Calcd for $Ni(NH_2CH_2CH_2SCH_2COO)_2$: C, 29.38; H, 4.93; N, 8.57; S, 19.61. Found: C, 29.39; H, 5.14; N, 8.46; S, 19.40. The deuterated sample was prepared by recrystallizing an analytical sample of the complex from deuterium oxide and drying as indicated above.

Bis(5-N,N-dimethylamino-3-thiapentanoato)nickel(II).—Chloroacetic acid was added to a mixture of 100 ml of water and sodium hydroxide (20 ml of 0.100 *N*) until the pH was 7.7. To this solution, bis(N,N-dimethyl-2-aminoethanethiolo)nickel(II) (0.27 g, 1 mmole) was added and the resulting reaction mixture was stirred for 5 hr at approximately 60°. The hot mixture was filtered, concentrated to about 2 ml, and cooled. On standing the solution deposited blue crystals which were dried as above; yield 0.13 g (30%). *Anal.* Calcd for $Ni\{(CH_3)_2NCH_2CH_2SCH_2COO\}_2$: C, 37.61; H, 6.31; N, 7.31; S, 16.74. Found: C, 37.09; H, 6.30; N, 7.18; S, 16.19.

Bis(5-N-*n*-propylamino-3-thiapentanoato)nickel(II).—This complex was prepared by the same method as for the dimethyl derivative. An isopropyl alcohol solution of the crude product deposited crystals of the desired composition after addition of chloroform. The sample was dried as above; yield 11%. *Anal.* Calcd for $Ni(C_3H_7NHCH_2CH_2SCH_2COO)_2$: C, 40.89; H, 6.86; N, 6.81; S, 15.60. Found: C, 40.72; H, 6.64; N, 6.72; S, 15.82.

Physical Measurements.—Molecular weights were obtained with a Mechrolab osmometer. Infrared spectra were determined by the KBr pellet technique and in Nujol mulls with a Perkin-Elmer 337 or Beckman IR 9 recording spectrophotometer. A Cary Model 14 spectrophotometer was used for measurements in the ultraviolet, visible, and near-infrared spectral ranges. Magnetic susceptibility data were obtained at room temperature by the Gouy technique.

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Preparation of Lanthanide Chloride Methanolates Using 2,2-Dimethoxypropane

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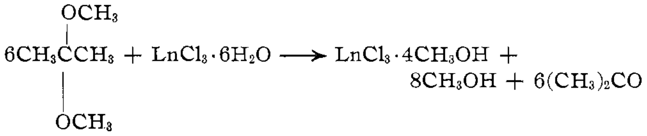
Although the alcoholates of the lanthanide halides have not been studied in detail, it is well known that both the anhydrous and hydrated chlorides are soluble in methyl, ethyl, isopropyl, and *n*-butyl alcohols and in glycerine.[2,3] Few observations have been made on the solid phases obtained from alcoholic solutions of the anhydrous chlorides.

Essentially, the procedures cited in previous studies[4-7] to make the alcoholates have been either (a) direct combination of the anhydrous chlorides with an alcohol, (b) a variation of an azeotropic drying of a hydrated chloride, or (c) an alcohol interchange. In the present investigation, the behavior of several hydrated lanthanide chlorides with easily hydrolyzable compounds was studied to learn whether the water of hydration of the lanthanide chlorides would react with selected reagents to form anhydrous lanthanide chlorides, or hydrates of lower water content, or other complexes.

Several investigators[8-12] have utilized 2,2-dimethoxypropane to obtain dehydrated chlorides, nitrates, and perchlorates in solution, but information about the actual isolation of the dehydrated salts is meager. The dehydrated products were used in solution as intermediates in the preparation of other complexes. 2,2-Dimethoxypropane was selected from among several possible reagents not only because of its strong tendency to react with water but because the reaction products, methanol and acetone, do not enter into bothersome side reactions. However, there is some tendency for polymerization which can be controlled.

