

portion of polymeric species. Our results at pH 4 are wholly consistent with an equilibrium of monomeric $\text{In}^{\text{III}}\text{L}_2$ complexes with polymeric species and mmc's. We observe that the ratio of $\text{In}:\text{L}$ in polymeric complexes is less than 0.5. The degree of polymerization is much reduced at values of pH less than 4³ but the extent of mmc formation also becomes much less. Nothing is known of the structure of the $\text{In}^{\text{III}}\text{L}_2$ complexes which exist in very dilute solutions of pH 4, but both ligands are quite tightly bound to the metal ion since no dissociation of these complexes was detected when the concentration of free ligand was as low as $10^{-2} M$.

The general picture which emerges from this investigation is one of the coexistence of very stable polymeric complexes of each metal ion with an mmc where the most stable species is the mmc. The data allow estimations of monomeric, polymeric, and mmc concentrations to be made in solutions containing either or both $\text{In}(\text{III})$ and $\text{U}(\text{VI})$ in malate, citrate, or tartrate media. These calculations and the experimental results show that mmc formation and polymerization can drastically affect the distribution coefficient of a metal ion present in concentrations at the $10^{-6} M$ level (under certain conditions the distribution coefficient of $\text{In}(\text{III})$ was reduced by a factor of 10^2).

CONTRIBUTION FROM THE CHEMICAL LABORATORIES,
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Preparation and Some Reactions of Alkoxides of Gadolinium and Erbium

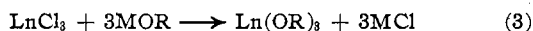
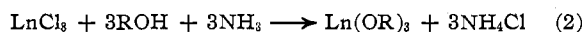
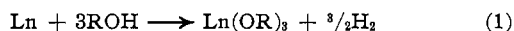
By R. C. MEHROTRA* AND J. M. BATWARA

Received April 8, 1970

Convenient methods for the preparation of alkoxides of gadolinium and erbium have been described. The pure isopropoxides can be obtained in quantitative yields by treating the 2-propanolates of the respective lanthanide chlorides with stoichiometric amounts of alkali isopropoxide. Alcoholysis of isopropoxides yields higher alkoxides. Reactions of isopropoxides with dry hydrogen chloride, *tert*-butyl acetate, and phenol were also carried out to yield chloride alcoholates, *tert*-butoxides, and phenoxides, respectively. Molecular complexity data show the soluble alkoxides to be oligomers in boiling benzene. Further identification of the products was made by infrared spectra.

In spite of considerable interest in the chemistry of alkoxides¹ of transition elements during the last decade only a few scattered references are available on similar derivatives of inner transition elements²⁻⁹ but these do not include any on gadolinium or erbium.

Experience in our laboratories and elsewhere^{1,8} suggested that the following general methods might be applicable for the preparation of the alkoxides of gadolinium and erbium



where Ln is lanthanide metal or ion, M is an alkali metal ion, and R is an alkyl group.

Method 1 has been used for the preparation of isopropoxides of dysprosium and ytterbium⁸ by treating

(1) R. C. Mehrotra, *Inorg. Chim. Acta, Rev.*, **1**, 99 (1967); D. C. Bradley, *Prog. Inorg. Chem.*, **2**, 303 (1960), and references cited therein.

(2) D. C. Bradley and M. M. Faktor, *Chem. Ind. (London)*, 1332 (1958).

(3) R. P. N. Sinha, *Sci. Cult.*, **25**, 494 (1960).

(4) D. C. Bradley, A. K. Chatterjee, and W. Wardlaw, *J. Chem. Soc.*, 2260, 3460 (1956); 2600 (1957).

(5) S. N. Misra, T. N. Misra, R. N. Kapoor, and R. C. Mehrotra, *Chem. Ind. (London)*, 120 (1963).

(6) B. S. Sankhla, S. N. Misra, and R. N. Kapoor, *ibid.*, 382 (1965).

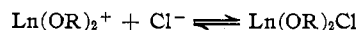
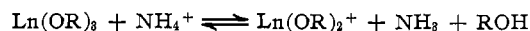
(7) J. M. Batwara, U. D. Tripathi, R. K. Mehrotra, and R. C. Mehrotra, *ibid.*, 1379 (1966).

(8) K. S. Mazdiyasi, C. T. Lynch, and J. S. Smith, *Inorg. Chem.*, **5**, 342 (1966).

(9) U. D. Tripathi, J. M. Batwara, and R. C. Mehrotra, *J. Chem. Soc. A*, 991 (1967).

metal shavings with isopropyl alcohol in the presence of the catalyst mercuric chloride. The method was attempted a number of times for gadolinium and erbium but was not pursued as the products could not be purified to a sufficient degree.

