hexagonal $BaTiO_3$ structure are reported by Blasse.[8] In this publication an explanation for the adoption of this structure in terms of anion polarization is presented.

A study of the magnetic properties of a series of these compounds is contemplated in the hope that the function of the d electrons may be revealed.

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(8) G. Blasse, *J. Inorg. Nucl. Chem.*, **27**, 993 (1965).

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The Preparation and Some Properties of Yttrium, Dysprosium, and Ytterbium Alkoxides

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Isopropoxides of yttrium, dysprosium, and ytterbium have been prepared by treating the metals with isopropyl alcohol using mercuric chloride as a catalyst. The reactants were refluxed for 24 hr at 82°, and the isopropoxides were recrystallized from isopropyl alcohol. The use of stoichiometric amounts of mercuric chloride resulted in chloride contamination and alkene alkoxide formation. High-purity isopropoxides of these metals could not be made by the metal chloride–ammonia method commonly employed to make group IV-B transition metal alkoxides. Heavier alkoxides were made by an alcoholysis reaction of the isopropoxides with the appropriate higher boiling alcohol in benzene. Compounds prepared by alcoholysis methods included the 2-pentoxides of yttrium, dysprosium, and ytterbium and yttrium *t*-butoxide, 3-methyl-2-butoxide, 2-hexoxide, 3-ethyl-3-pentoxide, 3-hexoxide, 2-ethyl-1-hexoxide, and phenoxide. All the alkoxides were solids which sublimed or decomposed on melting at 200° or higher. The alkoxides with heavier and branched-chain alkoxy groups were the most stable, but all differences were small and the chemistry was virtually identical for the three metals with the same alkoxy group attached. Thermal and hydrolytic decomposition was quantitative to the oxides.

Introduction

Only during the past 15 years have major efforts been directed toward a systematic investigation of metal alkoxides. Particularly important has been the work of Bradley.[1,2] Most metal alkoxides can be readily prepared and afford an opportunity for fundamental investigations of the metal–oxygen bond as influenced by adjacent organic groups. It was found, however, that classical methods of alkoxide synthesis failed to produce high-purity compounds of yttrium, dysprosium, and ytterbium. Preliminary work with other lanthanides indicates that the reactions are general to the series.

Metal alkoxides provide a direct route to ultra-high-purity, fine-particulate oxides by thermal and hydrolytic decomposition.[3] Transition metal alkoxides have previously been investigated for vapor deposition of oxides on refractory substrates.[4]

Owing to the lanthanide contraction there is little difference in the atomic size of these three elements. Yttrium, dysprosium, and ytterbium have covalent radii[5] of 1.62, 1.59, and 1.70 A and electronegativities[6] of 1.11, 1.10, and 1.06, respectively. Therefore, the reactions they undergo and the properties of the alkoxides formed are expected to be quite similar. For more electronegative elements such as titanium, zirconium, and aluminum, many of the alkoxides are liquids. In this instance the nature of the alkoxide group determines whether the compound is a solid or a liquid. For the electropositive elements such as lithium, sodium, and potassium, the alkoxides are always solids regardless of the alkoxide group. The alkoxides of yttrium, dysprosium, and ytterbium fall intermediate between these extremes, and, thus far, the alkoxides prepared by us have been solids. Volatility has been found to vary appreciably with the length and branching of the alkoxide group, however.

The rates of reactions for preparation of the alkoxides are faster for the compounds which have smaller covalent radii. The covalent radii[5] of aluminum, lithium, and titanium are 1.25, 1.23, and 1.32 A, and the reactions are relatively rapid. The covalent radii[5] of zirconium and hafnium are 1.45 and 1.44 A, and the reactions are considerably slower. For yttrium, dysprosium, and ytterbium, the reactions are much

(1) D. C. Bradley, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **21**, 179 (1960).

(2) D. C. Bradley, "Metal-Organic Compounds," Advances in Chemistry Series, No. 23, American Chemical Society, Washington, D. C., 1959, pp 10-36.

(3) K. S. Mazdiyasni, C. T. Lynch, and J. S. Smith, *J. Am. Ceram. Soc.*, **48**, 372 (1965).

(4) K. S. Mazdiyasni and C. T. Lynch, ASD-TDR 63-322, May, 1963.

(5) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1954, p 135.

