[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, HARVARD UNIVERSITY]

The Cyclopentadienides of Scandium, Yttrium and Some Rare Earth Elements

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RECEIVED AUGUST 25, 1955

Compounds of the formula $(C_5H_5)_3M$ where M is Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb have been prepared by reaction of the metal chloride with sodium cyclopentadienide in tetrahydrofuran solution, followed by sublimation of the compounds from the dry reaction mixture at 200–250° *in vacuo*, They are crystalline solids which react rapidly with air. The metal to C_5H_5 ring bonds are shown to be ionic in nature. Magnetic properties and absorption spectra of some of the compounds have been studied. Ammoniates of $(C_5H_5)_3Pr$ and $(C_5H_5)_3Sm$ have been noted.

I. Introduction

It seems to be fairly certain that alkyl and aryl derivatives of scandium, yttrium, lanthanum and the rare earth elements either do not exist or have an existence so transitory that they cannot be isolated.[1] The best chance of isolating organometallic compounds of these highly electropositive elements appeared to lie with the cyclopentadienide ion, since some ionic derivatives of electropositive elements, *e.g.*, C_5H_5K[2] and C_5H_5MgBr[3] have long been known, and others, $(C_5H_5)_2Mg$ and $(C_5H_5)_2Mn$ have been recently characterized.[4a,b]

By the reaction of the metal chloride with sodium cyclopentadienide in tetrahydrofuran solution, we have prepared the compounds $(C_5H_5)_3M$ where M is Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb; some of these compounds have been noted in a preliminary communication.[5]

II. Experimental

Materials.—The scandium oxide was prepared from thortveitite ore by the late Professor G. P. Baxter of this Department. Spectroscopic analysis showed impurities of approximately 1% Ca, 1% Zr, 0.5% Th, 0.5% combined rare earths and traces of other elements. Since calcium cyclopentadienide is non-volatile, the biscyclopentadienyl halides of Zr and Th sublime only very slowly at the temperatures used for sublimations in this work, and since $(C_5H_5)_3Sc$ sublimes at a temperature 20–30° lower than the compounds of the most abundant rare earth elements, no special purification of scandium oxide was made.

The following oxides were obtained from Research Chemicals, Inc. (Burbank, Calif.); Y_2O_3 99%, La_2O_3 99.9%, Ce_2O_3 99.8%, Pr_6O_{11} 98%, Nd_2O_3 99%, Sm_2O_3 99.9%, Gd_2O_3 98%. The following oxides were obtained from the loan collection of the Ames Laboratory of the Atomic Energy Commission, Iowa State University, Ames, Iowa, and were of 99.9% purity or better; Dy_2O_3, Er_2O_3, Yb_2O_3.

Tetrahydrofuran was purified by treatment in a 1 m. × 3 cm. column of Linde Air Products "Molecular Sieves" Type 13A, 1/16" pellets with a flow rate of 20 ml./min. For special purposes, the prepurified solvent was distilled in nitrogen over lithium aluminum hydride.

Preparations.—All the compounds described in this paper were prepared in an identical manner, by the reaction of the metal chloride with sodium cyclopentadienide in tetrahydrofuran solution. These reactions and all subsequent operations on the compounds were carried out either in an inert atmosphere, using a gloved box where necessary, or in a vacuum apparatus.

The metal chlorides were prepared from the oxides by the reaction with ammonium chloride at 300°.[6] Sodium cyclopentadienide was prepared in tetrahydrofuran by the reaction of sodium shot with cyclopentadiene (*cf.* ref. 4b). In each case, 0.04 mole of the anhydrous metal chloride was added to 0.20 mole of sodium cyclopentadienide in 200 ml. of tetrahydrofuran. The mixture was refluxed with rapid stirring for 2–4 hours. The solvent was removed under reduced pressure, and the dry residue transferred to a sublimation apparatus. On heating at 220–250° at 10^{-3}–10^{-4} mm. pressure, the crude cyclopentadienides sublimed and were collected on a water-cooled probe. The products were purified by resublimation along a Pyrex tube having constrictions to allow the samples to be sealed off *in vacuo*.

