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THE METHANOLATES OF LANTHANUM, PRASEODYMIUM AND NEODYMIUM CHLORIDES

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ABSTRACT

THE REACTION OF 2,2-DIMETHOXYPROPANE
WITH RARE EARTH HYDRATES:
THE METHANOLATES OF LANTHANUM, PRASEODYMIUM
AND NEODYMIUM CHLORIDES

by George L. Clink

In efforts to prepare the anhydrous chlorides, investigations of the reactions of the hydrated chlorides of the lanthanons with easily hydrolyzable compounds were made.

The hydrated chlorides of lanthanum, praseodymium and neodymium were prepared by reacting the appropriate oxides with concentrated hydrochloric acid, and evaporation of the solutions to effect crystallization. The hydrates were maintained in desiccators containing appropriate sulfuric acid-water solutions to afford constant humidity. Drying studies of the hydrates were made with Anhydrone and with sulfuric acid. Limited infra-red spectral studies of the hydrates were made to determine the positions of the bands due to H-OH bending frequencies.

Crystalline tetramethanolates of the lanthanon chlorides were made by reacting the hydrated chlorides with 2,2-dimethoxypropane-methanol solutions. Mother liquor was removed from the tetramethanolates by evacuation. Extended evacuation

resulted in a loss of some methanol, with a trend in composition toward the trimethanolates.

Infra-red spectral studies of the hydrates and the tetramethanolates show each series of salts to be very similar. The tetramethanolates are very reactive toward water as shown by infra-red studies and Karl Fischer water analyses. These compounds tend to go to the normal hydrates upon extended exposure to moist air.

Attempts to produce the anhydrous chlorides by refluxing the hydrated salts with acetyl chloride and with toluene were unsuccessful.

Preparation of the anhydrous chlorides by passing a stream of chlorine over the oxychlorides at elevated temperatures was ineffective.

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I. INTRODUCTION

In recent years, because of increased commercial and scientific interest in the lanthanon metals and the chemistry of their compounds, preparation of metals of high purity is receiving increased attention. The most universally applied methods employ the anhydrous halides, particularly the chlorides. One of the most widely applied older techniques is the electrolytic reduction of the fused halides. Other extensively used methods involve the reduction of the halides by a very active metal, such as calcium or magnesium. As a result, improved methods for the preparation of anhydrous halides, especially from the hydrated lanthanon salts, are continually sought. Many of the methods of preparation in the literature employ a reagent capable of reacting with the water of hydration. This investigation has been a partial study of the reactions of the hydrated chlorides of the lanthanons with easily hydrolyzable organic compounds to determine if either anhydrous chlorides or complexes other than hydrates could be prepared.

II. HISTORICAL

A. Methods for Preparing the Anhydrous Halides

The anhydrous halides are starting materials for the preparation of the free elements or metals, and since the original intention of this study was to determine if anhydrous halides might be made by either a new or modified procedure, a short review of the methods of preparation of the anhydrous halides will be made. Taylor (1) in 1962, and Thoma (2) in 1965 completed reviews of the various methods of preparation. More emphasis will be placed upon chloride preparatory procedures because they are employed most frequently.

The anhydrous halides of the lanthanons can be prepared 1) from the metals, 2) from the oxides, 3) from other binary lanthanon compounds, 4) from lanthanon salts of organic acids. 5) from the hydrated halides and 6) from other anhydrous lanthanon halides.

1. From the Metals

Ideally, the most applicable method for anhydrous halide preparation should be the reaction of the pure metals with pure halogens or hydrogen halides under suitable conditions. This was one of the earliest methods, but due to the limited

availability of pure lanthanon metals this technique is of very limited application (3-5). The reaction of the metals with methyl chloride has been reported (6). Heating of a mixture of mercuric iodide with lanthanon metal has resulted in the preparation of several lanthanon triiodides (7).

2. From the Oxides

The most readily available starting materials are the lanthanon sesquioxides, and their use in anhydrous halide preparation has received much attention. The anhydrous fluorides of most of the lanthanons were obtained by heating the appropriate lanthanon oxide in a stream of hydrogen fluoride (8,9). Popov and Glockler prepared the anhydrous fluorides by heating the moist lanthanon oxides in a stream of chlorine trifluoride, ClF_3 (10,11).