2,2-Dimethoxypropane reacts with water in an endothermic reaction to form methanol and acetone. The rate of reaction is proportional to the acidity of the reaction medium, and is impeded by basic conditions.

Experimentally, it was found that a typical reaction with the hydrated lanthanide chlorides was



$$6CH_3\overset{OCH_3}{\underset{OCH_3}{C}}CH_3 + LnCl_3\cdot 6H_2O \longrightarrow LnCl_3\cdot 4CH_3OH + 8CH_3OH + 6(CH_3)_2CO$$

Experimental Section

Materials.—2,2-Dimethoxypropane (98%) was used as obtained from The Dow Chemical Co. Infrared analysis showed the absence of water and that it contained methanol and acetone which are the other constituents of the azeotropic mixture. The absolute methyl alcohol was Fisher ACS Reagent Grade. The lanthanide oxides of 99% or better content were used as obtained from the Lindsay Chemical Co. or the Michigan Chemical Corp.

Analytical.—Infrared analyses were made with a Unicam SP-200, using sodium chloride optics. Fluorolube mulls were employed for sample analyses. The 1603 cm^{-1} band of polyethylene standard was used for calibration of the instrument. The presence of water, methanol, acetone, and 2,2-dimethoxypropane was determined by infrared procedures. The lanthanide content was determined by precipitation with oxalic acid and subsequent ignition of the oxalate to the oxide at 800° for 1 hr. The chloride content was determined by precipitation of silver chloride. The precipitated chloride was filtered on an asbestos mat, then dried at 110° for 1 hr.

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Methanol was determined by dichromate oxidation in sulfuric acid solution. The standard method for the determination of primary alcohols was varied to have the oxidizing solution at room temperature prior to the addition of the methanol sample; 2 hr standing at room temperature followed by 10 min of refluxing the solution assured complete oxidation of the formic acid formed to carbon dioxide. Addition of excess ferrous ammonium sulfate to the solution followed by back titration with standard dichromate solution permitted calculation of the methanol. Diphenylamine sulfonate was used as an indicator. Analyses of standard methanol samples indicated that this method gave an average level of 99.66% of the stoichiometric values; the deviation was 3.4 parts per thousand.

Water was determined by the Karl Fischer method, using ethanol as a solvent. Blank analyses to determine the correction factor for the water content of the ethanol were made.

Preparation.—To prepare the tetramethanolates of the lanthanide chlorides, the hydrated chlorides were used. Each of the hydrated chlorides was prepared by sifting the oxide into concentrated hydrochloric acid; after all the oxide was added, the reaction mixture was heated to 80–90° to effect complete solution. The crystalline hydrates were obtained by partial evaporation and then cooling of the resulting solutions. The crystals were thoroughly washed with ethyl ether to remove residual hydrochloric acid since it can cause rapid cracking and polymerization of the 2,2-dimethoxypropane. The crystalline hydrates were equilibrated with moisture by storing in desiccators containing sulfuric acid solutions exerting vapor pressures of about 7.8–6.9 mm (about 51.5–53.5% by weight H_2SO_4). After equilibration, the hydrated salts were free flowing. Analyses showed the lanthanum and praseodymium compounds to be heptahydrates, the others to be hexahydrates.

The infrared absorption frequencies of the hydrated chlorides of La, Pr, Nd, Gd, Tb, Ho, and Lu for the O–H stretch are 3375, 3375, 3360, 3350, 3350, and 3370 cm^{-1} (greatest values at ends, lowest values in center of lanthanide series); for the H–OH bend 1630 cm^{-1} (Nd 1633 cm^{-1}).

