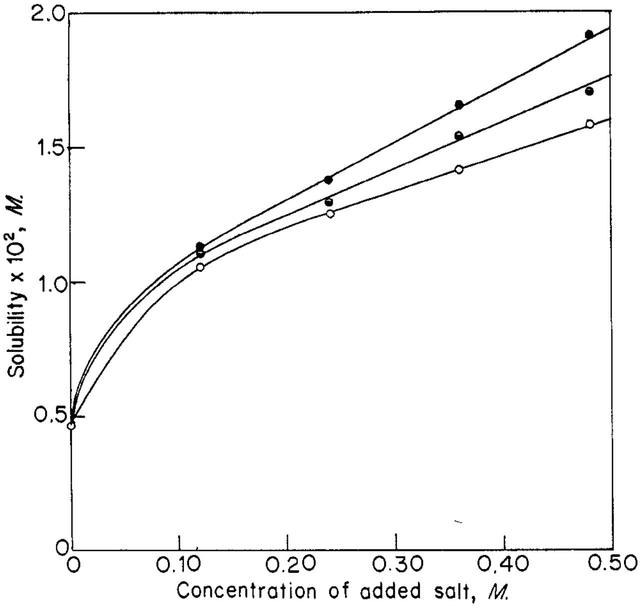

Figure 2.—Plot of solubility (*M*) of $Tl_4Fe(CN)_6$ against concentration of added salt: ●, $(CH_3)_4NO_3$; ◒, KNO_3; ○, $LiNO_3$.

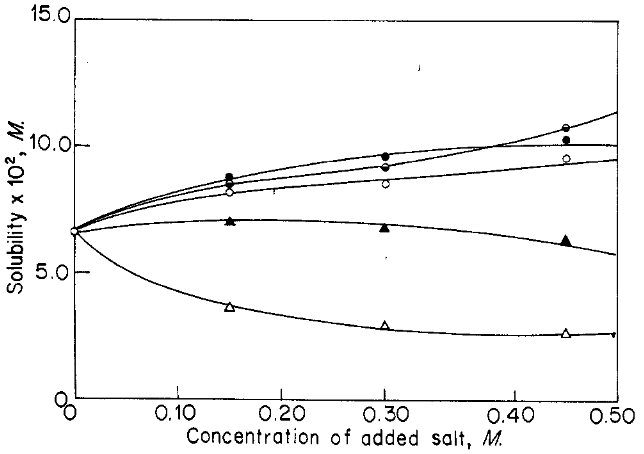

Figure 3.—Plot of solubility (*M*) of $K_2BaFe(CN)_6$ against concentration of added salt: ●, NaCl; ○, LiCl; ◒, $(CH_3)_4NCl$; ▲, $(C_2H_5)_4NCl$; △, KCl.

"common ion effect," since the saturating salt, $K_2BaFe(CN)_6$, itself gives rise to K^+ ions in solution.

Figure 4 shows that the increase in solubility of $Co(NH_3)_6Fe(CN)_6$ in the presence of $(CH_3)_4NCl$ and $(C_2H_5)_4NCl$ is much higher than in the presence of KCl, NaCl, and LiCl. In fact, two families of curves are obtained, one for the alkali metal chlorides and the other for the quaternary salts. The rather abnormally large effect of the tetraalkylammonium salts on the solubility may reasonably be attributed to an abnormally large decrease in the activity coefficient of the $Fe(CN)_6^{3-}$ ion in the presence of the quaternary ions.

Conclusion

From the results, it seems reasonable to conclude that at the same ionic strength, the tetramethylammonium ion decreases the activity coefficient of the triply charged $Fe(CN)_6^{3-}$ ion (f_{III}) by a larger extent than that of the quadruply charged $Fe(CN)_6^{4-}$ ion (f_{IV}), and that f_{III} decreases more rapidly with increasing ionic strength than f_{IV}, although the opposite might be expected from a simple consideration of interionic forces.