Oersted prepared the anhydrous chlorides by passing a stream of chlorine over a heated mixture of the oxide and carbon (12). This method has the disadvantage that the anhydrous salt is contaminated with carbon. Other investigators eliminated this problem by introducing carbon monoxide as the reducing agent since a reducing agent is necessary if chlorine is to react with the oxides (12-17). The reaction of phosphorus pentachloride with the oxides at elevated temperatures results in incomplete chlorination (18,19). Reaction of the oxides with a mixture of sulfur monochloride and chlorine was reported (20,21). However, pure europium(III) chloride cannot be prepared by this method because of partial

reduction of the product to europium(II) chloride (22). Conversion of the oxides to the anhydrous chlorides by using sulfur monochloride without chlorine usually result in a more complete conversion (23).

Ammonium chloride reacts with the oxides at temperatures near 250° to form the anhydrous chlorides; the excess ammonium chloride is removed by heating in vacuo (24). This method is reported to give neither high purity nor high quantitative yields (1). The anhydrous salts have been prepared by mixing a solution of the oxide and ammonium chloride in concentrated hydrochloric acid, evaporating the mixture to a thick paste, and heating it in vacuo at 300° for two hours prior to fusing it at 900° (25).

Both phosgene and carbon tetrachloride have been used to prepare the anhydrous chlorides from the oxides (26,27). When chlorine is used with carbon tetrachloride, the chlorinating ability is increased (1). Reaction of methyl chloride with the oxides gives the anhydrous chlorides, but the data are conflicting as to whether salts of good purity can be produced (28,29). Thionyl chloride effectively chlorinates the oxides to the anhydrous salts at elevated temperatures, but above 400°C it dissociates into sulfur dioxide, sulfur monochloride and chlorine (30). Thus, the actual chlorinating agent may be the sulfur monochloride. The use of sulfuryl chloride with the oxides produced only impure lanthanon chlorides (31).

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Only incompletely brominated oxides are obtained when a mixture of carbon monoxide and bromine is passed over the heated oxides (32). Iodides may be prepared from the oxides by a method similar to that of Hopkins, Reed and Audrieth for the preparation of the anhydrous chlorides (24). The oxide is heated with a large excess of ammonium iodide at 325°, the excess ammonium iodide being removed by heating *in vacuo* at 250° (33). Purity of the products is poor, the best reported value being ninety-five per cent (34). Aluminum iodide is reported to be capable of reacting with the oxides to produce the anhydrous iodides (35). However, the aluminum oxide which forms is very difficult to separate from non volatile chlorides.

3. From Other Binary Lanthanon Compounds

Lanthanon carbides react with halogen or hydrogen halide at elevated temperatures to form anhydrous halides. As carbides of the lanthanons of high purity are difficult to obtain in quantity, this method offers no advantage (36,37). Other binary lanthanon compounds, such as the hydrides, nitrides and sulfides have not proved satisfactory for the preparation of anhydrous halides because of their limited availability (16,28-40).

4. From Lanthanon Salts of Organic Acids

Certain organic compounds of the lanthanons have been utilized in the preparation of anhydrous chlorides.

The anhydrous chlorides of lanthanum, neodymium and samarium(III) have been made by treating suspensions of lanthanon benzoates in anhydrous ethyl ether by passing dry hydrogen chloride through the mixtures (41). Other investigators report poor results by this method which is not applicable to anhydrous bromides or iodides (1). The reaction of hydrogen bromide or hydrogen iodide with ethyl ether to form ethyl bromide or ethyl iodide eliminates this method for preparing the anhydrous bromides and iodides. Oxalates of the lanthanons have been used. Anhydrous cerium(III) chloride has been prepared by the reaction of hydrogen chloride and the oxalate (42).

5. From the Hydrated Halides

Since the hydrated halides of the lanthanons are readily prepared, they have received greater attention as intermediates in the preparation of the anhydrous chlorides. Many methods using the hydrated chlorides are analogous to methods using the oxides.

