CONTRIBUTION FROM THE RESEARCH LABORATORIES,
ETHYL CORPORATION, FERNDALE 20, DETROIT, MICHIGAN

The Preparation of Cyclopentadienyllanthanide Dichlorides

BY S. MANASTYRSKYJ, R. E. MAGINN, AND M. DUBECK[1]

Received April 6, 1963

The cyclopentadienyl dichlorides of samarium, europium, gadolinium, dysprosium, holmium, erbium, ytterbium, and lutetium can be formed by treating the respective trichlorides with one equivalent of cyclopentadienylsodium. When prepared in tetrahydrofuran the complexes are all isolated as the tris-(tetrahydrofuranates), $C_5H_5MCl_2\cdot(C_4H_8O)_3$. Magnetic susceptibility measurements on the europium, dysprosium, erbium, and ytterbium complexes show that the central lanthanide possesses a magnetic moment characteristic of the tripositive state.

The only organic derivatives of the lanthanides presently known, apart from a variety of chelate derivatives, are the tricyclopentadienyllanthanides[2] and the dicyclopentadienyllanthanide dichlorides recently reported by us.[3] On the basis of chemical and physical properties, both of these cyclopentadienyl type complexes are believed to be held together by essentially ionic bonds as opposed to the highly delocalized bonding present in the cyclopentadienyls of the transition metals. Our work in the organo-lanthanide field has led us to another group of cyclopentadienyl compounds—the cyclopentadienyllanthanide dichlorides—which completes the series of cyclopentadienyllanthanide type complexes. This new group of complexes is quite similar chemically to the tri[2] and dicyclopentadienyllanthanide compounds and it is believed that they are also bonded with essentially localized ionic metal–ligand interactions.

The cyclopentadienyllanthanide dichlorides are easily prepared by treating the respective trichlorides with one equivalent of cyclopentadienylsodium at room temperature. Isolation of the complexes can only be achieved by crystallization as they are nonvolatile and decompose on heating at reduced pressures. When prepared in tetrahydrofuran they are all isolated as tris-(tetrahydrofuranates), $C_5H_5MCl_2\cdot(C_4H_8O)_3$. Their preparation is also achieved by allowing a tricyclopentadienyllanthanide to react with an equivalent of the respective trichloride, or by treating a dicyclopentadienyllanthanide chloride with an equivalent of hydrogen chloride. These modes of preparation are illustrated in the equations

$$C_5H_5Na + MCl_3 + 3C_4H_8O \xrightarrow{C_4H_8O} C_5H_5MCl_2\cdot(C_4H_8O)_3 + NaCl$$

M = Sm, Eu, Gd, Dy, Ho, Er, Lu

$$(C_5H_5)_3Er + 2ErCl_3 + 9C_4H_8O \xrightarrow{C_4H_8O} 3C_5H_5ErCl_2\cdot(C_4H_8O)_3$$

$$(C_5H_5)_2YbCl + HCl + 3C_4H_8O \xrightarrow{C_4H_8O} (C_5H_5)YbCl_2\cdot(C_4H_8O)_3 + C_5H_6$$

The elemental analyses together with some physical properties are summarized in Table I. A molecular weight determination on the holmium derivative in boiling tetrahydrofuran indicates that it is a monomer and it can be concluded that the remaining complexes are also monomeric. All the complexes are reasonably soluble in tetrahydrofuran and can be crystallized from this medium; they are slightly soluble in benzene but completely insoluble in petroleum ether. They are very unstable both oxidatively and hydrolytically, decomposing in a matter of minutes on exposure to air and instantaneously in water. Properties of this nature, coupled with the color and magnetic moments of the complexes which resemble those of the lanthanide salts, strongly suggest that the cyclopentadienyl dichlorides are held together with ionic bonds. The magnetic moments of a representative sampling of the cyclopentadienyllanthanide chlorides as the tris-(tetrahydrofuranates) are shown in Table II.[4] The molar susceptibilities were measured at 300 and 194°K. The moments were determined from the Curie–Weiss law and are similar to the moments of the lanthanides in a +3 state. Spin coupling of the inner 4f electrons due to ligand field interaction is precluded in view of these magnetic data.