For the various compounds, Table I presents the temperature for moderate rates of sublimation (~ 10 g. per hour in the 4 cm. diameter Pyrex vessel used) of the crude product at ~10^{-4} mm., the yields and the melting point and color of the compounds. The melting points were determined in sealed tubes using high boiling oil and fused salt baths; temperatures were measured with a calibrated thermometer and a thermocouple and melting points are believed to be in error by no more than ±2°.

TABLE I

PREPARATION AND SOME PHYSICAL PROPERTIES OF CYCLOPENTADIENIDES

Compd. $(C_5H_5)_3$-M	Subli. temp., °C. at 10^{-4} mm.	Yield G.	Yield % theory	Color	M.p., °C.	Melt color
Sc	200	7.3	75	Straw	240	Red
Y	220	9.7	85	V. pale yellow	295	Greenish yellow
La	260	3.3	25	Colorless	395[a]	Colorless
Ce	230	9.6	72	Orange-yellow	435[a,b]	Yellow
Pr	220	11.1	83	Pale green	415[a]	Green
Nd	220	10.5	78	Reddish-blue	380	Reddish-blue[c]
Sm	220	10.4	75	Orange	365	Orange
Gd	220	11.9	84	Yellow	350	Yellow
Dy	220	12.9	85	Yellow	302	Yellow
Er	200	12.8	88	Pink	285	Pink
Yb	150	12.0	82	Dark green	273[a]	Green

[a] Slight decomposition occurs. [b] Blue-green vapor formed. [c] Red by transmitted light.

Analyses.—Analyses for metals were made by destruction of the compounds first with water and then by fuming with perchloric acid. The oxalate was then precipitated and this was ignited to the oxide for weighing. We are indebted to Dr. E. O. Brimm for arranging for carbon and hydrogen analyses on these reactive materials in the laboratories of the Linde Air Products Co., Tonawanda, N. Y.

Analyses of the compounds of Sc, Ce, Nd and Sm have been given previously.[5] The remaining analyses are given in Table II.

TABLE II

ANALYSES OF $(C_5H_5)_3M$ COMPOUNDS

Metal	Required C	Required H	Required M	Found C	Found H	Found M
Y	63.4	5.32	31.28	62.8	5.1	31.35
La	53.90	4.52	41.58	53.4	4.5	41.53
Pr	53.61	4.49	41.88	52.9	4.1	41.92
Gd	51.15	4.29	44.55	50.8	4.2	44.81
Dy			45.44			45.62
Er			46.15			46.10
Yb	48.9	4.10	47.00	48.4	4.1	47.22

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[1] For references see F. A. Cotton, *Chemical Revs.*, **55**, 554 (1955).

[2] J. Thiele, *Ber.*, **34**, 68 (1901).

[3] V. Grignard and C. Courtant, *Compt. rend.*, **158**, 1763 (1914).

[4] (a) G. Wilkinson and F. A. Cotton, *Chemistry and Industry (London)*, **11**, 307 (1954); (b) G. Wilkinson, J. M. Birmingham and F. A. Cotton, *J. Inorg. Nuclear Chem.*, in press.

[5] G. Wilkinson and J. M. Birmingham, THIS JOURNAL, **76**, 6210 (1954).

[6] "Inorganic Syntheses," H. S. Booth, Editor, McGraw-Hill Book Co., New York, N. Y., 1931, Vol. I, p. 28.

Chemical Properties.—The compounds have very similar chemical properties. They are all decomposed rapidly by water to give cyclopentadiene and the metal hydroxide, together with some polymeric organic material. Dilute acids cause effervescence and liberation of cyclopentadiene. The compounds are all sensitive to air and are decomposed on exposure. The cerium compound is the most reactive compound, and on exposure to even traces of air it turns black. This exceedingly ready oxidation must be attributed to the ease of oxidation of cerous ions in the crystal lattice to the ceric state.

All the cyclopentadienides are virtually insoluble in petroleum ether, cyclohexane and benzene. They are moderately soluble in pyridine and in tetrahydrofuran, glycoldimethyl ether and dioxane. With carbon disulfide, carbon tetrachloride and chloroform, rapid decomposition occurs. The compounds slowly react with carbon dioxide (*cf.* ref. 4b). They react at once with maleic anhydride and with aldehydes and ketones in a manner similar to $(C_5H_5)_2Mn$ or C_5H_5Na (*cf.* ref. 4b).