Anhydrous lanthanon fluorides have been prepared by heating the hydrated fluoride in a stream of hydrogen fluoride. The hydrated fluoride is prepared by precipitating it from a solution of the chloride by the addition of fluoride (43-46). A moisture contaminated product results by drying the precipitated hydrated fluorides (47). Uniform products are obtained by digesting the fluoride on a steam bath and drying the precipitate *in vacuo* at 250°. Formation of the oxyfluoride is prevented by heating the hydrated fluoride in a

stream of hydrogen fluoride (46). Taylor (48) has prepared the anhydrous fluorides of the lanthanons by heating a mixture of the hydrate and ammonium fluoride *in vacuo*.

One of the earlier methods of preparation employing the hydrated chlorides entailed heating the hydrate to 100° to form the monohydrate. When the temperature is carefully increased to 190°, the anhydrous chloride is reportedly formed. The product is then heated to 350° in a stream of hydrogen chloride. The fact that chloride-oxychloride mixtures are formed at temperatures above 100° indicates that hydrogen chloride is required for the complete conversion to the anhydrous chloride (49-58). Conditions for this procedure are critical; nitrogen, used to flush the system, must be completely free of oxygen and water since formation of the oxychloride in the presence of these substances is quite rapid. Mixtures of the hydrates and anhydrous halides are obtained by heating at a very low rate the higher hydrates of lanthanum, neodymium and praseodymium halides (59). The hydrates are converted to the anhydrous salts by heating for several days in dry hydrogen chloride at reduced pressures (60). Harrison obtained poor results by this method, obtaining purer products by heating the hydrates at 500° in a stream of hydrogen chloride at a pressure at 760 mm (61). Richards obtained good results using these reactants at high temperatures and reduced pressures (62).

The anhydrous chlorides may be prepared by heating hydrated chloride-ammonium chloride mixtures *in vacuo* at 200° sufficiently long to drive off the water, and then increasing the temperature to 300° to remove the excess ammonium chloride. This method is applicable to large or small quantities and yields high purity products (63-68). Taylor and Carter have reported a general method for the preparation of anhydrous halides which involves heating *in vacuo* a mixture of hydrated lanthanon halide and the appropriate ammonium halide until all the water and excess ammonium halide are expelled from the system. Products are reported as pure (48).

Treatment of the hydrated chlorides with sulfur monochloride or chlorine mixed with hydrogen chloride has resulted in the preparation of the anhydrous salts (54,55,69-71). The hydrated chlorides are heated in air followed by treatment of the resulting mixture of chloride-oxychloride with sulfur monocchloride and chlorine, or a mixture of sulfur monochloride, chlorine and hydrogen chloride has been used. This is followed by extraction of the chloride-oxychloride mixture with anhydrous ethyl alcohol and filtration and evaporation of the filtrate, with subsequent removal of the organic matter by heating in a current of dry air (72). Anhydrous europium(III) chloride and other lanthanon chlorides have been prepared by drying the hydrate at 100° and treating with a stream of sulfur monochloride and chlorine (20).

Treatment of the hydrated chlorides with carbonyl chloride or a mixture of carbon monoxide and chlorine has given good results (15).

Most reagents which readily react with water are not applicable because of extensive exchange between the anion of the dehydrating agent and the halide ion of the hydrate. The use of acetyl chloride or acetic anhydride was not satisfactory to prepare the anhydrous chlorides (48).

Hydrated chlorides refluxed with thionyl chloride has been reported to be effective in the preparation of the anhydrous salt, and has several advantages over earlier methods (73). Apparatus is low in cost and easily obtainable; relatively low temperatures are required; the presence of water in the system is of no concern, and the by-products of the reaction are easily removed from the system. The preparation of the chlorides of the lighter lanthanons is fairly rapid, while those of the heavier lanthanons require considerable time. About 110 hours is required to prepare the chloride of erbium.

Most methods for making anhydrous lanthanon bromides are analogous to the chloride methods. Dry hydrogen bromide passed over the hydrated bromides produces the anhydrous salt (51,74,80). Poor yields have been reported by this method (75,76). The addition of ammonium bromide to the hydrate followed by treatment with hydrogen bromide has produced the anhydrous bromide (76). The system is heated to

250° to remove most of the water and then at 600°, at which temperature the ammonium bromide is sublimed away. Ammonium bromide has served as the sole dehydrating agent for the preparation of the anhydrous salt (75,77,78).