In method 2 also, the gadolinium and erbium products were found to be contaminated with appreciable amounts of chloride. This behavior is understandable with the analogy of similar observations in the case of thorium alkoxides.¹⁰ As gadolinium and erbium alkoxides are more basic than ammonia, the following equilibria may be feasible



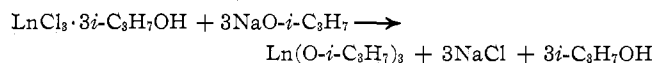
However, method 3 employing alkali metal alkoxides and anhydrous metal chlorides was found to be of general applicability for the preparation of pure soluble isopropoxides and insoluble methoxides of lanthanum, praseodymium, neodymium,⁵ and samarium⁶ and after a little modification was used for the preparation of alkoxides of gadolinium and erbium.

Results and Discussion

Soluble Alkoxides.—When gadolinium and erbium (hereafter described as lanthanide, abbreviated as Ln) chlorides suspended in benzene-isopropyl alcohol were

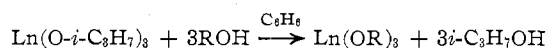
(10) D. C. Bradley, M. A. Saad, and W. Wardlaw, *ibid.*, 1091 (1954).

made to react with sodium isopropoxide, the ensuing reaction did not appear to proceed to completion as the products were contaminated with chloride. After repeated failures in the preparation of $\text{Ln}(\text{O-}i\text{-C}_3\text{H}_7)_3$ by this method, it was modified by taking the tri-2-propanolate of lanthanon chloride ($\text{LnCl}_3 \cdot 3i\text{-C}_3\text{H}_7\text{OH}$) in benzene-2-propanol and treating the solution with a stoichiometric quantity of sodium isopropoxide also in benzene-isopropyl alcohol solution



The alcoholate for the above reaction could also be prepared by refluxing the anhydrous chloride with isopropyl alcohol. It appears that the formation of alcoholate makes the lanthanide chloride more reactive and facilitates the completion of the reaction. Repeated experiments have shown that for a convenient separation of easily filtrable sodium chloride, it is essential that sodium isopropoxide in benzene solution is added to lanthanide chloride 2-propanolates and not in the reverse direction.

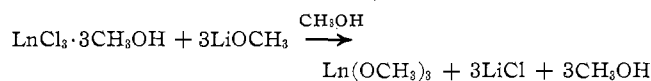
An alcohol interchange technique¹ has been employed subsequently by us for the synthesis of a large number of higher alkoxides of gadolinium and erbium by simple metathetic reactions in the presence of benzene



where R = *n*-C₄H₉, *sec*-C₄H₉, *tert*-C₄H₉, *n*-C₅H₁₁, *i*-C₅H₁₁, and *tert*-C₅H₁₁.

It was observed in these reactions that rate and facility were slower in the cases of branched alcohols in the order primary > secondary > tertiary, and the interchange reactions, as described, took about 5, 8, and 10 hr, respectively, for completion.

Insoluble Alkoxides.—The method suggested by Bradley and Faktor² for the preparation of lanthanum methoxide was employed for the preparation of methoxides of gadolinium and erbium



In view of their insoluble character, the lanthanide methoxides do not appear to interchange the methoxy groups readily with higher alkoxy groups. The ethoxides were prepared by adding excess of dry ethyl alcohol to benzene solution of lanthanide isopropoxides, whereby the ethoxides, being sparingly soluble in benzene, could be precipitated out. Unlike methoxides, ethoxides were found to interchange their ethoxy groups with higher alcohols more readily.

The trends in the chief characteristics of the lanthanides are largely governed by their highly electro-positive character and by the size of the Ln³⁺ ions. These are reflected in the chemistry of their alkoxides also. Probably the most notable action of an alkoxy (-OR) group is to impart a certain degree of covalent character to the metal compounds. Thus isopropoxides of lanthanides could be sublimed unchanged *in vacuo*. The lowest sublimation temperature at 0.01

mm pressure for $\text{Ln}(\text{O-}i\text{-C}_3\text{H}_7)_3$ appears to vary as follows: La, 250–280°; Nd, 230–250°; Sm, 210–230°; Gd, 200–210°; Er, 180–190°.^{5–7} Although these temperatures cannot be determined with accuracy, their trend might be ascribed to the variation of covalent character with atomic number in the lanthanide series.

Recently Mazdiyasi and coworkers¹¹ have tried to correlate the ionic character and the physical state (solid or liquid) of the metal alkoxides at room temperature and pressure with the electronegativity difference ($\chi_{\text{O}} - \chi_{\text{M}}$). According to these authors, for differences of less than 2.3, liquid metal alkoxides were usually found. We think a more appropriate calculation would be the determination of percentage covalent character of M–O bond by the method of Hannay and Smyth¹² using the equation

$$\text{ionic character} = 0.16(\chi_{\text{O}} - \chi_{\text{M}}) + 0.035(\chi_{\text{O}} - \chi_{\text{M}})^2$$