The crystalline tetramethanolates of the chlorides of La, Pr, Nd, and Gd were obtained by dissolving 4 g of the appropriate lanthanide chloride hydrate in 65 ml of a solution consisting of reagent grade methanol, 30%, and 2,2-dimethoxypropane, 70%. The resultant solution was evaporated on a steam bath, to approximately 20 ml. After cooling the solution for about 3 min, 25 ml of 2,2-dimethoxypropane was added resulting in the formation of two layers, one a heavier, viscous layer containing the product. The added 2,2-dimethoxypropane also served to protect the product layer from moisture. Crystals of the tetramethanolated chloride formed from the more viscous or lower layer. The crystals were of good size (2–3 mm long) and tended to absorb the mother liquor. A "dried" product was obtained by pulverizing the crystals in the mother liquor followed by evacuative drying at a pressure of 90–100 mm to remove the methanol, acetone, and dimethoxypropane of the mother liquor. The "drying" was carried out only to the first visual dryness. Too extended an evacuation resulted in partial loss of the coordinately bound methanol so that the product did not analyze to the tetramethanolate.

In general, crystallization of the neodymium product from the lower layer occurred within 1–2 hr, and of the lanthanum and praseodymium products in 5–6 hr. The hydrated chlorides of the heavier earths (Gd, Tb, Ho, and Lu) react with 2,2-dimethoxypropane–methanol solution with the same ease as do those of the lighter earths, but crystals of the gadolinium product formed after about 36 hr. Small amounts of the holmium and terbium product crystals form within 50–60 days. At the end of this time, nucleation of crystals in the lutetium mixture had not occurred. The lutetium product layer appeared much less viscous than others prepared in this study. Analyses of the crystals of the lanthanum, praseodymium, neodymium, and gadolinium salts are given in Table I.

The tetramethanolates were found to be very hygroscopic. When crystals of the tetramethanolate were placed over water in a desiccator, the methanol of crystallization was displaced to form the aqueous chloride solution, usually within 24 hr.

TABLE I

ANALYSES OF THE METHANOLATES OF LANTHANUM, PRASEODYMIUM, NEODYMIUM, AND GADOLINIUM CHLORIDES

	% metal		% Cl		% CH_3OH	
$LaCl_3\cdot4CH_3OH$	37.03	37.19	28.34	28.49	33.69	34.32
	36.94				33.39	
	37.09				33.06	
$PrCl_3\cdot4CH_3OH$	36.97	37.53	28.12	28.34	33.19	34.13
	36.98				33.24	
$NdCl_3\cdot4CH_3OH$	38.42	38.08	28.16	28.09	33.11	33.83
	37.91				32.92	
	37.80				33.07	
$GdCl_3\cdot4CH_3OH$	39.48	40.13	26.68	27.14	32.58	32.71
	40.04		27.03		31.97	

Infrared analyses demonstrated the complete removal of the dimethoxypropane in the evacuative drying process. 2,2-Dimethoxypropane contains a O–C–O linkge; in the 840 cm^{-1} frequency range there is a strong absorption band due to the O–C–O asymmetric stretching. The infrared spectra of the "dried" tetramethanolates of lanthanum, praseodymium, neodymium, and gadolinium chlorides did not show any absorption at 840 cm^{-1}, thus indicating the absence of any 2,2-dimethoxypropane.

Since the tetramethanolates of the lanthanide chlorides were readily made, it was questioned as to whether the methanol could be eliminated from the compounds more easily than water is removed from the hydrates by an evacuative process. The tetramethanolates of lanthanum and neodymium chlorides were subjected to reduced pressures of about 26 mm. After about 4 hr under the lower pressures, the products were close to the trimethanolates in composition as noted in Figure 1. Methanol analyses for the lanthanum product showed 28.41% exptl, 28.16% calcd; for the neodymium product 27.95% exptl, 27.72% calcd, indicating that the obtained products were the trimethanolates. Karl Fischer analyses of the products showed only traces of water. These observations confirm the formation of trialcoholates previously reported.[3,6] None of the analyses indicated dialcoholates as reported by Meyer and Koss.[4]

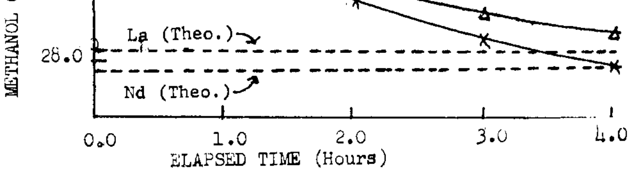

Figure 1.—Change of methanol content *vs.* time.