Hydrated lanthanon iodides can be converted to the anhydrous salt by treating them in a stream of dry hydrogen iodide (51,79,80). Others have added hydrogen to the hydrogen iodide after mixing the hydrate with ammonium iodide (79-81). The anhydrous iodides of the heavier lanthanons in the pure state have not been prepared by this method (2, 75-77,81). Taylor, Stubblefield and Carter have prepared the anhydrous triiodides of all the lanthanons except those of samarium and europium, which reduce to the diiodides (48,68). In the preparation of the iodides, the oxide is dissolved in a solution of hydrogen iodide; ammonium iodide is added to the resultant solution in a twelve to one molar ratio of ammonium salt to oxide. The mixture is evaporated to dryness and heated in vacuo; heating at 200° expels most of the water, and excess ammonium iodide sublimed away at 350°.

6. From Other Anhydrous Halides

The reaction between anhydrous lanthanon chlorides and either hydrogen bromide or hydrogen iodide to prepare the anhydrous bromides or iodides has been reported. The method is limited, since oxybromide formation increases with time, thus obviating complete conversion. The iodide is prepared

by reacting a mixture of hydrogen iodide and hydrogen with the anhydrous chloride (82).

Ternary lanthanon salts, such as sulfates and carbonates, can be converted to the anhydrous chloride by treatment with sulfur monochloride and chlorine (20,22,56,83).

B. Preparation and Properties of the Lanthanon Chloride Alcoholates

The lanthanon ions, in spite of their high nuclear charge, are too large to effect appreciable polarization, which causes the electrostatic forces of attraction to be smaller. The sizes of the lanthanon ions, as compared to those of the transition groups, would indicate a lower tendency to coordinate. The unavailability of the 4f orbitals for bonding, due to their relatively deep position in the ions, tends to prevent the formation of hybrid orbitals which could lead to covalent bond strength.

Since the hydrates are so readily formed, it is reasonable to assume that there would be a tendency for the anhydrous chlorides to coordinate with other species capable of the lone pair electron type bonding characteristic of many oxygen containing ligands. Various alcohols do form the alcoholates, with several preparations having been reported.

Matignon prepared the triethanolate of neodymium chloride by crystallizing the salt from an ethanol solution of the anhydrous chloride (85). Meyer and Koss prepared the

ethanolates of didymium and lanthanum chlorides by dissolving the anhydrous chlorides in anhydrous ethanol with subsequent crystallization of the ethanolates. The products were reported to be $DiCl_3.3C_2H_5OH$ and $LaCl_3.2C_2H_5OH$ (87).

Although the alcoholates of compounds of many elements have been prepared and studied, this phase of the chemistry of the lanthanons has received little attention. The availability of modern preparatory techniques and methods of analysis should prompt increased attention in this area. Bradley and co-workers (88) used the azeotropic drying of lanthanum chloride hydrate with anhydrous ethanol to prepare the triethanolate of lanthanum chloride. Lanthanum chloride triethanolate was converted to the triisopropanolate by alcohol exchange by reflux techniques.

Recently, Mehrotra and co-workers prepared and studied some properties of the alcoholates of the general composition $LnCl_3(H_2O)(ROH)_2$ and $LnCl_3.3ROH$. The alcohols employed were methyl, ethyl, isopropyl and n-butyl. The monohydrate dialcoholates were prepared by dissolving the monohydrated chlorides in anhydrous alcohol and crystallizing the salts by cooling and evaporation under reduced pressure. The monohydrate dialcoholates were converted to the trialcoholates by refluxing the former in the respective alcohol to which a small amount of benzene had been added. Water was removed as a component of the ternary azeotrope, alcohol-benzene-water, by distillation. Subsequent crystallization and drying

yielded a product which, on analysis, was found to be the trialcoholate.