With ferrous chloride, prepared in tetrahydrofuran solution by reduction of anhydrous ferric chloride with iron powder,[4b] selected $(C_5H_5)_2M$ compounds reacted instantaneously and quantitatively at 25° to form ferrocene. The ferrocene was recovered from the reaction mixture by extraction with petroleum ether after the tetrahydrofuran had been removed first.

The cyclopentadienides are only sparingly soluble in liquid ammonia; the conductance of these solutions is qualitatively of the same order as the conductivity of $(C_5H_5)_2Mn$ in liquid ammonia.[4b] Ammoniates are formed and the ammonia is not removed by pumping at 25°, although on heating the ammoniates at 100–150° ammonia is lost and the cyclopentadienides are recovered. For praseodymium, the ammoniate is a very pale green, almost white, and for samarium the ammoniate is yellow. After pumping on the samples for an hour at 25° in both cases the compounds analyzed approximately for $(C_5H_5)_3M.NH_3$. (*Anal.* Calcd.: Pr, 39.8; N, 3.96. Found: Pr, 40.0; N, 3.6. Calcd.: Sm, 41.50; N, 3.86. Found: Sm, 41.65; N, 3.7.)

As originally obtained by sublimation, the cyclopentadienides are often microcrystalline; on annealing sealed tubes of the compounds at 220–250°, or by subliming the compounds on to hot surfaces, well defined single crystals can be obtained. The lanthanum compound we have been unable to crystallize, while the cerium and praseodymium compounds are more difficult than the others to crystallize.

Physical Properties.—The molecular weight of $(C_5H_5)_3Nd$ was determined by the method of isothermal distillation,[7] using tetrahydrofuran as the solvent and ferrocene as a reference. The neodymium compound was sublimed into one arm of the apparatus; a weighed pellet of ferrocene was introduced into the other arm and, after admission of solvent from a vacuum system, the apparatus was sealed off. The neodymium content of the solution was determined subsequently by analysis. The molecular weight was 341 ± 5 (theory 339.54). For $(C_5H_5)_3Sc$ and $(C_5H_5)_3Y$, the molecular weights were similarly close to the theoretical value. These results, together with the fact that the electrical conductivities in tetrahydrofuran are only slightly greater than that of the solvent indicates that the compounds are essentially undissociated in tetrahydrofuran solution.

The absorption spectra in the visible region of tetrahydrofuran solutions of some of the compounds have been measured using a Cary Model 11 B spectrophotometer; in Figs. 1 and 2 are shown as examples the spectra of $(C_5H_5)_3Pr$ and $(C_5H_5)_3Er$.

The magnetic properties of the $(C_5H_5)_3M$ compounds have been studied by methods previously described for $(C_5H_5)_2Mn$[4b]; no dependence of the susceptibility on field strength was noted. The values of the susceptibilities (Table III) are good to ±2%. In Table III are also given the experimentally determined effective magnetic moments calculated using the Curie–Weiss law, $\mu_{\text{eff}} = 2.83\sqrt{\chi^{\text{cor}}_{\text{mol}}(T + \Delta)}$, together with the theoretical moments of Van Vleck and Frank,[8] and the range of previous determined moments of various rare earth compounds.[9] None of the paramagnetic compounds with the exception $(C_5H_5)_3Gd$ satisfy Curie's Law; as in other compounds, Sm shows temperature dependent effects due to multiplet intervals being comparable to kT.

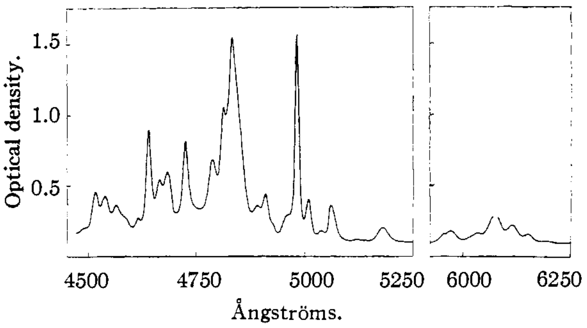

Fig. 1.—Absorption spectrum of $(C_5H_5)_3Pr$, 0.045 *M* in tetrahydrofuran, 1 cm. cell.