(6) M. M. Jones, *J. Chem. Educ.*, **37**, 231 (1961).

slower than for zirconium and hafnium and harder to drive to completion.

Experimental Section

Apparatus.—All preparative work was carried out in glass apparatus with ground-glass joints. The reaction steps were done under vacuum or under an atmosphere of dry nitrogen. Compounds were handled in a drybox under dry nitrogen and stored in evacuated desiccators over magnesium perchlorate. Molecular weights were determined with a vapor pressure osmometer. Concentrations were 0.01 to 0.1 *M* in benzene. The accuracy of the method was 1%. Several compounds were not determined as decomposition occurred on the thermistor beads.

Materials.—Reagent grade isopropyl alcohol from Matheson Coleman and Bell was dried for 24 hr over calcium sulfate and then distilled at 82.4° using a molecular still. Thiophene-free benzene from Matheson Coleman and Bell was dried for 24 hr over magnesium perchlorate, decanted, and used. Metal shavings of yttrium, dysprosium, and ytterbium from American Potash and Chemical Co. with analyzed purity of 99.9% were used as received.

The higher boiling alcohols were obtained from Matheson Coleman and Bell. The alcohols were dried over calcium sulfate and redistilled in a Vigreux or Fenske helices-packed fractionating column at their boiling points. All other chemicals were reagent grade.

Methods of Preparation.—The preparative methods for any given alkoxide of Y, Dy, and Yb are essentially alike. The rate of reaction was qualitatively observed to be Yb > Dy > Y, and product alkoxide stability toward hydrolytic decomposition was Y > Dy > Yb. Differences were not large. Infrared spectra have proved useful in checking the results of synthesis for completeness of reaction and product identification. The infrared spectra of yttrium, dysprosium, and ytterbium isopropoxides from 5000 to 625 cm^{-1} are given in Table I. The spectra are almost identical for the three compounds. Absorptions characteristic of the isopropoxy group are found at 1168 to 1176 cm^{-1} and at 1127 to 1136 cm^{-1}. These bands and the doublet characteristic of the *gem*-dimethyl structure at 1359 and 1372 cm^{-1} for the yttrium and dysprosium isopropoxides and at 1364 and 1377 cm^{-1} for ytterbium isopropoxide can be used to identify the reaction products.[7,8] The C-O stretch vibration at 1006 to 1012 cm^{-1} is enhanced as a result of the M-O-C bond.[8] Yttrium tri-*t*-butoxide has four strong absorptions at 1212, 1010, 973, and 755 cm^{-1} characteristic of the *t*-butoxy group which can be used to identify this compound.[8] The typical C-H deformation vibration of the *t*-butoxy group is observed at 1355 cm^{-1} with a weaker band at 1379 cm^{-1} and also is useful for distinguishing yttrium *t*-butoxide. The spectra of alkoxides of heavier alcohols are similar to those of the substituent alcohols themselves without the hydroxyl group absorption. Yttrium tri-2-pentoxide, for example, has the fingerprint skeletal vibration region absorptions (1200 to 900 cm^{-1}) identical with those of 2-pentanol, and no 3333 cm^{-1} band is observed.[8] The spectral region at 1000 cm^{-1} is complex, and the effect of the metal on the intensity of the C-O stretch vibration is not clear.

Yttrium Isopropoxide.—To 250 ml of isopropyl alcohol were added 17.0 g of yttrium metal shavings and 10 mg of mercuric chloride. The mixture was refluxed at 80° for 24 hr, then cooled and filtered. The excess alcohol was distilled off until the product was nearly dry. The crude isopropoxide was dissolved in benzene, filtered, and evaporated to dryness at reduced pressure at 50°. The solid was further purified by dissolving it in hot isopropyl alcohol and recrystallizing the white crystalline product; yield 47%; sublimes at 200–210° at 0.1 mm; mol wt 544 (dimer); soluble in C_6H_6, CCl_4, and CS_2.