These investigators also prepared the trialcoholates by dissolving the anhydrous lanthanon chlorides in the chosen alcohol. The alcoholic solution was refluxed and cooled. The solvent was then evaporated and the crystals were dried under reduced pressure to yield the product. Anhydrous chlorides of the following were treated as described above: lanthanum, cerium(III), praseodymium and neodymium. Attempts to interchange the bound alcohol with secondary and tertiary alcohols resulted in side reactions which were accompanied by some loss of chloride. Refluxing of the triisopropanolate of lanthanum chloride with n-butanol reportedly gives the n-butyl trialcoholate.

Mehrotra and co-workers (89,91) found the trialcoholates to be very soluble in the parent alcohol. The alcoholates of lanthanum and cerium(III) chlorides are sparingly soluble in benzene, while those of praseodymium and neodymium are insoluble.

These investigators also found that the monohydrate diisopropanolate can be converted to the di-n-butanolate when treated with molar equivalents of n-butanol. Attempts were made to prepare the monohydrate dialcoholate from the anhydrous chlorides. The relatively strong attraction of lanthanon chlorides for water molecules is indicated by the formation of almost pure trihydrate of the chloride when the

anhydrous chloride is treated with water and isopropyl alcohol, even when the water to alcohol molar ratio is one to fourteen. The monohydrate dialcoholate is isolated only when the molar ratio of water to alcohol is increased to one to forty-three.

When the trialcoholates were heated extensive loss of alcohol and slight decomposition of the chloride resulted. For the triisopropanolate of lanthanum chloride, after heating at 100° and at 0.05 mm of pressure, the metal to chloride ratio is found to be 1:2.89, and of metal to alcohol 1:0.29.

C. Preparation of Other Solvates

Although the tendency of the lanthanon ions to coordinate with monodentates is more pronounced with oxygen lone pair bonding, several complexes containing nitrogen lone pair bonding have been reported. Matignon and Trannoy (47) prepared the ammoniates of neodymium chloride of the general composition $NdCl_3 \cdot nNH_3$, where n is 1, 2, 4, 5, 8, 11 and 12. Anhydrous neodymium chloride absorbs ammonia, either gaseous or liquid, to produce these complexes. Cerium(III) chloride ammoniates have been prepared by reacting anhydrous cerium trichloride with ammonia at -80°. They are reported to have the general composition $CeCl_3.nNH_3$, where n is 2, 4, 8 and 20 (84).

The pyridine complex of neodymium chloride crystallizes from a solution of anhydrous neodymium chloride and pyridine,

and its composition reported as $NdCl_3.3C_5H_5N$ (85).

Popov and Wendlandt have prepared methylamine complexes of chlorides of the lighter lanthanons, by reacting methylamine with the anhydrous chlorides at 0° (86). All lanthanon chlorides so treated formed complexes of the type $LnCl_3.nMeNH_2$ where n is found to range from one to five; lanthanum and neodymium form the monomethylamine complexes.

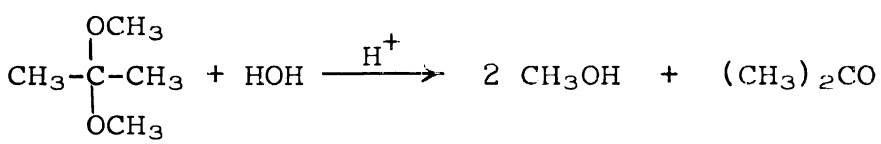
III. EXPERIMENTAL

A. Introduction

The behavior of the hydrated lanthanon chlorides with easily hydrolyzable compounds was studied. 2,2-Dimethoxypropane and acetyl chloride were used. The basic concept was to learn if the anhydrous chlorides, lower hydrated chlorides or other complexes might result if the water of hydration of the lanthanon chlorides reacted with the selected reagents.

The 2,2-dimethoxypropane was selected because other investigators had dehydrated several metal chlorides, nitrates and perchlorates with the material (92-96). Acetyl chloride was chosen because it reacts readily with water, is readily available and inexpensive.

2,2-Dimethoxypropane reacts with water in an endothermic reaction to form methanol and acetone (102). The rate of reaction is proportional to the acidity of the reaction medium, and is impeded by basic conditions.