Thus merely on the basis of the electronegativities of metal and oxygen, the percentages of covalent character of sodium, lanthanides, aluminium, and boron alkoxides come out in the order of about 38, 48, 59, and 70, respectively. The effects of alkyl groups in metal alkoxide volatilities are well known but no effect of alkyl group is accounted for here. The methoxides are generally the least volatile and usually insoluble in inert solvents like benzene. The reason for this has been ascribed by Mehrotra¹ to the special inductive effect of the methyl group. The polymerization of molecules to give larger aggregates (due to lower steric factors) can also be another obvious reason. Polymerization in metal alkoxides occurs due to intermolecular coordination through oxygens in order to satisfy the tendency of central metal ion to expand its covalency or coordination number. Thus the atoms with large covalent radii have a tendency to form larger aggregates or polymeric compounds. The steric effect endowed by larger or ramified branched alkyl groups appears to check the polymerization process and, on the other hand, induces, by virtue of the +I inductive effect, covalency to M–O bond. Hence ethoxides of a large number of metals are soluble in inert solvents like benzene and are less polymeric, but with metals of large covalent radii, *e.g.*, lanthanides or thorium,¹⁰ ethoxides are also sparingly soluble. For soluble alkoxides there seems to exist a direct relation between covalent radii and molecular complexity. In Table I are depicted values of covalent radii and observed molecular complexities of a few metal alkoxides;¹ the foregoing correlation fits the alkoxides of gadolinium and erbium in the third group in the same manner as tetravalent cerium and thorium find places along with group IV elements.

Some Reactions of Lanthanide Isopropoxides.—Like the alkoxides of most transition metals, alkoxides of gadolinium and erbium are also highly sensitive to hydrolysis. In view of the high solubility of isopropox-

(11) K. S. Mazdiyasi, C. T. Lynch, and J. S. Smith, *J. Amer. Ceram. Soc.*, **50**, 532 (1967).

(12) N. B. Hannay and C. P. Smyth, *J. Amer. Chem. Soc.*, **68**, 171 (1946).

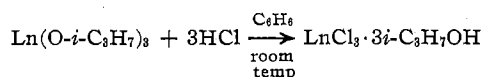
TABLE I
RELATIVE MOLECULAR COMPLEXITIES OF A
FEW METAL ALKOXIDES

Element	Covalent radii ^a	Molecular complexity in benzene			
		<i>n</i> - Butoxide	<i>sec</i> - Butoxide	<i>tert</i> - Butoxide	Iso- propoxide
Si	1.173	1.0	1.0	1.0	1.0
Ti	1.324	1.0	1.4
Zr	1.454	3.4	2.5	1.0	3.0
Th	1.652	6.4	4.2	3.4	3.8
Ce(IV)	1.646	4.2	3.0	2.5	3.1
B	0.80	1.0	1.0	1.0	1.0
Al	1.248	3.9	2.4	1.9	3.0
Gd	1.614	4.3	3.3	3.0	3.9
Er	1.567	4.2	3.5	2.9	3.8

^a Values taken from T. Moeller, "Inorganic Chemistry. An Advanced Textbook," Wiley, New York, N. Y., 1952, p 135.

ides in anhydrous benzene, these were chosen for further reactions.

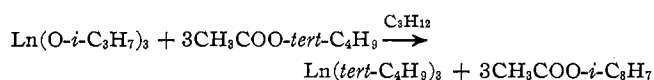
(i) **Action of Dry Hydrogen Chloride Gas.**—When a slow stream of dry hydrogen chloride gas was passed through a solution of lanthanide isopropoxides in benzene, precipitation of $\text{LnCl}_3 \cdot 3i\text{-C}_3\text{H}_7\text{OH}$ occurs in exothermic reactions of the type



It is interesting to note that the same product has been formed by reaction of anhydrous lanthanide chloride and 2-propanol.

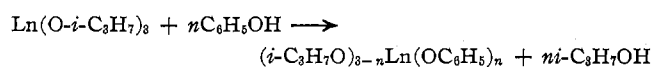
This observation appears to be in conformity with the generalization shown by Mehrotra¹³ that the action of hydrogen chloride with metal alkoxides results in the formation of essentially the same products as obtained by the reaction of the corresponding *anhydrous metal chloride with the alcohol*.

(ii) **Reaction with Ester.**—Reaction of lanthanide isopropoxides with slight excess of *tert*-butyl acetate in cyclohexane solution results in the formation of lanthanide *tert*-butoxides in quantitative yields



In this transesterification reaction, the isopropyl acetate formed was fractionated out azeotropically with cyclohexane.

(iii) **Reactions with Phenol.**—In view of the easy replacement of lower by higher alkoxy groups, the reactions of lanthanide isopropoxides with phenol were undertaken in benzene in molar ratios of 1:1, 1:2, and 1:3 in order to prepare mono-, di-, and triphenoxides, respectively



where $n = 1, 2, \text{ or } 3$. All the phenoxide products are sparingly soluble in benzene; as a matter of fact solubility decreases with the increasing number of phenoxy groups. The diisopropoxide monophenoxides of lanthanides retain the color of the respective ions but di-

(13) R. C. Mehrotra, *J. Indian Chem. Soc.*, **30**, 731 (1953).

and triphenoxides are yellow to brown. The products are sparingly soluble in cyclohexane also and no adduct with cyclohexane is obtained for gadolinium or erbium triphenoxides unlike that reported for the triphenoxide of yttrium.⁸