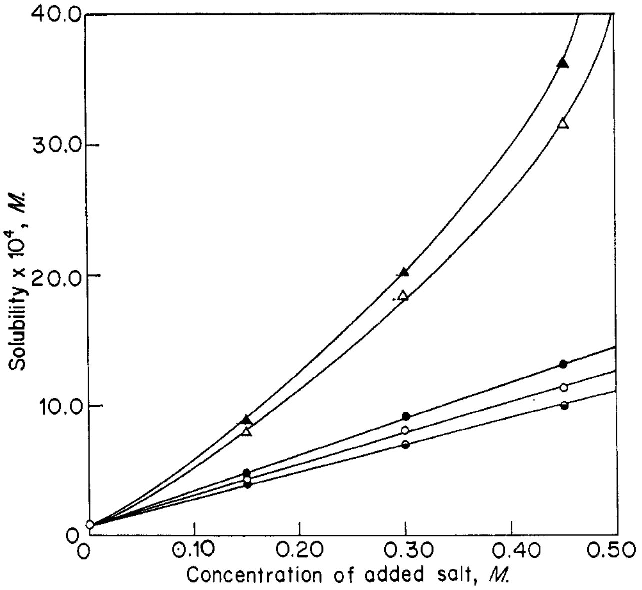

Figure 4.—Plot of solubility (*M*) of $Co(NH_3)_6Fe(CN)_6$ against concentration of added salt: ▲, $(C_2H_5)_4NCl$; △$(CH_3)_4NCl$; ●, KCl; ○, NaCl; ◒, LiCl.

Rather high salt concentrations have been used in the present work, and under these conditions specific interaction between ions, arising out of short-range forces, is likely to preponderate over normal electrostatic factors. It appears that specific interaction between a tetraalkylammonium ion and the $Fe(CN)_6^{3-}$ ion is stronger than that between this cation and $Fe(CN)_6^{4-}$ ion and also stronger than that between an alkali metal ion and the $Fe(CN)_6^{3-}$ ion. However, no quantitative treatment can be attempted at this stage.

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Synthesis and Some Properties of Yttrium and Lanthanide Isopropoxides[1]

BY L. M. BROWN AND K. S. MAZDIYASNI*

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Transition metal alkoxides have been studied extensively in the past two decades by a number of investigators. This work has been reviewed by Bradley[2,3]

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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 7-12, 1969.

[2] D. C. Bradley, *Advan. Chem. Ser.*, **No. 23**, 10 (1959).

[3] D. C. Bradley, "Preparative Inorganic Reactions," Vol. 2, W. L. Jolly, Ed., Wiley, New York, N. Y., 1962, pp 169-186.

and Mehrotra.[4] However, alkoxides of the inner transition elements, particularly the lanthanide series, have received little attention. Mazdiyasni, *et al.*,[5] and Mehrotra and coworkers[6] reported the synthesis of some lanthanide alkoxides but presented very limited properties to characterize effectively the whole series of rare earth alkoxides.

In this paper, the methods of synthesis of yttrium and the lanthanide tris(isopropoxides) are discussed. Some of the properties of these compounds reported are elemental analysis, thermogravimetric analysis, infrared absorption frequencies, and uv and visible absorption data. Nmr and mass spectral data have been obtained for some representative isopropoxides.

Experimental Section

The preparative work was carried out in glass apparatus with ground-glass joints under reduced pressure or under an atmosphere of dry helium. Compounds were handled at all times in an inert atmosphere and were stored in an evacuated desiccator over calcium sulfate. Reagent grade isopropyl alcohol was purchased from Matheson Coleman and Bell and further dried before being used. Metal turnings with analyzed purity of 99.9% were purchased from Michigan Chemical Corp. and American Potash & Chemical Corp. All other chemicals were reagent grade. The quantitative analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Sublimation data were obtained with a McCarter vacuum sublimer immersed in a silicone oil bath.

Thermogravimetric analysis was performed in air from room temperature to 1000° with a Burrell Stanton Model TR-1 thermobalance. Ir spectra in the 4000–250-cm^{-1} region were recorded on a Perkin-Elmer 521 grating spectrophotometer using Nujol mulls and CsI windows. Absorption spectra in the 220–650-mμ range were obtained with a Cary Model 14 recording spectrophotometer using 1–2% cyclohexane solutions and 1-cm path length absorption cells. A Varian Associates Model A-56/60 spectrometer was used to measure the nmr spectra of the isopropoxides in saturated benzene solutions at 60 MHz at a probe temperature of 37°. Mass spectra were recorded on a CEC Model 21-110B double-focusing mass spectrometer at temperatures of 120–250°.

