparently more complex because of the greater number of f electrons. This dependence of absorption maxima on the central metal would tend to rule out ligand–ligand transfers as a cause of the absorption. Furthermore, the π–π^* absorptions of cyclooctatetraene and its dianion actually occur in the uv region.

Although we cannot rule out 4f → 5d transitions, we can cite results from the cyclooctatetraene actinides which relate directly to this question. Streitwieser and Harmon[39] have observed shifts in the visible absorption of alkyl-substituted $U(C_8H_8)_2$ derivatives toward the red. Similar effects have been observed by Karraker on alkyl-substituted $Pu(C_8H_8)_2$ and $Np(C_8H_8)_2$ derivatives.[40] Alkyl substituents make the rings more reducing and would make ligand to metal charge transfer more facile. Similar experiments with lanthanides would be valuable in this regard and are in progress.

The charge-transfer mechanism from ligand to the lanthanide ion is also in agreement with the spectral behavior of the lanthanide triscyclopentadienides. A reasonable explanation of the $Eu(C_5H_5)_3$ spectrum is that oxidation of the ligand to a C_5H_5 radical is not particularly facile, and only in the case where a very stable electronic configuration of the metal cation results (for example the f^7 configuration of Eu^{2+}) does the transition occur in the visible. Since cyclooctatetraene dianion is more easily oxidized to the corresponding radical anion than is cyclopentadienyl anion, ligand to metal charge transfer is expected at longer wavelengths in the $C_8H_8^{2-}$ complexes.

The visible spectra of the mono-C_8H_8 dianion chloride complexes in THF also show characteristic broad absorptions with ϵ of around 10^2. The absorptions are, however, of generally lower ϵ than for the corresponding biscyclooctatetraene complexes and do not follow a clear monotonic trend in energy as one goes across the lanthanide series. The other interesting observation is that as the coordinated solvent is removed under vacuum from the cerium or samarium complexes, the color becomes much less intense. This desolvated material still has chemical, physical, and spectral properties which establish the structures as being fundamentally the same except for the coordinatedTHF molecules; in particular the colors of the cerium and samarium complexes are regenerated when the desolvated powders are added to

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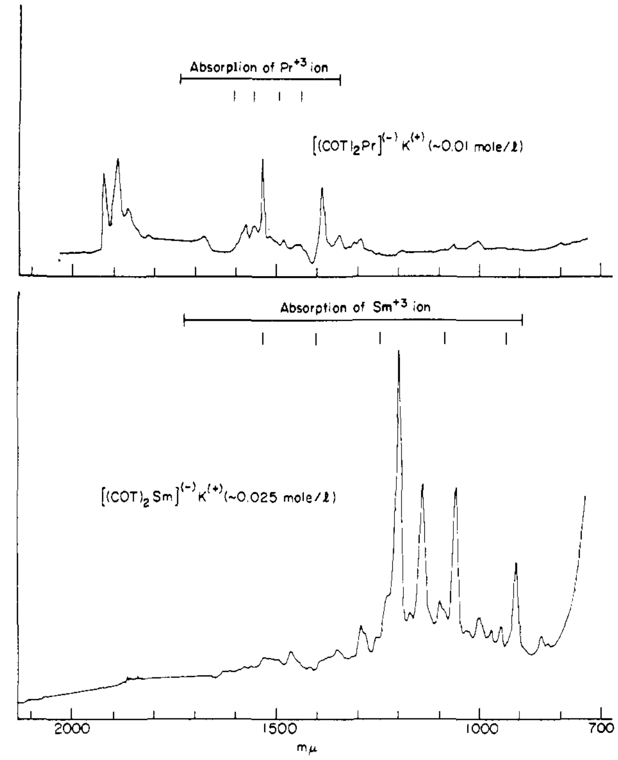

Figure 2. Near-infrared spectra of $[Pr(C_8H_8)_2]K$ and $[Sm(C_8H_8)_2]K$ in tetrahyrofuran solution.