TABLE II
INFRARED ABSORPTION PEAKS OF A FEW
ALKOXIDES AND PHENOXIDE (cm^{-1})^a

$\text{Er}(\text{OCH}_3)_3$	$\text{Er}(\text{O}-i\text{-C}_3\text{H}_7)_3$	$\text{Er}(\text{O}-\text{tert}-\text{C}_4\text{H}_9)_3$	$\text{Er}(\text{OC}_6\text{H}_5)_3$
3350 m	3350 w	3350 w	3350 w
1565 w	1615 w	1601 m	1590 s
1450* s	1460* s	1502 m	1460* s
1360* s	1380 s	1450* s	1450 s
1190 s	1350* s	1375 m	1365* s
1160 m	1340 m	1355* s	1310 m
1090 m	1315 m	1253 m	1270 s
1050 m	1165 s	1208 s	1238 m
942 m	1135 s	1170 m	1162 m
720 w	1008 m	1135 m	1112 m
610 w	975 m	1005 s	1070 w
482 w	952 m	972 m	1020 w
	820 m	910 w	995 m
	720 w	785 m	935 m
	510 m	770 w	880 m
	430 w	745 m	835 m
		524 w	750 s
		472 w	685 m
			580 w
			560 m
			510 w
			430 w

^a The asterisk-marked wave numbers are either pure or overlap of Nujol peaks.

Infrared Studies.—In Table II are listed the infrared absorption maxima and relative intensities of a few representative compounds. In general weak- to medium-intensity bands appear in most of the spectra in the 3400-cm^{-1} region and these may be due to unavoidable slight hydrolysis of the compounds during mulling and recording. The region $1470\text{-}1200\text{ cm}^{-1}$ contains a few peaks which may be due to the usual deformation modes of CH_3 , CH_2 , and CH groups. The compounds have been identified by the presence of characteristic absorption of alkoxy groups as mentioned by earlier authors.¹⁴⁻¹⁹ The methoxy group has a characteristic band at 1190 cm^{-1} which is also observed in lanthanide methoxides along with bands at 1160, 1090, and 1050 cm^{-1} which may be assigned to C-O stretching modes. The presence of a larger number of C-O stretching bands than expected on theoretical grounds may be due to the polymeric nature of the methoxides. The isopropoxy group exhibits its characteristic absorption at $1175\text{-}1160$ and $1140\text{-}1120\text{ cm}^{-1}$; these are found as strong bands at 1165 and 1135 cm^{-1} ,

(14) C. T. Lynch, K. S. Mazdiyasi, J. S. Smith, and W. J. Crawford, *Anal. Chem.*, **36**, 2332 (1964).

(15) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 2601 (1961).

(16) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963.

(17) J. Bellamy, "Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1954; "Advances in Infrared Group Frequencies," Methuen, London, 1968.

(18) K. Nakanishi, "Infrared Absorption Spectroscopy, Practical," Holden-Day, San Francisco, Calif., 1962.

(19) D. C. Bradley and A. H. Westlake, private communication.

respectively, in lanthanide isopropoxides. A strong peak at 1380 cm^{-1} may be assigned to the *gem*-dimethyl structure. The bands at $1010\text{--}1005$, 975 , and 950 cm^{-1} in isopropoxides may be assigned to various (terminal and bridged) C–O stretching vibrations. The characteristic bands of *tert*-butoxide appear at 1253 , 1208 , 1170 , 1005 , 972 , 910 , and 945 cm^{-1} ; of these, those at 1208 and 1170 cm^{-1} may be due to skeletal vibrations of *tert*-butoxy groups and those at 1005 and 972 cm^{-1} may be due to C–O stretching vibrations. The phenoxides have been identified by the presence of characteristic deformation bands of phenol at 1450 , 1270 , 1162 , and 995 cm^{-1} . A large number of additional peaks is probably suggestive of the polymeric nature of these compounds.

Experimental Section

Apparatus.—All-glass apparatus with standard Quickfit joints were used throughout. Extreme precautions were taken to exclude moisture. The interchange reactions were done on a column packed with Raschig rings having a still head, the latter being fitted with a thermometer pocket condenser and a stop-cock.

Materials.—Rare earth oxides (99.9%) were obtained from American Potash and Chemical Corp., New York, N. Y., and Johnson Matthey. Benzene, cyclohexane, and alcohols were dried by usual procedures.

Anhydrous Lanthanum Chlorides.—Anhydrous GdCl_3 and ErCl_3 were prepared by heating a mixture of the hydrated lanthanide chloride and ammonium chloride in a current of dry hydrogen chloride and chlorine; the temperature was carefully regulated to avoid the formation of fusible oxychlorides.

Analyses.—Gadolinium and erbium were weighed as oxides after ignition of precipitated oxalates. Methoxy, ethoxy, and isopropoxy contents were estimated by the oxidimetric method^{20,21} using standard chromic acid.

Molecular Weight.—A semimicrobulliometer (Gallenkemp) with thermistor sensing was used for molecular weight determinations.

Infrared Spectra.—All the infrared spectra were recorded on a Perkin-Elmer Infracord 337, in Nujol mulls. The wave numbers at 1601.4 and 1028.0 cm^{-1} of polystyrene were used as calibrants.