Methods of Preparation.—Efforts to synthesize the rare earth isopropoxides by a previously reported method resulted in impure products and poor yield.[6,7] The yttrium and lanthanide tris(isopropoxides) were prepared by the reaction of 5 g of metal turnings with 300 ml of isopropyl alcohol and a small amount of $HgCl_2$ (10^{-4} mol/g-atom of metal) as a catalyst. The mixture was refluxed at 82° for 24 hr and then cooled and filtered. After filtration the crude product was purified by recrystallization from hot isopropyl alcohol or vacuum sublimation. Yields of 75% or better were realized with this method. For some of the larger metal ions, lanthanum through neodymium, the reaction rate and per cent yield were increased by using for the catalyst a mixture of $HgCl_2$ and $Hg(C_2H_3O_2)_2$ or HgI_2. Yttrium and the lanthanide isopropoxides are readily soluble in common organic solvents. These compounds are extremely moisture sensitive; the presence of <10 ppm of water is sufficient to initiate hydrolytic decomposition.

Results and Discussion

Synthesis of Isopropoxides.—Mazdiyasni, *et al.*,[5] prepared yttrium, dysprosium, and ytterbium tris(isopropoxides) from the metal and alcohol using $HgCl_2$ as a catalyst

$$M + 3C_3H_7OH \xrightarrow[82°]{HgCl_2} M(OC_3H_7)_3 + 1.5H_2\uparrow + Hg$$

This reaction was previously thought to be confined to the alkali metals magnesium and aluminum; however, it was found that the method could be extended to the synthesis of yttrium and all of the lanthanide isopropoxides. For the lower lanthanides, namely, lanthanum, cerium, praseodymium, and neodymium, a mixture of $HgCl_2$ and $Hg(C_2H_3O_2)_2$ or HgI_2 was used to increase both the rate of reaction and per cent yield. The reactions within the series are slow and follow no significant trend. The size, shape, and oxygen content of the metal turnings used vary the surface area and thus influence the reaction rate and per cent yield.

Chemical Analysis.—The results of elemental analysis and sublimation temperatures are listed in Table I.

TABLE I

ANALYTICAL DATA FOR YTTRIUM AND LANTHANIDE ISOPROPOXIDES

COMPOUND	COLOR	SUBLIMATION POINT (°C/mmHg)		ELEMENTAL ANALYSIS* % METAL	% CARBON	% HYDROGEN
$Y(OC_3H_7)_3$	White	200/0.10	Calcd	33.40	40.60	7.97
			Found	33.06	40.39	7.87
$Pr(OC_3H_7)_3$	Green	175/0.04	Calcd	44.29	33.98	6.65
			Found	43.80	33.55	6.82
$Nd(OC_3H_7)_3$	Blue		Calcd	44.86	33.62	6.58
			Found	45.70	33.19	6.36
$Sm(OC_3H_7)_3$	Lt. yellow	180/0.04	Calcd	45.89	33.00	6.46
			Found	46.39	32.56	6.18
$Eu(OC_3H_7)_2$	Orange		Calcd	56.25	26.68	5.22
			Found	55.53	26.82	5.30
$Gd(OC_3H_7)_3$	White	200/0.15	Calcd	47.01	32.31	6.33
			Found	47.78	31.63	6.04
$Tb(OC_3H_7)_3$	White	190/0.10	Calcd	47.27	32.15	6.30
			Found	47.56	31.94	6.37
$Dy(OC_3H_7)_3$	Lt. yellow	190/0.17	Calcd	47.83	31.81	6.23
			Found	48.43	31.49	6.04
$Ho(OC_3H_7)_3$	Peach	195/0.18	Calcd	48.20	31.59	6.18
			Found	49.02	30.85	5.98
$Er(OC_3H_7)_3$	Pink	195/0.35	Calcd	48.55	31.38	6.14
			Found	49.25	30.02	5.97
$Tm(OC_3H_7)_3$	Lt. green	185/0.06	Calcd	48.80	31.22	6.11
			Found	49.64	30.64	5.93
$Yb(OC_3H_7)_3$	White	195/0.02	Calcd	49.40	30.86	6.04
			Found	49.80	30.55	6.00
$Lu(OC_3H_7)_3$	White	198/0.10	Calcd	49.67	30.69	6.01
			Found	50.39	30.14	5.94

* Analyses for Cl and Hg were negative.

Analyses for chlorine, iodine, and mercury were negative. Routine combustion analysis sometimes had to be corrected for a high residue result which is a consequence of premature sample decomposition.