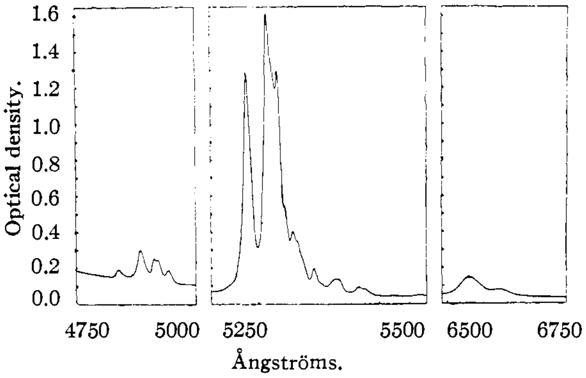

Fig. 2.—Absorption spectrum of $(C_5H_5)_3Er$, 0.0014 *M* in tetrahydrofuran, 1 cm. cell.

TABLE III

MAGNETIC DATA FOR SOME RARE EARTH CYCLOPENTADIENIDES

Compd.	Ground term of metal ion	Temp., °K.	$\chi^{\text{cor}}_{\text{mol}} \times 10^{6a}$	Δ, °C.	Exptl. μ_{eff}	Calcd. $\mu_{\text{eff}}{}^{b}$	Ranges of $\mu_{\text{eff}}{}^{c}$
$(C_5H_5)_3Ce$	$^2F_{5/2}$	295	2,230		2.46		
		194	3,420	15	2.46	2.54	2.10–2.77
		77	8,000		2.46		
$(C_5H_5)_3Pr$	$^3H_4$	295	4,700		3.61		
		194	6,780	37	3.59	3.62	3.41–3.62
		77	14,100		3.61		
$(C_5H_5)_3Nd$	$^4I_{9/2}$	295	4,260		3.63		
		194	5,960	72	3.62	3.68	3.43–3.62
		77	10,800		3.63		
$(C_5H_5)_3Sm$	$^6H_{5/2}$	295	1,080	0			
		194	1,160	60	1.54	1.65	1.32–1.63
		77	1,550	113			
$(C_5H_5)_3Gd$	$^8S_{7/2}$	295	26,800		7.98		
		194	40,500	0	7.95	7.94	7.46–8.1
		77	103,000		7.95		
$(C_5H_5)_3Dy$	$^6H_{15/2}$	295	40,000		10.0		
		194	59,200	15	10.0	10.6	10.0–10.6
		77	133,000		10.0		
$(C_5H_5)_3Er$	$^4I_{7/2}$	295	35,600		9.45		
		194	52,500	17	9.44	9.8	9.0–9.5
		77	118,200		9.45		
$(C_5H_5)_3Yb$	$^2F_{7/2}$	295	6,160		4.00		
		194	9,070	21	4.00	4.5	4.3–4.6
		77	20,350		4.00		

[a] Values include diamagnetic correction for the C_5H_5 rings of -135×10^{-6} c.g.s.u. Reference: Mohr's salt $\chi_g^{295°} = +32.0 \times 10^{-6}$ c.g.s.u. [b] Data from ref. 8. [c] Data from ref. 9. The compounds of Sc, Y and La are diamagnetic.

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(7) E. D. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941).

(8) J. H. Van Vleck and N. Frank, *Phys. Rev.*, **34**, 1494 (1929).

(9) D. M. Yost, H. Russell, Jr., and C. S. Garner, "The Rare Earth Elements and their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 14.

In Fig. 3 are plotted the melting points of the compounds as a function of the empirical ionic radii for the oxides.[10] The melting points lie on a smooth curve with the exception of $(C_5H_5)_3La$; unlike the melting points of the halides there is no reversal in the region of terbium with a subsequent increase in melting point in going towards Lu, although there is a change in the slope of the curve.

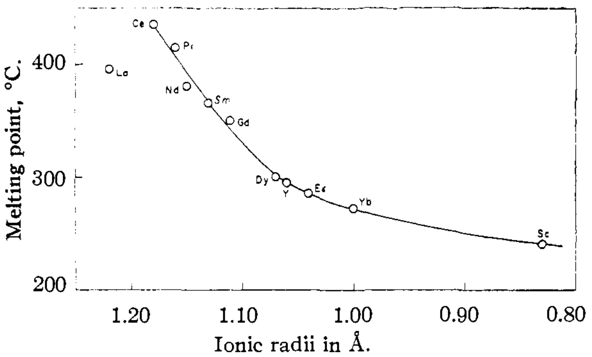

Fig. 3.—Melting points of the $(C_5H_5)_3M$ compounds *vs.* ionic radii of M^{3+}.