Soluble Alkoxides. Preparation of Gadolinium Isopropoxide.—Anhydrous gadolinium chloride (12.28 g) was dissolved in refluxing isopropyl alcohol (36 g). On cooling, crystals of tri-2-propanolate of gadolinium chloride separated out. A solution of sodium isopropoxide, prepared by dissolving metallic sodium (3.21 g) in a mixture of 2-propanol (52 g) and benzene (90 g) was transferred to the above reaction mixture. As soon as the two solutions came in contact, instantaneous precipitation of sodium chloride occurred with the evolution of heat. To ensure completion of the reaction the contents were allowed to reflux for about 2 hr (bath temperature of 120°). After cooling overnight, the precipitated sodium chloride was filtered under vacuum through a G-4 sintered funnel and excess benzene and 2-propanol were distilled out from the filtrate. The final drying of the product under reduced pressure at room temperature (28° (0.1 mm)) yielded a white crystalline solid (15.27 g , yield 98%) which was readily soluble in benzene and 2-propanol. *Anal.* Calcd for $\text{Gd}(\text{O}-i\text{-C}_3\text{H}_7)_3$: Gd, 47.03; $i\text{-C}_3\text{H}_7\text{O}$, 52.97. Found: Gd, 47.0; $i\text{-C}_3\text{H}_7\text{O}$, 52.6. Mol wt: calcd, 334.5; found (in boiling benzene), 1304.

The above compound (4.85 g), when heated under reduced pressure (0.1 mm) at about 210° (bath temperature), sublimed (0.66 g , yield 13.6%). The sublimate was analyzed for gadolinium and isopropoxy contents. Found: Gd, 47.0; $i\text{-C}_3\text{H}_7\text{O}$, 52.9.

(20) D. C. Bradley, F. M. A. Halim, and W. Wardlaw, *J. Chem. Soc.*, 3450 (1950).

(21) R. C. Mehrotra, *J. Indian Chem. Soc.*, **31**, 904 (1954).

Preparation of Erbium Isopropoxide.—The procedure was essentially the same as mentioned above for the preparation of gadolinium isopropoxide. Sodium (3.38 g) was dissolved in the mixture of isopropyl alcohol and benzene for preparing its isopropoxide and mixed with the solution of erbium chloride (13.39 g) in isopropyl alcohol. Pink erbium isopropoxide (16.64 g , yield 98.7%) was obtained after filtering out the precipitated sodium chloride and removing the volatile solvents under reduced pressure. *Anal.* Calcd for $\text{Er}(\text{O}-i\text{-C}_3\text{H}_7)_3$: Er, 48.54; $i\text{-C}_3\text{H}_7\text{O}$, 51.46. Found: Er, 48.51; $i\text{-C}_3\text{H}_7\text{O}$, 51.1. Mol wt: calcd, 344.5; found, 1309.

The above compound (3.35 g) was heated to $180\text{--}190^\circ$ (0.1 mm); a pink sublimate (0.54 g , 16.5%) was obtained. Found: Er, 48.52; $i\text{-C}_3\text{H}_7\text{O}$, 51.2.

Preparation of Higher Alkoxides of Gadolinium and Erbium.—The various butoxides and amyl oxides of gadolinium and erbium were prepared by alcohol interchange reactions involving metal isopropoxides and the respective higher alcohols in the presence of benzene. The liberated isopropyl alcohol in the azeotrope could be estimated quantitatively in the reactions of tertiary alcohols. The alcohol interchange technique employed is similar for all such reactions, and for brevity, these are summarized in Table III.

Insoluble Alkoxides. Preparation of Gadolinium Methoxide.

(a) **Lithium Method.**—Anhydrous gadolinium chloride (3.20 g) was dissolved in dry methyl alcohol (46 g). A solution of lithium methoxide prepared by dissolving lithium metal (0.256 g) in methyl alcohol (12 g) was added dropwise to the refluxing chloride solution. A white precipitate appeared during addition. The contents were allowed to reflux for about 2 hr and cooled to room temperature. The upper clear solution containing most of the lithium chloride was decanted off and the remaining solid portion was caused to reflux with methanol (30 g) again. The contents were then filtered while hot through a sintered (G-4) funnel. The solid was washed thoroughly with methyl alcohol until the filtrate gave a negative test for chloride. The product was finally dried under vacuum at 26° (0.1 mm) to yield a white solid (2.90 g , 94.3% yield), which was sparingly soluble in methanol, benzene, or ether. *Anal.* Calcd for $\text{Gd}(\text{OCH}_3)_3$: Gd, 62.82; OCH_3 , 37.18. Found: Gd, 62.75; OCH_3 , 37.2.

(b) **From Isopropoxide.**—Methyl alcohol (30 g) was added to benzene (12 g) solution of gadolinium isopropoxide (1.35 g). Instantaneous precipitation of white gadolinium methoxide accompanied by evolution of heat occurred. The contents were allowed to reflux for about 2 hr and cooled to room temperature. The supernatant liquid was decanted off and the precipitate was boiled again for about 2 hr with methyl alcohol (35 g). The precipitate was then filtered off and washed repeatedly with benzene and finally dried under vacuum at 25° (0.1 mm). A white solid (1.00 g , 99% yield) was obtained. *Anal.* Calcd for $\text{Gd}(\text{OCH}_3)_3$: Gd, 62.82; OCH_3 , 37.18. Found: Gd, 62.66; OCH_3 , 36.12.