Thermogravimetric Analysis.—The thermal hydrolytic decomposition of the isopropoxides to the respective metal oxides was studied by thermogravimetric analysis in air. Immediate dealkoxylation and formation of an intermediate hydroxide produces an approximately 30% weight loss from room temperature up to 200–250°. About 80% of the weight loss occurs during this stage of the decomposition reaction. The remaining weight loss occurs by the gradual conversion of the hydroxide to the oxide which is completed at 750–850°. The residue is identified by X-ray powder diffraction analysis.

Infrared Spectra.—The ir spectra of the yttrium and lanthanide isopropoxides are quite similar and compare

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[4] R. C. Mehrotra, *Inorg. Chim. Acta*, **1**, 99 (1967).

[5] K. S. Mazdiyasni, C. T. Lynch, and J. S. Smith, *Inorg. Chem.*, **5**, 342 (1966).

[6] R. C. Mehrotra, J. M. Batwara, S. N. Misra, T. N. Misra, and N. D. Tripathi, Proceedings of the 6th Rare Earth Conference, Oak Ridge, Tenn., May 3–5, 1967.

[7] R. N. P. Sinha, *Sci. Cult.*, **25**, 594 (1960).

TABLE II

NaCl REGION ABSORPTION FREQUENCIES OF YTTRIUM AND LANTHANIDE ISOPROPOXIDES (CM^{-1})

$Y(OC_3H_7)_3$	$La(OC_3H_7)_3$	$Ce(OC_3H_7)_4$	$Pr(OC_3H_7)_3$	$Nd(OC_3H_7)_3$	$Sm(OC_3H_7)_3$	$Eu(OC_3H_7)_2$	$Gd(OC_3H_7)_3$	$Tb(OC_3H_7)_3$	$Dy(OC_3H_7)_3$	$Ho(OC_3H_7)_3$	$Er(OC_3H_7)_3$	$Tm(OC_3H_7)_3$	$Yb(OC_3H_7)_3$	$Lu(OC_3H_7)_3$	$M(OC_3H_7)_3$**
2955vs*	2955vs*	2950vs*	2950vs*	2950vs*	2950vs*	2950vs*	2950vs*	2950vs*	2951vs*	2950vs*	2950vs*	2952vs*	2955vs*	2960vs*	2960vs*
2920vs*	2925vs*	2920vs*	2920vs*	2920vs*	2920vs*	2920vs*	2920vs*	2915vs*	2920vs*	2920vs*	2918vs*	2920vs*	2922vs*	2925vs*	2920vs*
2850vs*	2855vs*	2855vs*	2850vs*	2850vs*	2855vs*	2850vs*	2850vs*	2850vs*	2854vs*	2855vs*	2848vs*	2850vs*	2855vs*	2860vs*	2855vs*
2607w	2608w	2608w	2611w	2609w	2611w	2620w	2610w	2608w	2614w	2615w	2610w	2610w	2617w	2611w	2608w
1460vs*	1460s*	1460s*	1460s*	1459s*	1460s*	1460s*	1460s*	1466s*	1460s*	1460s*	1459s*	1457s*	1461s*	1462s*	1460s*
1376s*	1378s*	1378s*	1377s*	1376s*	1375s*	1378s*	1375s*	1372s*	1376s*	1376s*	1374s*	1373s*	1378s*	1372s*	1376s*
1363sh	1363sh	1376sh	1361sh	1361sh		1368sh	1362sh	1360sh		1363sh	1362sh	1362sh	1365sh	1365sh	1365sh
1354m	1357sh	1359sh	1355s	1346sh	1353s	1358sh	1354s	1350s	1350sh	1354s	1352s	1352m	1356s	1358s	1355m
1336m	1333m	1329m	1331 s	1330s	1332s	1336s	1333s	1330s	1335s	1335s	1333s	1334m	1337s	1339s	1336s
1168vs	1168vs	1158s	1156vs	1156vs	1160s	1164vs	1163vs	1163vs	1167vs	1167vs	1165vs	1167vs	1172vs	1173vs	1168vs
1123s	1127s	1130vs	1125vs	1121vs	1125vs	1120s	1123vs	1126s	1123s	1123vs	1120s	1121s	1123s	1125s	1128s
1005vs	992vs	980vs	994vs	993vs	997vs	1000s	1001vs	1001vs	1004vs	1005vs	1003vs	1004vs	1010vs	1011vs	1005vs
974s	965s	970sh	971s	968s	970s	973s	969s	970s	975s	975s	970s	973s	976s	977s	970s
950s	946m	952s	952s	950s	950s	958s	950s	948s	951s	950s	947s	948s	953s	952s	950s
835m	835m	836m	834m	832m	834m	836m	835m	834m	837m	836m	835m	835m	839m	840m	835sh
830m			827sh	825m	826sh	832sh	830sh	827sh	827sh	830m	828m	829m	833m	835sh	830m
822m	820m	824m	820m	819m	820m	823m	821m	820m	822m	821m	820m	821m	825m	828m	823sh