TABLE I

INFRARED ABSORPTION FREQUENCIES OF ISOPROPOXIDES (CM^{-1})

$Y(OC_3H_7)_3$	$Dy(OC_3H_7)_3$	$Yb(OC_3H_7)_3$
2941	2941	2941
2899	2899	2907
2857	2857	2857
2817	2820	2825
2597	2604	2611
1466	1466	1464
1387	1385	1377
1372	1372	1365
1359	1359	1351
1340	1333	1333
1176	1168	1170
1136	1130	1127
1012	1006	1009
980	975	967
958	951	946
840	838	837
836	831	828
828	823	816

Anal. Calcd for $Y(OC_3H_7)_3$: C, 40.7; H, 7.9; Y, 33.4. Found: C, 40.2; H, 7.8; Y, 33.8.

Yttrium Isopropoxide (from Lithium Isopropoxide).—To a rapidly stirred solution of 24.3 g of lithium isopropoxide in 150 ml of isopropyl alcohol were added 43.1 g of yttrium trichloride and 25 ml of tetrahydrofuran. The mixture reacted at 45° for 3 hr, and then the isopropyl alcohol and tetrahydrofuran were distilled off under reduced pressure until the product was nearly dry. The solid was dissolved in benzene, then filtered, and the filtrate was evaporated to dryness. The isopropoxide was further purified by recrystallization from isopropyl alcohol; yield 56%. (It is difficult to remove all of the lithium and chloride from the product. Consequently, the mercuric chloride method is preferred.) This method is similar to that employed to make uranium tetramethoxide in tetrahydrofuran.[9]

Dysprosium Isopropoxide.—To 700 ml of isopropyl alcohol were added 30.0 g of dysprosium metal shavings and 12 mg of mercuric chloride. The mixture was refluxed at 80° for 24 hr, then cooled and filtered. The excess alcohol was distilled off until the product was nearly dry. The crude isopropoxide was dissolved in benzene, filtered, and evaporated to dryness at reduced pressure at 50°. The solid was further purified by dissolving it in hot isopropyl alcohol and recrystallizing the white crystalline product; yield 27%; sublimes at 190–200° at 0.17 mm.

Anal. Calcd for $Dy(OC_3H_7)_3$: C, 31.85; H, 6.2; Dy, 47.9. Found: C, 31.5; H, 6.1; Dy, 48.4.

Ytterbium Isopropoxide.—To 250 ml of isopropyl alcohol were added 10 g of ytterbium metal shavings and 6 mg of mercuric chloride. The mixture was refluxed at 80° for 24 hr, then cooled and filtered. The excess alcohol was distilled off until the product was nearly dry. The crude isopropoxide was purified in analogous manner to the dysprosium isopropoxide; yield 21%; sublimes at 190–200° at 0.2 mm.

Anal. Calcd for $Yb(OC_3H_7)_3$: C, 30.85; H, 6.0; Yb, 49.5. Found: C, 30.5; H, 6.0; Yb, 49.8.

Yttrium Tri-*t*-butoxide.—To 15.0 g of yttrium isopropoxide were added 200 ml of *t*-butyl alcohol and 50 ml of benzene. The alcoholysis reaction proceeded with azeotropic distillation of the lower boiling alcohol–benzene azeotrope followed by distillation of the higher boiling alcohol–benzene azeotrope from 75 to 105° over a 24-hr period. The product was evaporated to dryness at reduced pressure. It was dissolved in hot benzene, filtered,

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[7] C. T. Lynch, K. S. Mazdiyasni, J. S. Smith, and W. J. Crawford, *Anal. Chem.*, **36**, 2332 (1965).

[8] C. T. Lynch, K. S. Mazdiyasni, J. S. Smith, and W. J. Crawford, "Application of Infrared Spectra in the Analysis of Yttrium, Dysprosium, and Ytterbium Alkoxides," 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1, 1964.

[9] H. Gilman, R. G. Jones, G. Karmas, and G. A. Martin, *J. Am. Chem. Soc.*, **78**, 4285 (1956).

and recrystallized. $Y(OC_4H_9)_3$ sublimed at 242° at 2 mm; yield 85%.

Anal. Calcd for $Y(OC_4H_9)_3$: C, 46.8; H, 8.8; Y, 28.8. Found: C, 46.4; H, 8.9; Y, 29.0.

Yttrium Tri-3-methyl-2-butoxide.—To 5.0 g of yttrium isopropoxide were added 24 ml of 3-methyl-2-butanol and 50 ml of benzene. The reaction mixture was heated to 75°, and then azeotropic distillation was carried out for 24 hr to a final temperature of 109°. The product was evaporated to dryness at reduced pressure. It was dissolved in hot benzene, filtered, and recrystallized; yield 70%; mp ~225° dec; mol wt 523 (molecular complexity of 1.5).