Preparation of Erbium Methoxide. Lithium Method.—The procedure was essentially the same as described above for the preparation of gadolinium methoxide. Lithium methoxide, obtained by dissolving lithium metal (0.217 g) in methyl alcohol (28 g), was added dropwise to the refluxing solution of erbium chloride (2.85 g) in methanol (64 g). A pink precipitate formed during the addition. The precipitate was treated similarly as described for gadolinium methoxide. A pink solid (2.52 g , yield 93%) was obtained. *Anal.* Calcd for $\text{Er}(\text{OCH}_3)_3$: Er, 64.22; OCH_3 , 35.78. Found: Er, 64.20; OCH_3 , 35.8.

Preparation of Gadolinium Ethoxide from Isopropoxide.—Dry ethyl alcohol (60 g) was added to a benzene (14 g) solution of gadolinium isopropoxide (2.36 g). A white precipitate immediately formed, the bulk of which increased on refluxing the contents. After cooling, the precipitate was filtered and residue was again refluxed with more (28 g) ethyl alcohol. A white solid was obtained after removing the volatile solvents under reduced pressure at 28° (0.1 mm). *Anal.* Calcd for $\text{Er}(\text{OC}_2\text{H}_5)_3$: Er, 55.29; OC_2H_5 , 44.71. Found: Er, 54.94; OC_2H_5 , 44.3.

Preparation of Gadolinium *n*-Propoxide from Gadolinium Eth-

TABLE III
 ALCOHOL INTERCHANGE REACTIONS OF GADOLINIUM AND ERBIUM ISOPROPOXIDES

Reactants		Product (yield, mmol)	% metal		Analyses Mmol of <i>i</i> -C ₃ H ₇ OH in azeotrope		Mol wt in benzene	
Isopropoxide (mmol)	Alcohol (mmol)		Calcd	Found	Calcd	Found	Calcd	Found
Gd(O- <i>i</i> -C ₃ H ₇) ₃ (5.054)	<i>n</i> -C ₄ H ₉ OH (107.9)	Gd(O- <i>n</i> -C ₄ H ₉) ₃ (4.965)	41.76	42.0	376.6	1613
Er(O- <i>i</i> -C ₃ H ₇) ₃ (2.571)	<i>n</i> -C ₄ H ₉ OH (91.75)	Er(O- <i>n</i> -C ₄ H ₉) ₃ (2.457)	43.26	43.5	386.6	1623
Gd(O- <i>i</i> -C ₃ H ₇) ₃ (3.110)	<i>sec</i> -C ₄ H ₉ OH (110.6)	Gd(O- <i>sec</i> -C ₄ H ₉) ₃ (2.974)	41.76	42.3	376.6	1243
Er(O- <i>i</i> -C ₃ H ₇) ₃ (1.828)	<i>sec</i> -C ₄ H ₉ OH (121.4)	Er(O- <i>sec</i> -C ₄ H ₉) ₃ (1.762)	43.26	43.7	386.6	1353
Gd(O- <i>i</i> -C ₃ H ₇) ₃ (2.380)	<i>tert</i> -C ₄ H ₉ OH (96.65)	Gd(O- <i>tert</i> -C ₄ H ₉) ₃ (2.390)	41.76	42.3	7.137	6.986	376.6	1130
Er(O- <i>i</i> -C ₃ H ₇) ₃ (2.961)	<i>tert</i> -C ₄ H ₉ OH (97.12)	Er(O- <i>tert</i> -C ₄ H ₉) ₃ (2.849)	43.26	43.9	8.883	8.654	386.6	1121
Gd(O- <i>i</i> -C ₃ H ₇) ₃ (3.948)	<i>n</i> -C ₅ H ₁₁ OH (104.3)	Gd(O- <i>n</i> -C ₅ H ₁₁) ₃ (3.821)	37.56	38.1
Er(O- <i>i</i> -C ₃ H ₇) ₃ (2.497)	<i>i</i> -C ₅ H ₁₁ OH (88.14)	Er(O- <i>i</i> -C ₅ H ₁₁) ₃ (2.380)	39.02	39.7
Gd(O- <i>i</i> -C ₃ H ₇) ₃ (6.131)	<i>tert</i> -C ₅ H ₁₁ OH (182.5)	Gd(O- <i>tert</i> -C ₅ H ₁₁) ₃ (5.971)	37.56	38.1	18.98	17.48	418.7	1252
Er(O- <i>i</i> -C ₃ H ₇) ₃ (2.583)	<i>tert</i> -C ₅ H ₁₁ OH (147.4)	Er(O- <i>tert</i> -C ₅ H ₁₁) ₃ (2.520)	39.02	39.5	7.750	7.489