vs = very strong, s = strong, m = medium, w = weak, sh = shoulder; * = Nujol; ** = misch metal isopropoxide

favorably with the spectra reported by Mazdiyasni, *et al.*,[5] for yttrium, dysprosium, and ytterbium isopropoxides. Table II lists the observed absorption frequencies in the NaCl region for the rare earth isopropoxides in Nujol mulls. The lanthanide isopropoxides exhibit a unique series of five bands in the CsBr region as illustrated in Table III. This series of bands on the spectra is useful for immediate identification of these compounds. As the mass of the central atom increases, there is some trend for the absorption bands to shift to higher frequency; however, this is not always the case and cannot be used to distinguish quantitatively the spectra of the isopropoxides. Although the spectra are too similar to permit differentiation of the separate isopropoxides, the ir spectra have proved to be invaluable in checking the results of synthesis for completeness of reaction and identification of products.

TABLE III

CsBr REGION ABSORPTION FREQUENCIES OF YTTRIUM AND LANTHANIDE ISOPROPOXIDES

COMPOUND	ABSORPTION FREQUENCIES (cm^{-1})				
$Y(OC_3H_7)_3$	532s	493s	450s	418m	393s
$La(OC_3H_7)_3$	520s	475m	441m	410m	391m
$Ce(OC_3H_7)_3$	520s	490m	443m	410m	391sh
$Pr(OC_3H_7)_3$	521s	480s	444m	402m	361s
$Nd(OC_3H_7)_3$	523s	484s	444m	403m	368s
$Sm(OC_3H_7)_3$	526m	486m	445m	406m	377m
$Eu(OC_3H_7)_3$	525s	490m	451m	410m	373m
$Gd(OC_3H_7)_3$	528s	493m	447m	411m	383m
$Tb(OC_3H_7)_3$	529s	493s	447m	413m	389s
$Dy(OC_3H_7)_3$	532s	495s	449s	414m	390m
$Ho(OC_3H_7)_3$	532s	498s	448m	414s	391s
$Er(OC_3H_7)_3$	533s	496m	447m	413m	391m
$Tm(OC_3H_7)_3$	533s	496s	448m	415m	394s
$Yb(OC_3H_7)_3$	534s	497m	447m	416m	393m
$Lu(OC_3H_7)_3$	546s	501s	480s	413m	398s
$M(OC_3H_7)_3$*	530s	491s	447m	415m	391m

s = strong m = medium, sh = shoulder

* Misch metal isopropoxide

Uv and Visible Absorption Data.—Since lanthanide complexes in general exhibit strong absorption frequencies in the visible and uv region, it is expected that uv and visible absorption spectra would provide useful information for differentiating the lanthanide isopropoxides. There is no known literature reference to indicate that this method has been applied to the characterization of alkoxides. Preliminary data have indicated that this analytical technique may indeed be valuable but the moisture sensitivity and rapid aging of these alkoxides are serious problems.

The observed absorption bands in the uv region (220–350 mμ) for some of the lanthanide isopropoxides are listed in Table IV. Many of the bands appear to be due to the isopropoxy group since several of the compounds, including the isopropoxides of Y(III) and Lu(III) which are said to exhibit no absorption in the region,[8] share many of the same absorption frequencies. In the visible region (350–650 mμ), as seen in Table V,

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[8] T. Moeller, "Inorganic Chemistry," Wiley, New York, N. Y., 1954, pp 127–226.

TABLE IV
UV ABSORPTION BANDS FOR SOME LANTHANIDE ISOPROPOXIDES

COMPOUND*	λ_{max} (mμ)									
$Y(OC_3H_7)_3$	270	260	255	249	243	238	234			
$Sm(OC_3H_7)_3$	262	258	252	245	240					
$Eu(OC_3H_7)_2$	265	259	253	246	232					
$Gd(OC_3H_7)_3$	297	278	276	243						
$Tb(OC_3H_7)_3$	302	264	257							
$Dy(OC_3H_7)_3$	296	260	254	248	240					
$Ho(OC_3H_7)_3$	338	292	289	281	260	254	249	242		
$Er(OC_3H_7)_3$	268	261	254	249	244	239	234	230		
$Tm(OC_3H_7)_3$	289	287	284	274	268	265	260	254	249	243
$Lu(OC_3H_7)_3$	260	255	249	243						

* Cyclohexane solution.