On the basis of the above evidence the exact spatial structure of the cyclopentadienyllanthanide dichloride tris-(tetrahydrofuranates) can only be inferred in the absence of unambiguous X-ray diffraction studies. However, it does appear that the complexes are octahedral with tetrahydrofuran occupying three of the sites with a fairly strong ligand bond *via* the oxygen atom, and the two chloride anions and the cyclopentadienyl group the remaining three positions. The fairly strong interaction between tetrahydrofuran and the central lanthanide is borne out by the facts that the ether is not easily lost from the complex at atmospheric pressures, and by the observation that on prolonged heating of the ytterbium derivative at 40° under high vacuum the ether is slowly lost and the material changes from an initial bright orange to a purple. This marked color change suggests some orbital interaction of the tetrahydrofuran with the ytterbium ion in the solvated complex.

Although the cyclopentadienyl dichlorides of the lanthanides from samarium to lutetium are readily

---

[1] To whom all inquiries should be addressed.

[2] J. M. Birmingham and G. J. Wilkinson, *J. Am. Chem. Soc.*, **78**, 42 (1956).

[3] R. E. Maginn, S. Manastyrskyj, and M. Dubeck, *ibid.*, **85**, 627 (1963).

[4] We are indebted to Professor Stanley Kirschner and Mr. John Bergman for the magnetic measurements.

TABLE I

TRIS-(TETRAHYDROFURANATES) OF THE CYCLOPENTADIENYLLANTHANIDE DICHLORIDES, $(C_5H_5)MCl_2 \cdot (C_4H_8O)_3$

Element M	Analysis, % Calculated C	H	Cl	M	Found C	H	Cl	M	Color	Thermal properties under N_2
Sm	40.6	5.82	14.1	29.9	40.7	5.77	14.4	29.9	Beige	No m.p.; color progressively darkens from 50 to 240°
Eu	40.5	5.80	14.1	30.1	40.4	5.83	14.6	30.3	Purple	No m.p.; color progressively darkens from 50 to 240°
Gd	40.1	5.74	13.9	30.9	39.4	5.90	14.3	31.1	Lavender	M.p. 82–86° dec.
Dy	39.7	5.68	13.8	31.6	39.0	5.72	13.9	32.1	Colorless	M.p. 85–90 dec.
Ho	39.5	5.65	13.7	31.9	39.6	5.74	13.8	31.7	Yellow	M.p. 84–92°
Er	39.3	5.63	13.7	32.2	38.6	5.52	14.0	32.6	Pink	M.p. 91–94°
Yb	38.9	5.56	13.5	32.9	38.2	5.56	13.8	33.5	Orange	M.p. 78–81°
Lu	38.7	5.54	13.5	33.2	37.9	5.30	13.2	33.4	Colorless	M.p. 76–78°

TABLE II

MAGNETIC SUSCEPTIBILITIES OF SOME CYCLOPENTADIENYLLANTHANIDE DICHLORIDE TRIS-(TETRAHYDROFURANATES), $C_5H_5MCl_2 \cdot (C_4H_8O)_3$

Lanthanide, M	$\chi_m^{corr} \times 10^{6a}$	Δ	Exptl. $\mu_{eff.}$	Theor.[b] $\mu_{eff.}$
Eu	4,870 6,336	157	4.24	3.5
Dy	44,254 60,744	90.9	11.81	10.6
Er	35,904 53,344	24.2	9.68	9.8
Yb	7,589	7.52	4.33	4.5

[a] The susceptibilities were corrected for the diamagnetic contributions of $C_5H_5^{(-)}$, $2Cl^{(-)}$, and $3C_5H_8O$. [b] Values taken from P. W. Selwood, "Magnetochemistry," Interscience Publ., Inc., New York, N. Y., 1956, p. 142.

prepared, all attempts to isolate similar complexes with lanthanum, praseodymium, and neodymium have failed. This same behavior of the lanthanide series was encountered with the lower lanthanides during the preparation of the dicyclopentadienyllanthanide chlorides.[3] As suggested then, the lanthanide contraction may be playing some subtle role in defining the stability of the mixed cyclopentadienyl chloride derivatives. Such a behavior is not present with the tricyclopentadienyllanthanides, as all members of the series readily yield this complex.[2] As yet, a thorough explanation for these observations cannot be offered.