 TABLE IV
 REACTIONS OF GADOLINIUM AND ERBIUM ISOPROPOXIDES WITH PHENOL

Reactants	[Reactant], mmol	Product, yield (mmol), nature	% metal		% O- <i>i</i> -C ₃ H ₇		Mmol of <i>i</i> -C ₃ H ₇ OH in azeotrope
			Calcd	Found	Calcd	Found	
Gd(O- <i>i</i> -C ₃ H ₇) ₃ C ₆ H ₅ OH	3.020 2.985	Gd(O- <i>i</i> -C ₃ H ₇) ₂ (OC ₆ H ₅), 2.985, yellow solid	42.68	42.52	32.09	31.7	3.060
Gd(O- <i>i</i> -C ₃ H ₇) ₃ C ₆ H ₅ OH	3.053 6.163	Gd(O- <i>i</i> -C ₃ H ₇)(OC ₆ H ₅) ₂ , 2.982, brown solid	38.88	38.32	14.61	14.5	5.824
Gd(O- <i>i</i> -C ₃ H ₇) ₃ C ₆ H ₅ OH	3.708 11.116	Gd(OC ₆ H ₅) ₃ , 3.664 brown solid, turned black on standing	36.04	36.20	11.16
Er(O- <i>i</i> -C ₃ H ₇) ₃ C ₆ H ₅ OH	3.483 3.558	Er(O- <i>i</i> -C ₃ H ₇) ₂ (OC ₆ H ₅), 3.434, yellow solid	44.19	44.31	31.22	31.3	3.327
Er(O- <i>i</i> -C ₃ H ₇) ₃ C ₆ H ₅ OH	3.686 7.331	Er(O- <i>i</i> -C ₃ H ₇)(OC ₆ H ₅) ₂ , 3.636, brown solid	40.55	40.72	14.32	14.3	6.996
Er(O- <i>i</i> -C ₃ H ₇) ₃ C ₆ H ₅ OH	4.306 12.85	Er(OC ₆ H ₅) ₃ , 4.277 brown solid	37.46	37.53	12.85

oxide.—*n*-Propyl alcohol (22.52 g) was added to a suspension of gadolinium ethoxide (0.89 g) in benzene (62 g). The contents were caused to reflux and the low-boiling azeotrope was fractionated out at a high reflux ratio. A clear solution was obtained after about 8 hr of fractionation. Excess solvent was distilled out and last traces of volatile fractions were removed under reduced pressure. A product (1.00 g, 98% yield) was finally obtained after drying at 28° (0.1 mm). *Anal.* Calcd for Gd(O-*n*-C₃H₇)₃: Gd, 47.03. Found: Gd, 47.34.

Reactions of Gadolinium and Erbium Isopropoxides. Action of Dry Hydrogen Chloride Gas on Gadolinium Isopropoxide.—Hydrogen chloride gas was slowly bubbled in a solution of gadolinium isopropoxide (1.26 g) in benzene (32 g). After the gas had been passed for a few minutes, the temperature of the solution appeared to rise, accompanied by the formation of a white precipitate. On further passing the gas, the solution became quite hot and bulk of the precipitate also increased. Hydrogen chloride gas was passed for about 3 hr more until the reaction mixture attained room temperature. The precipitate was filtered out and washed with benzene. A white crystalline solid (1.62 g) was obtained after drying under reduced pressure at 28° (0.1 mm). *Anal.* Calcd for GdCl₃·3*i*-C₃H₇OH: Gd, 35.44; Cl, 23.93; *i*-C₃H₇OH, 40.63. Found: Gd, 35.27; Cl, 23.71; *i*-C₃H₇OH, 40.2.

Action of Dry Hydrogen Chloride Gas on Erbium Isopropoxide.—The procedure followed in this reaction was similar as described

above. Hydrogen chloride gas was bubbled through a solution of erbium isopropoxide (1.82 g) in benzene (38 g). A pink crystalline solid (2.3 g) was obtained after removing the solvent. *Anal.* Calcd for ErCl₃·3*i*-C₃H₇OH: Er, 36.85; Cl, 23.43; *i*-C₃H₇OH, 39.72. Found: Er, 36.93; Cl, 23.21; *i*-C₃H₇OH, 38.5.

Reaction between Gadolinium Isopropoxide and *tert*-Butyl Acetate.—To a solution of gadolinium isopropoxide (3.04 g) in cyclohexane (62 g), freshly distilled *tert*-butyl acetate (32 g) was added. The contents were caused to reflux under a fractionating column. The azeotrope of isopropyl acetate and cyclohexane was distilled out at 79–80°, at a high reflux ratio. The fractionation was continued for about 7 hr after which excess of solvent was removed by distillation and finally the volatile fractions were removed under reduced pressure at 28° (0.1 mm). A white crystalline product (3.35 g, 98.5% yield) was obtained. *Anal.* Calcd for Gd(O-*tert*-C₄H₉)₃: Gd, 41.76. Found: Gd, 41.88.