Anal. Calcd for $Y(OC_5H_{11})_3$: C, 51.7; H, 9.4; Y, 25.3. Found: C, 51.1; H, 9.4; Y, 25.5.

Yttrium Tri-2-pentoxide.—To 5.0 g of yttrium isopropoxide were added 24 ml of 2-pentanol and 50 ml of benzene. The reaction mixture was heated to 75°, and then azeotropic distillation was carried out for 24 hr to a final temperature of 91°. The product was evaporated to dryness at reduced pressure. It was dissolved in hot benzene, filtered, and recrystallized; yield 75%; mp ~225° dec; mol wt 612 (molecular complexity of 1.7).

Anal. Calcd for $Y(OC_5H_{11})_3$: C, 51.7; H, 9.4; Y, 25.3. Found: C, 51.4; H, 9.5; Y, 25.4.

The 2-pentoxides of Dy and Yb were also made in this manner. The infrared spectra were almost identical with that of Y; no further analysis was done on these compounds.

Yttrium Tri-2-hexoxide.—To 9.5 g of yttrium isopropoxide were added 50 ml of 2-hexanol and 100 ml of benzene. The reaction mixture was heated to 72°, and then azeotropic distillation was carried out for 24 hr to a final temperature of 136°. The product was evaporated to dryness at reduced pressure. It was dissolved in hot benzene, filtered, and recrystallized; yield 80%; mp ~260° dec.

Anal. Calcd for $Y(OC_6H_{13})_3$: C, 55.1; H, 10.0; Y, 22.7. Found: C, 55.4; H, 10.1; Y, 22.4.

Yttrium Tri-3-ethyl-3-pentoxide.—To 85.9 g of yttrium isopropoxide were added 400 ml of *t*-heptyl alcohol and 100 ml of benzene. The reaction mixture was heated to 78°, and then azeotropic distillation was carried out for 24 hr to a final temperature of 97°. The product was evaporated to a semiliquid at reduced pressure. The product was distilled at 224° at 760 mm with partial decomposition; yield 77%.

Anal. Calcd for $Y(OC_7H_{15})_3$: C, 58.0; H, 10.4; Y, 20.5. Found: C, 58.2; H, 9.9; Y, 21.2.

Yttrium Tri-3-hexoxide.—To 5.0 g of yttrium isopropoxide were added 24 ml of 3-hexanol and 50 ml of benzene. The reaction mixture was heated to 75°, and then azeotropic distillation was carried out for 24 hr to a final temperature of 94°. The product was evaporated to dryness at reduced pressure. The product was dissolved in hot benzene, filtered, and recrystallized; yield 82%; mp ~265° dec.

Anal. Calcd for $Y(OC_6H_{13})_3$: C, 55.1; H, 10.0; Y, 22.7. Found: C, 54.2; H, 10.2; Y, 23.3.

Yttrium Tri-2-ethyl-1-hexoxide.—To 12.4 g of yttrium isopropoxide were added 235 ml of 2-ethylhexanol and 100 ml of benzene. The alcoholysis reaction proceeded with azeotropic distillation for 24 hr from 73° to a final temperature of 97°. The product was evaporated to dryness under reduced pressure. The solid was dissolved in hot benzene, filtered, and recrystallized; yield 84%; mp ~275° dec.

Anal. Calcd. for $Y(OC_8H_{17})_3$: C, 60.6; H, 10.8; Y, 18.6. Found: C, 60.9; H, 11.0; Y, 18.7.

Yttrium Phenoxide.—To 55 ml of phenol were added 2.7 g of yttrium metal shavings and 7 mg of mercuric chloride. The mixture was refluxed at 182° for 24 hr, then cooled and filtered. The excess alcohol was distilled off until the product was nearly dry. The crude phenoxide was dissolved in hot cyclohexane, filtered, and recrystallized; yield 77%; mp ~310° dec.

Anal. Calcd for $Y(OC_6H_5)_3{\cdot}4C_6H_{12}$: C, 71.7; H, 8.9; Y, 12.5. Found: C, 71.1; H, 8.7; Y, 12.2.