Experimental

All manipulations were performed under an atmosphere of prepurified nitrogen. The anhydrous solvents utilized were freshly distilled and protected from the atmosphere. The anhydrous lanthanide trichlorides were prepared by treating the commercially available hydrates with thionyl chloride.[5] Cyclopentadienylsodium was prepared by adding the freshly prepared monomer to a dispersion of sodium in tetrahydrofuran. After standardization, the solution was employed directly in the synthetic work.

The procedure for the preparation of cyclopentadienylsamarium dichloride tristetrahydrofuranate, outlined below, is applicable for all of the mentioned lanthanide complexes. The yield of product varied between 30 and 60% and seemed to depend on the care exercised in crystallization.

The Preparation of Cyclopentadienylsamarium Dichloride Tris-(tetrahydrofuranate).—Samarium trichloride, 4.9 g. (0.19 mole), was suspended in 125 ml. of tetrahydrofuran. To this stirred suspension 10 ml. of a 1.9 *M* solution of cyclopentadienylsodium in tetrahydrofuran was slowly added and the reaction mixture was stirred at room temperature overnight. The mixture was then filtered and the filtrate was concentrated under reduced pressures until crystallization was initiated and it was then kept at 0° until crystallization was complete. The fine light beige needles were filtered, washed with tetrahydrofuran at −50°, and dried under vacuum at room temperature for about 15 min. Cyclopentadienylsamarium dichloride tris-(tetrahydrofuranate) was isolated in a yield of 3.4 g. (35.4%), m.p. 91 to 94°, with an analysis shown in Table I. The infrared spectrum of the complex exhibited major peaks at 3350, 1640, 1450, 1360, 1050, and 1015 cm.$^{-1}$. All of the complexes presently prepared exhibited identical absorptions.

The Reaction of Dicyclopentadienylytterbium Chloride with One Equivalent of Hydrogen Chloride.—To a clear red-orange solution of 2.70 g. (0.00798 mole) of dicyclopentadienylytterbium chloride in 100 ml. of tetrahydrofuran was added dropwise 25 ml. of tetrahydrofuran solution containing 0.00798 mole of hydrogen chloride. During the addition, a slight darkening of the red color was observed. After stirring overnight, the solvent was removed at reduced pressure to approximately one-fourth the original volume, whereupon a considerable amount of orange solids precipitated from solution. After cooling 1 hr. at 0°, the suspension was filtered. The orange solids thus obtained were dissolved in the minimal amount of tetrahydrofuran, and, after filtration, the resulting solution was cooled at 0° overnight, yielding 1.3 g. (31%) of orange crystals of cyclopentadienylytterbium dichloride tris-(tetrahydrofuranate).

The Preparation of Cyclopentadienylerbium Chloride Tris-(tetrahydrofuranate) from Tricyclopentadienylerbium and Erbium Trichloride.—Erbium trichoride, 7.20 g. (0.0266 mole), was added to a stirred solution of tricyclopentadienylerbium, 4.40 g. (0.0121 mole), at room temperature. Pink crystals immediately appeared in the reaction mixture, but it was stirred for an additional 4 hr. These crystals were redissolved by heating the reaction flask in warm water and the clear solution was then slowly cooled to 0°, which caused a massive crystallization of the product. These crystals were filtered and dried under vacuum for about 15 min. The yield of cyclopentadienylerbium dichloride tris-(tetrahydrofuranate) was 11.5 g. (60.8%).

Molecular Weight Determinations.—Molecular weight measurements were made on the holmium derivative in tetrahydrofuran utilizing the standard differential ebulliometric techniques. Anthracene was employed as an internal standard to compensate for any impurities in the solvent. The results indicate that the complexes are monomers in boiling tetrahydrofuran as the holmium derivative was found to have a molecular weight of 579 (calculated 517).

Acknowledgments.—This study was partially supported by the Atomic Energy Commission under Contract No. AT(11-1)-999. The authors are indebted to Dr. A. H. Filbey for his helpful suggestions throughout the course of our work and to Mrs. Patricia Wilson and Mr. Paul Kemp for the analytical determinations.

---

(5) T. Moeller, *Inorg. Syn.*, **5**, 153 (1957).