Reaction between Erbium Isopropoxide and *tert*-Butyl Acetate.—The procedure was essentially similar to that mentioned above. To a cyclohexane (52 g) solution of erbium isopropoxide (2.10 g), was added *tert*-butyl acetate (27 g). A pink crystalline product (2.30 g, 97.5% yield) was isolated after fractionation for about 7–8 hr and drying at 28° (0.1 mm). *Anal.* Calcd for Er(O-*tert*-C₄H₉)₃: Er, 43.26. Found: Er, 43.53.

Reactions of Gadolinium and Erbium Isopropoxides with Phenol.—The reactions of gadolinium and erbium isopropoxides

with phenol were undertaken in various molar ratios (*i.e.*, 1:1, 1:2, and 1:3) in the presence of benzene. All the reactions were exothermic and resulted in instantaneous precipitation of sparingly soluble products during addition. The reaction mixtures were caused to reflux for about 3–4 hr and the liberated isopropyl alcohol was fractionated out. The presence of theoretically required isopropyl alcohol in the azeotrope in all the reactions confirm the completion of the reactions. The products were then isolated by stripping off the volatile solvent under vacuum and

finally drying at 27–29° (0.1 mm). As the procedure was similar for all these reactions, they are, for brevity, summarized in Table IV.

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Further Studies of the Thermal Decomposition of Europium Hexacyanoferrate(III) and Ammonium Europium Hexacyanoferrate(II)

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Mass spectrographic analysis of the evolved gases and infrared spectra of the solid residues are used to expand earlier studies concerning the thermal decomposition of $\text{EuFe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ and $\text{NH}_4\text{EuFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$. Under vacuum the decompositions are very complex. The chain of intermediates for iron is $(\text{Fe}(\text{CN})_6)^{3-}$ or $(\text{Fe}(\text{CN})_6)^{4-}$ — $\text{Fe}(\text{CN})_2$ — Fe_3C —Fe. Similarly the europium is shown to proceed *via* a hydrolytic decomposition to EuOOH and finally to EuO after interaction with the free carbon at elevated temperatures.

Introduction

Rare earth hexacyanoferrates(III) and ammonium rare earth hexacyanoferrates(II) have been shown to be useful precursors for the production of rare earth orthoferrites.¹ The conversion to the desired compound is accomplished through their thermal decomposition in an oxidizing atmosphere. The decomposition under vacuum or in nitrogen is very complex and incompletely understood.² It is the purpose herein to present the results of evolved gas analysis and infrared spectroscopic examination of the solid residue for the europium compounds and to indicate how they contribute to a more complete understanding of the decomposition in an inert atmosphere.

Experimental Procedures and Results

Evolved Gas Analysis (ega).—Approximately 25 mg of the compound to be studied was suspended in a small platinum crucible from a platinum wire within a closed platinum furnace tube. This tube was connected to a Veeco SPI-10 residual gas analyzer and the pressure was maintained between 10^{-5} and 10^{-4} Torr. The furnace surrounding the platinum tube was programmed to rise at about 3°/min. The mass range of the analyzer was repeatedly scanned between 0 and 55 $m\mu$ and the output was recorded on pen one. The output from a Pt—Pt-10% Rh thermocouple in close proximity to the sample was simultaneous recorded on pen two of the Bristol recorder.

Figures 1 and 2 show the relative intensities of the pertinent mass peaks for the ega of $\text{EuFe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ and $\text{NH}_4\text{EuFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, respectively.

Ir Spectra.—Infrared spectra of samples which had been

heated to various temperatures for 0.5 hr under a low pressure of 10^{-5} Torr or in air were recorded on a Model 421 Perkin-Elmer spectrometer. The instrument was continuously purged with dry nitrogen. Samples were run from 4000 to 250 cm^{-1} using KBr pellet technique with an appropriate KBr pellet in the reference beam. Selected spectra are given in Figures 3–5 for samples of $\text{EuFe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ heated in air and under vacuum and of $\text{NH}_4\text{EuFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ under vacuum. X-Ray diffraction patterns and Mössbauer spectra of these samples have been previously reported.²

Discussion

Previous work,² based primarily on the results of Mössbauer spectroscopy, had established that the hexacyanoferrate(III) and hexacyanoferrate(II) decomposed to $\text{Fe}(\text{CN})_2$, then to Fe_3C , and finally to metallic iron. This is consistent with the results presented herein. The reduction of iron during the change from hexacyanoferrate(III) to $\text{Fe}(\text{CN})_2$ is accomplished by the release of cyanogen, $(\text{CN})_2$, which can be plainly seen around 370° in Figure 1. Such a reduction is not necessary for the decomposition of the hexacyanoferrate(II) species and no mass peak corresponding to cyanogen is observed in Figure 2.

The decomposition of the $\text{Fe}(\text{CN})_2$ to form Fe_3C gives rise to the nitrogen peak at mass 28 around 600° in both Figures 1 and 2. The peak for this mass at higher temperature includes a large contribution from carbon monoxide as well as nitrogen. The origin of the carbon monoxide is discussed later.

Figure 4 shows the demise of the trivalent iron cyanide bands in accord with the reduction proposed earlier. The bands associated with divalent iron–cyanide interaction in Figures 4 and 5 gradually diminish and

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