Results and Discussion

Synthesis of Isopropoxides.—Bradley and Wardlaw[10] have prepared many of the group IV-B transition metal alkoxides from anhydrous metal halides and alcohol using anhydrous ammonia

$$MCl_4 + 4NH_3 + 4ROH \xrightarrow[5°]{C_6H_6} M(OR)_4 + 4NH_4Cl \qquad (1)$$

where M is Ti, Zr, Hf, or Th and R is an alkyl group.

Attempts to make isopropoxides of yttrium, dysprosium, and ytterbium by this method or by direct reaction with the alcohol were unsuccessful. This reaction (1) with these metals was extremely slow, producing very low yields of the yttrium, dysprosium, and ytterbium compounds, and the product was always contaminated with chloride. This contamination can be explained in terms of yttrium alkoxides being stronger bases than ammonia in an analogous way to thorium compounds[1] (made by the metal chloride–ammonia method) where

$$Y(OR)_3 \rightleftharpoons Y(OR)_2^+ + RO^- \qquad (2)$$

$$Y(OR)_2^+ + Cl^- \rightleftharpoons Y(OR)_2Cl \qquad (3)$$

Yttrium, dysprosium, and ytterbium isopropoxides were prepared using a reaction first employed by Adkins and Cox[11] to make aluminum isopropoxide

$$M + HgCl_2 + 3ROH \xrightarrow{82°} M(OR)_3 + Hg + 2HCl + {}^1/_2H_2 \qquad (4)$$

where M is Al, Y, Dy, or Yb, and R is the isopropyl group. The reaction with aluminum is exothermic and complete within a 4-hr reflux period; with yttrium, dysprosium, and ytterbium the reaction requires a minimum of 24 hr. The crude product is recovered from hot isopropyl alcohol. This reaction previously was thought to be confined to alkali metals, magnesium, and aluminum, the latter two with appropriate catalysts.[2] This reaction can be carried out in excess alcohol but not in excess mercuric chloride. However, when a stoichiometric amount of mercuric chloride is used for the reaction, up to 1% or more chloride is found in the product isopropoxide. A side reaction also is observed in which the alcohol reacts to form an alkene and to produce an alkene alkoxide as the final product. This reaction can be followed by observing the infrared spectra for the appearance of a C=C stretch vibration at 1616 cm^{-1} and terminal methylene deformation at 891 cm^{-1} which are present in the alkene and not in the alkoxy compounds.[8]

The formation of yttrium isopropeneoxide, $Y[OC(=CH_3)CH_3]$, has been confirmed from infrared spectral and proton nuclear magnetic resonance. The differences between the infrared and nmr spectra for yttrium isopropoxide and yttrium isopropeneoxide are given in Table II. The side reaction in excess $HgCl_2$ probably is

$$Y + 4HgCl_2 + 3C_3H_7OH \xrightarrow[82°]{HgCl_2} Y(OC_3H_5)_3 + 4Hg + 8HCl + {}^1/_2H_2 \qquad (5)$$

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[10] D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, 208 (1951).

[11] H. Adkins and F. W. Cox, *J. Am. Chem. Soc.*, **60**, 1151 (1938).

TABLE II

YTTRIUM ISOPROPOXIDE AND YTTRIUM ISOPROPENEOXIDE

A. Infrared Absorption Frequencies, Cm^{-1}

$Y(OC_3H_7)_3$	$Y(OC_3H_5)_3$
2941	3125
2899	2959
2857	2874
2817	2740
2597	2618
1466	1953
1387	1616
1372	1580
1359	1493
1340	1481
1176	1449
1136	1414
1012	1387
980	1333
958	1190
840	1163
836	1106
828	1058
	971
	891
	826
	789
	717

B. Nuclear Magnetic Resonance Data (TMS Standard)

	$Y(OC_3H_7)_3$		$Y(OC_3H_5)_3$	
Chemical shift, ppm	4.28	1.35	4.0	1.29
Assignment	α-Hydrogen	Methyl	Methylene	Methyl
Relative no. of protons	1.0	6.1	2.0	3.3

The yttrium isopropeneoxide was obtained as the main product after a 48-hr reflux but was contaminated with mercury, chlorine, and yttrium isopropoxide.