TABLE V
VISIBLE REGION ABSORPTION BANDS FOR COLORED LANTHANIDE ISOPROPOXIDES

COMPOUND*	λ_{max} (mμ)													
$Pr(OC_3H_7)_3$	494	484	475	458										
$Nd(OC_3H_7)_3$	601	598	594	590	584	582	579	536	532	528	434	432	361	354
$Sm(OC_3H_7)_3$	408	404	478	372										
$Ho(OC_3H_7)_3$	631	462	460	452	447	416	366	362						
$Er(OC_3H_7)_3$	545	531	525	522	521	520	385	382	381	379	366			

*Cyclohexane solution.

the bands observed for the different alkoxides are unique and characteristic of each highly colored species.

Nmr Spectra.—Although nmr spectroscopy has been used for structure analysis of metal isopropoxides,[9,10] most of the lanthanide ions are paramagnetic and their isopropoxides cannot be analyzed by this method. However, the trivalent ions of Y, La, and Lu are diamagnetic and nmr spectra were obtained for these isopropoxides. The characteristic spectrum of a monomeric isopropoxide consists of a doublet in the τ 7–9 region resulting from the resonance of the CH_3 protons and a septet in the τ 5–7 region due to the CH proton. Polymeric species give spectra with overlapping doublets and septets. Bradley[10] has indicated that this overlapping is due to the chemical shifts of two or more differently situated alkoxy groups, such as terminal or bridging sites. Bridging tends to deshield the protons causing the resonance signals to occur at lower field.

The three nmr spectra obtained for the lanthanide isopropoxides were characteristic of polymeric isopropoxides although some of the peaks were somewhat broadened due to the inherent poor nmr resolution generally observed in rare earth metal complexes. The spectrum of $La(OC_3H_7)_3$ in benzene consisted of two doublets at 91.3 and 112.3 Hz and a broad septet around 272 Hz. Only one broad doublet was observed at 83 Hz for the $Y(OC_3H_7)_3$–benzene solution with the septet at 264 Hz. The $Lu(OC_3H_7)_3$ spectrum exhibited three overlapping doublets at 42.4, 49.0, and 69.5 Hz and the broad septet at about 230 Hz. The progressive lower field chemical shifts from Lu to La may be attributed to the combination of the deshielding of the CH_3 protons, the nature of covalency of the metal ions, and/or an increase in the degree of polymerization. It should be noted, however, that there is no definite correlation of the mass of the metal atom with the observed degree of lower field chemical shift.

Mass Spectrometry.—Mass spectra of some of the isopropoxides were recorded to obtain molecular weight measurements since the extreme moisture sensitivity of these alkoxides limits molecular weight determinations by the conventional method of vapor pressure osmometry. Previously Mazdiyasni, *et al.*,[5] had proposed the dimeric structure similar to that of the smallest tris(aluminum alkoxide) involving a four-covalent metal with the tetrahedral configuration for aluminum.[3] Misra and coworkers,[11] however, found the isopropoxides of La, Pr, and Nd to be monomeric in benzene.

Preliminary mass spectra recorded of the isopropoxides of Nd, Er, Tb, and Lu have shown peaks at low mass numbers corresponding to the isopropoxy group and its fragmentation and the next significant peaks in the mass number ranges for dimeric and tetrameric species. The tetrameric structure is postulated to be quite similar to the aluminum tris(isopropoxide) structure reported by Brown and Mazdiyasni.[9] This part of the investigation is continuing with high-resolution mass spectrometric measurements of the molecular ion peaks and construction of the possible empirical formula by computer calculation.

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[9] L. M. Brown and K. S. Mazdiyasni, *Anal. Chem.*, **41**, 1243 (1969).

[10] D. C. Bradley and C. T. Holloway, *Offic. Dig. J. Paint Technol. Eng.*, **37**, 487 (1965).

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

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The Synthesis, Characterization, and Some Reactions of *trans*-Diacetatobis(trimethylenediamine)-chromium(III) Chloride Monohydrate

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The reaction of an aqueous solution of hydrated chromium(III) chloride, hydrofluoric acid, and various diamines such as ethylenediamine (en) or trimethylene-

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