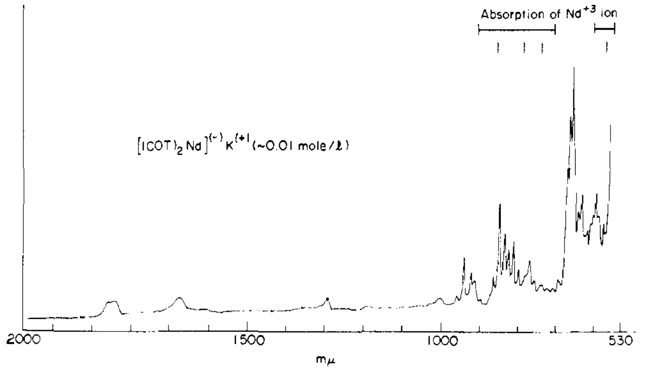

Figure 3. Near-infrared spectrum of $[Nd(C_8H_8)_2]K$ in tetrahydrofuran solution.

THF. This result suggests involvement of solvent in the inner coordination sphere in those transitions responsible for the colors of the mono-C_8H_8 chloride complexes; that is, the absorption in the visible region presumably does not result from solvent to metal charge transfer but rather the position of the ligand to metal band is shifted to higher energy as a result of the change in coordination around the central metal. Especially in the case of the neodymium complex, it appears that there may be less overall charge-transfer character since the absorption is split into three more distinct bands of lower extinction coefficient. Neodymium trichloride in acidic solution has an absorption centered at 579 nm (ϵ = 7). Further assignments of these absorptions cannot be made without additional studies.

Near Infrared. The near-ir spectra (1000–2000 nm) for several of the complexes were also measured using similar techniques except that saturated solutions in THF were used. Figure 2 shows the near-ir spectra in the region of 700–2000 nm for the complexes $K[Ln(C_8H_8)_2]$ in THF where Ln is Pr and Sm. Figure 3 is the spectrum of $K[Nd(C_8H_8)_2]$ in THF in this same spectral region. The cerium complex showed no absorption in this region. Only two of the monocyclooctatetraene chlorides were studied. The complex $[Ce(C_8H_8)Cl\cdot 2C_4H_8O]_2$ also showed no absorption and the absorption of the analogous samarium complex in THF from 800–2000 nm is shown in Figure 4.

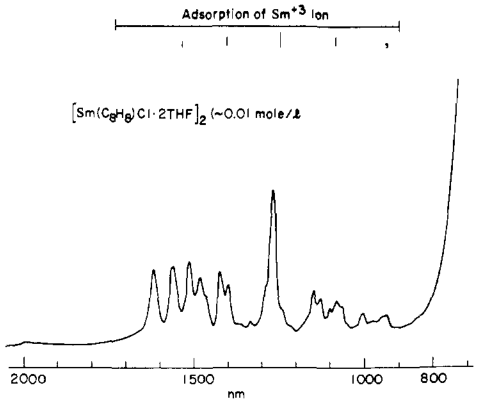

Figure 4. Near-infrared spectrum of $[Sm(C_8H_8)Cl\cdot 2C_4H_8O]_2$ in tetrahydrofuran solution.

These sharp transitions with low extinction coefficients (ϵ = 5–10) are characteristic of f^n transitions of the corresponding free ions in acidic solution or vapor phase. In each of the spectra (Figures 2–4), the absorption of the corresponding free ions in solution as measured from acidic solutions of the corresponding aquo-lanthanide halides[35] is indicated above the observed spectra of the complexes. The free ion extinction coefficients are, as expected, somewhat solvent dependent. Although the absorptions occur in the same region as the free ions, the band structure for these complexes is different from the aquo ions and the extinction coefficients are several times higher. The higher extinctions undoubtedly result from a decrease in the symmetry forbiddenness of the f^n transitions. The degeneracy of the normally spherically symmetric functions is split by the ligand field and f^n transitions become more allowed from vibronic coupling with the ligand field. It is thus reasonable to conclude that the absorptions in this region are f-orbital transitions with enhanced extinction coefficients resulting from the ligand field.