Using mercuric chloride as catalyst in the amount of 10^{-3} to 10^{-4} mole of mercuric chloride per mole of metal, reaction 4 proceeds to completion with the mercury formed acting as a catalyst as

$$M + Hg \longrightarrow M(Hg) \qquad (6)$$

$$M(Hg) + 3ROH \longrightarrow M(OR)_3 + Hg + {}^3/_2H_2 \qquad (7)$$

The alkoxide product of this reaction is not contaminated with chloride, and no alkene formation is observed. Evidence for this mechanism was the evolution of hydrogen and the failure of the reaction to proceed when the Hg was removed from the reactants. When large amounts of $HgCl_2$ were used, the formation of free Hg and amalgamation with the metal (Y, Dy, Yb) were readily observed.

Synthesis of Heavier Alkoxides.—Substitution of other R groups for the isopropoxy group is done by an alcoholysis reaction.[12] For example, the *sec*-pentoxides of yttrium, dysprosium, and ytterbium (and other $C_5H_{11}OH$ derivative isomers) are prepared by treating the isopropoxides with *sec*-pentyl alcohol in the presence of benzene

$$M(OC_3H_7)_3 + 3C_5H_{11}OH + n\text{-}C_6H_6 \xrightarrow[C_6H_6]{C_5H_{11}OH} M(OC_5H_{11})_3 + 3[C_3H_7OH \cdot n\text{-}C_6H_6] \qquad (8)$$

The distillation of an azeotrope drives the reaction to completion. The rise in temperature to the higher boiling azeotrope of $C_5H_{11}OH \cdot n\text{-}C_6H_6$ signals the end of the reaction. Compounds prepared by this method include the *sec*-pentoxide, *sec*-hexoxide, sec-heptoxide, *t*-butoxide, *t*-heptoxide, and phenoxide of yttrium. Synthesis of these alkoxides was done to determine the importance of the degree of branching and alkoxide group length to volatility. (It is not unusual for branched alkyl groups of higher molecular weight to impart increased volatility to alkoxides.[13] For example, zirconium tetra-*t*-butoxide is a liquid and zirconium isopropoxide is a solid at STP. The effect has been attributed to a decrease in intermolecular association due to steric hindrance.[2])

The compounds with the higher molecular weights were found to have greater stability to hydrolysis and thermal decomposition. Often higher melting or sublimation points were also observed with several exceptions, particularly yttrium 3-ethyl-3-pentoxide, which was significantly more volatile than other pentoxides and the *t*-butoxide compound. The differences in volatility, however, were not great compared with, for example, zirconium alkoxides. With four alkoxy groups around the smaller zirconium atom compared to three alkoxy groups around the larger yttrium atom, this is an expected result. Aluminum alkoxides are also much less volatile than analogous zirconium compounds but more volatile than yttrium alkoxides, probably because of the electronegativity difference. A considerably greater number of examples would have to be studied, however, to determine the importance of electronegativity of the metal relative to the nature of the alkoxide group.

Thermal Decomposition.—The alkoxides of Y, Dy, and Yb decompose quantitatively to the respective oxides, an olefin, and alcohol. For yttrium isopropoxide

$$2Y(OC_3H_7)_3 \longrightarrow Y_2O_3 + 3C_3H_7OH + 3CH_3CH{=}CH_2 \qquad (9)$$

The thermal gravimetric curves for the decomposition of yttrium isopropoxide to the oxide showed that decomposition was over 90% completed in air at 200° and in nitrogen at 300° using heating rates of 5°/min or less and 0.1-g samples. The Y_2O_3 formed had no carbon contamination and a purity of 99.9+%. No evidence of a stable intermediate oxy–alkoxide was found in thermal decomposition. Slow spontaneous decomposition was found at room temperature in a desiccator unless the product was stored in the dark.

The alkoxides hydrolyze rapidly to form the oxides

$$2M(OR)_3 + 3H_2O \longrightarrow M_2O_3 + 6ROH \qquad (10)$$

Reaction 10 produces a fine-particulate, high-purity oxide of Y, Dy, or Yb. The alkoxide is dissolved in an organic solvent such as benzene or isopropyl alcohol and water added slowly to a stirred solution. Complete dealkoxylation occurs immediately with no evi-

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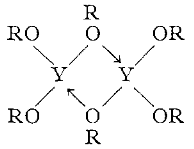
(12) R. C. Mehrotra, *J. Am. Chem. Soc.*, **76**, 2266 (1954).