Discussion

The chemical and physical properties of the $(C_5H_5)_3M$ compounds clearly indicate their ionic nature. Thus while the dissociation, *e.g.*

$$(C_5H_5)_3Nd \rightleftarrows (C_5H_5)_2Nd^+ + C_5H_5^-, \text{ etc.}$$

is very small, perhaps attributable in part to a low tendency of the anion to solvate, the instantaneous liberation of cyclopentadiene with water or acids, and the instantaneous quantitative reaction with ferrous chloride to form ferrocene, show that the above type of equilibria are labile, and that agents attacking the cyclopentadienide ion will rapidly displace the equilibrium. The reactivity of the compounds toward maleic anhydride, aldehydes, ketones and halogenated solvents is due to this fact also.

The ionic nature of the compounds is also shown by properties dependent upon the metal atom. Thus the magnetic susceptibility values are very close to those for the rare earth ions in other compounds and there is little doubt that the metal to ring bonds in $(C_5H_5)_3M$ compounds are electrostatic in nature. The similarity of the absorption spectra of the $(C_5H_5)_3M$ compounds in tetrahydrofuran to those of the ions in aqueous solution is also in agreement with the ionic nature of the bonding; in the cyclopentadienides the bands are sharper and somewhat shifted to longer wave lengths.

In the absence of X-ray data, little can be said concerning the structure of the cyclopentadienides in the crystal or as the free molecules. Since the metal to ring bonds are electrostatic the $C_5H_5^-$ ions may be expected to lie with their centers at the vertices of an equilateral triangle at whose center is placed the metal ion; with such an arrangement the electrostatic energy would be at a minimum. The comparatively low melting points and ready volatilities suggest that the compounds exist, even in the crystals, as ionically bonded molecules. It is noteworthy that methyl substitution in the anion lowers the melting point for the neodymium cyclopentadienide by 215°[11]; ethylcyclopentadienides may be expected to melt at even lower temperatures and since steric hindrance may be expected with bulky substituents on the $C_5H_5^-$ ion, even greater differences may be found in melting points and volatilities over the range of the rare earth elements than occur with the $(C_5H_5)_3M$ compounds.

Acknowledgments.—We are indebted to Professor W. Moffitt for his helpful advice and criticism. Thanks are due to the National Institutes of Health for a fellowship and to the Mallinckrodt Chemical Company for their generous support of research expenses (J.M.B.).

This work was supported in part by the Atomic Energy Commission.

Cambridge, Mass.

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[10] T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 147.

[11] L. T. Reynolds and G. Wilkinson (unpublished work).

[Contribution from the Kedzie Chemical Laboratory, Michigan State University]

Bromine Pentafluoride. The Electric Dipole Moment in the Vapor State and the Dielectric Constant of the Liquid[1]

By Max T. Rogers. Richard D. Pruett, H. Bradford Thompson and John L. Speirs

Received August 2, 1955

The electric moment of bromine pentafluoride, determined from the dielectric constant of the vapor at several temperatures, is 1.51 ± 0.10 *D*. This value is consistent with a square prismatic structure for the molecule and excludes the trigonal bipyramidal and pentagonal planar configurations. The dielectric constant of the liquid in the range −12 to 25° may be represented by the equation $\epsilon = 8.20 - 0.0177\,t$. This is close to the value calculated theoretically from the gas dipole moment and indicates that bromine pentafluoride is not an associated liquid (in the conventional sense).

Introduction

Since the structure of bromine pentafluoride is not known we have measured the electric moment in the vapor state to provide information concerning the structure. A comparison of the dielectric constants of liquid chlorine trifluoride and iodine pentafluoride with the values calculated theoretically seemed to indicate that these are associated liquids.[2] This study has been extended to bromine pentafluoride by measurement of its dielectric constant over a range of temperature.

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[1] Physical properties of the halogen fluorides V. For preceding article of this series see M. T. Rogers, J. L. Speirs and M. B. Panish, This Journal, **77**, 5280 (1955).

[2] M. T. Rogers, H. B. Thompson and J. L. Speirs, *ibid.*, **76**, 4841 (1954).