Magnetic Susceptibilities. The magnetic susceptibilities of the complexes have been measured at ambient temperature as described in the experimental section. Table VII compares the observed magnetic moments for the $K[Ln(C_8H_8)_2]$ complexes with the moments of the free ions. The analogous magnetic data for the mono-C_8H_8 lanthanide chloride complexes are summarized in Table VIII. In each case for both series of complexes the moments of the complexes as calculated by the normal Gouy procedure with diamagnetic corrections[24] correspond closely with the moments of the free ions. The outerlying $5s^2$ and $5p^6$ electrons effectively shield the 4f electrons from interaction with external ligand fields, and thus the 4f ion electronic configurations are given to a good degree of approximation by the Russell–Saunders coupling pattern, except in the case of Sm(III)

Table VIII. Visible Spectra and Magnetic Moments of the $[Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2$

Ln	λ_{max}, nm	ϵ	Magnetic moment, BM
Ce	477	419	1.79
Pr			3.39
Nd	578	58	3.37
	605	93	
	623	51	
Sm	542	243	1.36

where a low-lying excited state appears to be appreciably populated at room temperature.

The similarity in magnetic susceptibility for each of the paramagnetic complexes suggests similarity of their electronic configurations with those of the corresponding free ions.

Chemical Properties and Reactions. The most striking property common to all of the complexes reported here is their often violent air oxidation. Even small amounts will spark or ignite. After air oxidation, the odor of C_8H_8 is easily detectable. Under controlled oxidation at low temperature both series of complexes give C_8H_8 in nearly quantitative yield. This technique was used to first establish the stoichiometry of the complex. A weighed amount of complex was oxidized in CCl_4 at $-15°$ by bubbling dry oxygen through a stirred suspension of the complex. The solution was filtered through a fine fritted disk and a weighed amount of benzene was added as an internal reference. In the 60-MHz nmr spectrum of this solution the only peak resulting from the sample oxidation was a sharp singlet at δ 5.9 ppm corresponding to C_8H_8 with a C_8H_8 : metal molar ratio of close to 2:1. Similar quantitative results were difficult to obtain for the mono-C_8H_8 chloride complexes because of the variable amount of solvation. They do, however, give only C_8H_8 from the π-carbocyclic ligand on air oxidation as determined by nmr.

A second category of chemical reaction for the complexes is their hydrolysis and solvolysis. The two series of complexes are much more similar to $Th(C_8H_8)_2$[4] in their solvolytic behavior than to $U(C_8H_8)_2$ in that they are rapidly decomposed by water. To establish the identity of the organic reaction products of hydrolysis of $K[Ce(C_8H_8)_2]$ and $[Ce(CeH_8)Cl \cdot 2C_4H_8O]_2$, degassed water was vacuum transferred onto the frozen solid at liquid nitrogen temperature and the mixtures were allowed to warm slowly to 0°. In both cases hydrolysis began to occur at around -30 to $-20°$ and took about 5 min to complete giving a white insoluble powder, probably cerium hydroxide, and an organic liquid as a second layer. No gas was evolved during the reactions. The organic layers were each extracted with CCl_4, and the CCl_4 was dried with anhydrous $MgSO_4$ and filtered into nmr tubes. The spectra of both hydrolysis reactions were superimposable except for the presence of THF in the spectrum of the $[Ce(C_8H_8)Cl \cdot 2C_4H_8O]_2$ reaction mixture. The spectra showed *no* sharp singlet at δ 5.9 ppm; hence, C_8H_8 was absent. A broad methylene peak at δ 2.4 ppm and a multiplet centered around δ 5.9 ppm integrated with area ratios of 4:6.1, indicative of cyclooctatrienes. The same spectrum was given by an authentic equimolar mixture of the two isomeric cyclooctatrienes. Thus, the products are the same as given by hydrolysis of C_8H_8 dianion itself.

All of the complexes undergo solvolysis in protic solvents such as amines, alcohols, and acids. In fact, even small amounts of cyclohexylamine in the inert atmosphere box caused decomposition of the complexes. For the series of $K[Ln(C_8H_8)_2]$ complexes the rate of solvolysis at ambient temperature is qualitatively greater for $K[Tb(C_8H_8)_2]$ and slowest for $K[Ce(C_8H_8)_2]$ with the other members of the series falling in between. This may be due to the increased solubility in polar solvents as one goes across the lanthanide series.