Conclusions

The reaction of 2,2-dimethoxypropane with the hydrated lanthanide chlorides provides a simple method of preparing the tetramethanolated chlorides. The trimethanolated lanthanide chlorides can be obtained from the tetramethanolated salts by evacuative drying. The preparation of these alcoholates opens the way for molecular weight, conductivity, and structural studies of the compounds, and for their use as intermediates in preparing other lanthanide complexes difficult to prepare in aqueous solutions. The use of tertiary alcohols, with subsequent heating of the obtained alcoholates, could conceivably result in the synthesis of other organic groups.

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Correspondence

The Deprotonation of Weak Acids

Sir:

Alkali metal salts of very weak protonic acids commonly have been prepared by three methods that do not require a metal salt of the acid as a starting material: (1) reaction with strong bases, (2) direct reaction with alkali metals, and (3) cleavage of halo derivatives with alkali metals. It is the purpose of this communication to show that the thermodynamic limitations of each of these methods may be defined in terms of acid pK values.

Reaction with Strong Bases.—In this method the weak acid is treated with an alkali metal salt of a still weaker protonic acid, sometimes using one of the protonic acids as a solvent. The pK of the acid whose salt is used as a reactant is an approximate upper limit to the pK values of the acids whose salts can be formed in this type reaction. Tables of weak acids and their aqueous pK values may be found in various references.[1-3] However these tables must be used with caution, because the pK values listed for hydroxylic acids (*e.g.*, water, ethanol, and acetic acid) are valid only in water, where the anions of these acids are abnormally stabilized by hydrogen bonding. In nonhydroxylic solvents such as ammonia, ethers, and dimethyl sulfoxide, the hydroxylic acids are *relatively* much weaker.[4-6] For example, it has been estimated[3] that if the hydroxide ion in water were not stabilized by hydrogen bonding, the pK of water would be about 28. This latter pK value would be the appropriate one to use when comparing water with nonhydroxylic acids in a nonhydroxylic solvent.

Alkali metal hydroxides are very strong bases, but their base strengths are greatly reduced by dissolving them in hydroxylic solvents such as water or alcohols. The intrinsic basicity of hydroxides can be achieved by using them in the solid form in conjunction with nonhydroxylic solvents, in which they are essentially insoluble.[7,8] In such cases the driving force for the deprotonation of an acid is markedly increased when the solid hydroxide is in excess, because the excess hydroxide can react with the water formed in the reaction to form a stable hydrate. Thus the net reaction in the case of potassium hydroxide is

$$2\mathrm{KOH(s)} + \mathrm{HA} \longrightarrow \mathrm{K}^+ + \mathrm{A}^- + \mathrm{KOH}\cdot\mathrm{H_2O(s)}$$

By making the approximation that the free energies of transfer of $K^+ + A^-$ and HA from water to the nonhydroxylic solvent are negligible,[9-13] we may calculate (using available thermodynamic data)[14,15] that the equilibrium constant for the latter reaction is 10^{31-pK}, where pK refers to the aqueous pK of the acid HA. We see that anhydrous KOH[16] is capable of deprotonating acids with pK values as high as 31. We have found several reactions of this type to have synthetic utility.[17] By simply stirring a suspension of powdered KOH in 1,2-dimethoxyethane with cyclopentadiene (p$K \approx 16$), indene (p$K \approx 20$), germane (p$K \approx 25$), or phosphine (p$K \approx 27$), we have obtained essentially quantitative yields of the corresponding potassium salts. These potassium salts have been used as intermediates for the preparation of various organometallic compounds such as ferrocene, bisindenyliron, ethylgermane, and methylphosphine. Undoubtedly many

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(16) It may be similarly shown that potassium oxide is potentially capable of deprotonating acids with pK values as high as 69. However, the relative unavailability and difficulty of handling $\mathrm{K_2O}$ makes it less attractive as a deprotonating agent.

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