(13) D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 4204 (1952).

dence of the formation of oxy–alkoxy polymers of the type suggested for zirconium alkoxides.[14] The isopropoxides of Y, Dy, and Yb react rapidly with water vapor in the air. As the size of the R group increases, the compounds are more stable (particularly alkoxides of C_5H_{11} and larger derivatives).

The X-ray spectrum of yttrium isopropoxide gave a powder pattern with broad, overlapping lines. Adequate resolution was achieved using a special collimator,[15] a copper target, and very long exposure times. Small crystals of purified yttrium isopropoxide were analyzed by infrared, nuclear magnetic resonance, and combustion analysis with no substantial impurities or second phase found. These crystals were ground and loaded into capillaries in an inert atmosphere. No oxide phase was found in the results, and it is believed that no other second phase was present considering prior chemical analysis. The lines are given in Table III. The pattern has not yet been indexed; however, several transition metal isopropoxides have been reported to have a monoclinic structure.[16]

The molecular weight determination of yttrium isopropoxide indicated that it exists as a dimer. A probable structure would be[2]



The infrared spectra of Yb and Dy isopropoxide suggest structures identical with that of the Y compound.

TABLE III

$Y(OC_3H_7)_3$ X-RAY DIFFRACTION POWDER LINE DATA (Cu $K\alpha$ RADIATION)

I/I_0	d, A	I/I_0	d, A
30	11.2	5	4.33
100	10.79	10	3.63
100	9.81	5	3.58
5	9.03	5	3.46
5	8.27	10	3.20
30	7.70	30	3.00
20	6.57	10	2.853
10	6.03	5	2.768
10	5.40	5	2.723
10	5.01	5	2.176

Molecular weights for yttrium 3-methyl-2-butoxide and yttrium 2-pentoxide averaged out between a monomer and dimer at 1.5 and 1.7, respectively. The lowered tendency for intermolecular association correlates with the increased branching of these compounds and higher volatility compared with the isopropoxide.[17]

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[14] W. B. Blumenthal, *Ind. Eng. Chem.*, **55**, 51 (1963).

[15] The offset collimator, developed by R. L. Prickett, had a 0.015-in. diameter collimator offset of 0.020 in.

[16] S. A. Iman and B. R. Rao, *Naturwissenschaften*, **50**, 517 (1963).

[17] This paper was presented in part at the 147th National Meeting of the American Chemical Society, Inorganic Division, Philadelphia, Pa., April 10, 1964.

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Magnetism, Electronic Spectra, and Structure of Transition Metal Alkoxides. III. Spin–Spin Coupling in Trinuclear Fe_3 Systems[1]

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The anomalous temperature dependence of the magnetic susceptibility of trimeric *n*-alkoxides of tervalent iron, $[Fe_3(OR)_9]$, is interpreted in terms of cooperative spin coupling between the three iron atoms which constitute the Fe_3 core of a model involving FeO_4 tetrahedra sharing corners to give the point group symmetry D_{3h}. The magnitude of the isotropic coupling constant J in the spin–spin Hamiltonian $\hat{\mathcal{H}} = -2J\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$ is estimated from the $\chi_M(T)$ data to be $J = -10\ \mathrm{cm}^{-1}$, and this value is compared with those observed for some related polynuclear systems.

Introduction

The trimeric *n*-alkoxides of tervalent iron[1] provide a favorable new class of polynuclear compound with which to test current concepts of metal–metal interaction.

The effective magnetic moments of $Fe_3(OCH_3)_9$, $Fe_3(OC_2H_5)_9$, and $Fe_3(OC_4H_9)_9$ fall in the range 4.4–4.5 BM at room temperature and are strongly dependent on temperature. The three compounds follow a Curie–Weiss law with θ values between -170 and $-200°$, and the inclusion of these values gives corrected moments of 5.5–5.9 BM, which are then independent of temperature. Dissolution of the iron(III) alkoxides in benzene at room temperature does not simplify this anomalous behavior, the effective magnetic moments remaining at 4.2–4.4 BM and being independent of solute concentration. This provides good evidence that the magnetic anomaly is intramolecular in its origin and that the molecular species in benzene is the one also present in the pure liquid *n*-butoxide and the crystalline methoxide and ethoxide. Cryoscopy in

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