The complexes are destroyed immediately by aqueous acid. Concentrated HCl or HNO_3 induced rapid polymerization of the organic products to yield intractable tars.

One important reaction of the lanthanide complexes is that with UCl_4. Solid $K[Ce(C_8H_8)_2]$ or $K[Sm(C_8H_8)_2]$ when added to a THF solution of UCl_4 in the glove box produced the green color of uranocene instantly; spectral analysis using the visible band of uranocene shows an 89% yield of uranocene produced from the Ce complex. This result suggests greater thermodynamic stability of $U(C_8H_8)_2$ relative to the lanthanide complexes.

To completely clarify the series of equilibria relating the lanthanide trichloride, the mono-C_8H_8 lanthanide chloride and the bis-C_8H_8 lanthanide salt, summarized in Scheme I, we carried out the equilibrium reaction between $CeCl_3$ and $K[Ce(C_8H_8)_2]$ described in the Experimental Section. The rate of the reaction was limited by the solubility of $CeCl_3$ in the THF solution, but after 20 min all of the $K[Ce(C_8H_8)_2]$ was quantitatively converted to $[Ce(C_8H_8)Cl \cdot 2C_4H_8O]_2$ as determined by the visible spectrum. We also found that $[Ce(C_8H_8)Cl \cdot 2C_4H_8O]_2$ reacts with additional $K_2(C_8H_8)$ to yield the $K[Ce(C_8H_8)_2]$ complex. Thus, in the reaction of $CeCl_3$, with 2 equiv of $K_2(C_8H_8)$ the first formed product is clearly $[Ce(C_8H_8)Cl \cdot 2C_4H_8O]_2$ which subsequently reacts with more $K_2(C_8H_8)$ *via* reaction B. When $K_2(C_8H_8)$ is not present in excess, little of the bis-C_8H_8 product is formed.

Scheme I. Equilibria Relating the Lanthanide Trichloride and the Two Complexes $[Ln(C_8H_8)_2]K$ and $[Ln(C_8H_8)Cl \cdot 2THF]_2$ in THF

$$2LnCl_3 + 2K_2C_8H_8 \rightleftharpoons [Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2 + 4KCl$$

$$[Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2 + 2K_2C_8H_8 \rightleftharpoons 2[Ln(C_8H_8)_2]K + 2KCl$$

$$[Ln(C_8H_8)_2]K + LnCl_3 \rightleftharpoons [Ln(C_8H_8)Cl \cdot 2C_4H_8O]_2 + KCl$$

Finally, we call attention to the importance of the effective basicity of the co-ligand as in the bridged chloride complexes. We actually first obtained such complexes in attempts to prepare the neutral mixed complexes $Ln(C_8H_8)(C_9H_9)$. The inability of cyclononatetraenyl anion to compete with chloride ion as a ligand undoubtedly reflects the diffuse charge density of the large ring anion. We did succeed in preparing the mixed complex $Ce(C_8H_8)(C_5H_5)$ whose visible absorption spectrum differed from other cerium complexes, but complete characterization was not pursued. Such neutral complexes have since been prepared and characterized by J. Takats (personal communication). The charge density of cyclopentadienyl anion is clearly sufficient to provide effective competition with chloride ion as a lanthanide ligand together with $C_8H_8^{2-}$.

Conclusions

Two series of cyclooctatetraene lanthanide complexes are described, $K[Ln(C_8H_8)_2]$ and $[(C_8H_8)LnCl\cdot 2THF]_2$. The empirical composition of both series of complexes has been well established by analysis and low-temperature oxidation. The molecular structures of both series are established by comparison of spectral characteristics with the corresponding cerium complex for which in both cases the single crystal X-ray structure has been determined.

The chemical and spectral results demonstrate that these complexes involve no chemically significant amount of covalent interaction with the metal. The ease of hydrolysis and the hydrolysis products are characteristic of ionic salts of C_8H_8 dianion. The facile interconversion of the two series of complexes is also indicative of highly ionic bonding. The near-ir spectra are characteristic of f^n transitions in the central metal ion with only mild perturbation by the ligand field. The magnetic susceptibility results lead to a similar conclusion. The assignment of visible bands as ligand to metal charge-transfer transitions, however, does imply some overlap of ligand π MO's and metal atomic orbitals. Nevertheless, even if the 4f orbitals are involved in such transitions, the actual amount of overlap need only be minute and without chemical significance. Such minute overlap could still correspond to essentially ionic ligand–metal bonding. Furthermore, included among these sandwich complexes is that with yttrium which is not a lanthanide rare earth and which has no 4f electrons or accessible 4f orbitals; yet its complex has properties similar to those of the lanthanide rare earth complexes.

These results provide a valuable contrast to the corresponding actinide complexes and suggest that the actinides do have significant ring–metal covalent bonding. The Raman spectral results show that the M–C bond strength in uranocene is greater than in the corresponding lanthanide complexes.

Finally, the rapid and complete conversion of the cerium complex to uranocene on treatment with UCl_4 also emphasizes the greater thermodynamic stability of the actinide complex. Thus, all of this chemistry is consistent with the simple hypothesis that the lanthanide C_8H_8 complexes are almost wholly ionic whereas the actinide C_8H_8 complexes have significant ring-metal covalent bonding involving metal orbitals; these differences suggest strongly that the actinite orbitals involved in such covalent interaction are 5f orbitals.

Acknowledgment. We thank Dr. Norman Edelstein of the Lawrence Berkeley Laboratory and Professor Gerd M. LaMar of University of California, Davis, who measured preliminary nmr spectra of the paramagnetic complexes. We also thank Professor Kenneth Raymond for his helpful discussions and suggestions.

Pentachlorocyclopentadienylmercurials

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received June 11, 1973*

Abstract: The first σ-bonded organometallic derivatives of the pentachlorocyclopentadienide anion, $C_5Cl_5^-$, are reported. The compounds $Hg(C_5Cl_5)_2$, C_5Cl_5HgCl, C_5Cl_5HgBr, and $C_6H_5HgC_5Cl_5$ are prepared either by the reaction of mercuric halides with thallium pentachlorocyclopentadienide or by the reaction of methoxides of mercury with pentachlorocyclopentadiene. Different crystalline phases of these compounds and adducts of these compounds with ethers and with mercuric halides are described and characterized. The presence of a σ-bonded C_5Cl_5 ring rather than a π-bonded ring is deduced from ir, nqr, and uv spectra of the mercurials. The electronic spectra of substituted cyclopentadienes are discussed; those for the mercurials are interpreted in terms of σ–π conjugation between the C–Hg bond and the cyclopentadiene π orbitals.

Organometallic derivatives of chlorocarbons were little known until recently, but this field has grown rapidly in the last few years, as shown in the review by Chivers.[1] Organometallic derivatives of the interesting pentachlorocyclopentadienide anion,[2] $C_5Cl_5^-$ (**1**), were not isolated until 1970, when perchloroferrocene, $Fe(C_5Cl_5)_2$, and perchlororuthenocene, $Ru(C_5Cl_5)_2$, were prepared.[3] This preparation of π-bonded organometallic derivatives of **1** was supplemented in 1971 by the isolation of an ionic organometallic derivative $Tl^+C_5Cl_5^-$ (**1a**).[2] We wish to report a series of σ-bonded organometallic derivatives of mercury including bis(pentachlorocyclopentadienyl)mercury (**2**) and several compounds (**3–5**) of the general formula C_5Cl_5HgX, some ether adducts, and double salts.[4]

Synthesis

Compounds **2e** and **3a** were prepared by the action of **1a** on solutions of $HgCl_2$ in tetrahydrofuran at −78°. When 2 mol of **1a** was allowed to react with 1 mol of $HgCl_2$, **2e** was produced as colorless flat crystals. However, use of only 1 mol of **1a** furnished

$$2Tl^+C_5Cl_5^- + HgCl_2 \xrightarrow{THF} 2TlCl + Hg(C_5Cl_5)_2\text{-}THF$$

3a as lemon-yellow crystals. Mixing of equimolar amounts of **1a** and **3a** in tetrahydrofuran afforded **2e**.

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