If the source of water is a hydrate, possible reactions, which were considered in this study, could yield:

a) an anhydrous halide

$$6\ CH_3-C(OCH_3)_2-CH_3 + LnCl_3 \cdot 6H_2O \rightarrow LnCl_3 + 12\ CH_3OH + 6\ (CH_3)_2CO$$

b) a lower hydrate

$$x\ CH_3-C(OCH_3)_2-CH_3 + LnCl_3 \cdot 6H_2O \rightarrow LnCl_3 \cdot (6-x)\ H_2O + 2xCH_3OH + x(CH_3)_2CO$$

c) a methanolate hydrate

$$x\ CH_3-C(OCH_3)_2-CH_3 + LnCl_3 \cdot 6H_2O \rightarrow LnCl_3(6-x)H_2O(y)CH_3OH + (2x-y)CH_3OH + x(CH_3)_2CO$$

d) a methanolate

$$6\ CH_3-C(OCH_3)_2-CH_3 + LnCl_3 \cdot 6H_2O \rightarrow LnCl_3 \cdot xCH_3OH + (12-x)CH_3OH + 6(CH_3)_2CO$$

Acetyl chloride hydrolyzes according to the following:

$$CH_3COCl + HOH \longrightarrow HCl + CH_3COOH$$

If the source of water is the hydrate, it could be assumed that a) an anhydrous chloride could result

$$6CH_3COCl + LnCl_3.6H_2O \longrightarrow LnCl_3 + 6HCl + 6CH_3COOH$$

or b) an acetate could form

$$6CH_3COCl + LnCl_3.6H_2O \longrightarrow Ln(C_2H_3O_2)_3 + 9HCl + 3CH_3COOH$$

or c) a mixture of acetates and chlorides, or an aceto-chloride could form.

A limited number of experiments using acetyl chloride and hydrated lanthanum chloride yielded products containing both acetate and chloride, so this phase of the investigations was not carried out too extensively.

B. Analytical Methods

Lanthanon Content Determination

Lanthanon content was determined by the oxalate method. A weighed sample was dissolved in water and the solution heated to 90°. The solution was made approximately 0.05N with nitric acid to prevent formation of oxalochlorides. The oxalate precipitate was filtered on paper, washed thoroughly with oxalic acid solution and ignited at 800° for one hour. The temperature was elevated gradually to prevent splattering of the oxalate.

Chloride Content Determination

Chloride was determined by the usual silver nitrate precipitation method. The precipitate was filtered in a Gooch crucible with an asbestos mat and dried one hour at 110°.

Methanol Determination

Methanol content was determined by dichromate oxidation in an acid medium. A measured excess of standard potassium dichromate solution was acidified with sulfuric acid and allowed to cool to room temperature. The weighed methanolate sample was placed in water, dissolved and added to the oxidant. When the methanol-dichromate solution had remained at room temperature for two hours, it was refluxed for ten minutes. After the solution had cooled to room temperature, a measured excess of standard ferrous ammonium sulfate solution was added. Back titration was with standard dichromate solution, using diphenylamine sulfonate as the indicator.

Water Content Determination

The determination of water was made by the Karl Fischer method. Ethanol was used as a solvent for all determinations. Blanks were run on the ethanol to determine its water content.

Infra-red Analysis

Infra-red spectral studies were made with a UNICAM SP-200, with sodium chloride optics. Fluorolube mulls were

employed for sample analyses. The $1603^{cm^{-1}}$ band of a polyethylene standard was used for calibration of the instrument.

C. Preparation of Some Lanthanon Chloride Hydrates

The hydrates of lanthanum, praseodymium and neodymium chlorides were prepared according to the following empirical reactions:

$$Ln_2O_3 + xH_2O + yHCl \longrightarrow LnCl_3.zH_2O \quad (La, Nd)$$

$$Pr_6O_{11} + uH_2O + vHCl \longrightarrow 6PrCl_3.zH_2O + wO_2$$

With adequate water present, the lanthanum and praseodymium chlorides form the heptahydrates while the neodymium chloride forms the hexahydrate. The oxide of praseodymium, Pr_6O_{11}, contains the element in both the three and four oxidation states. This oxide dissolves in acids, aided by heating, with reduction of the tetra valent praseodymium to the tri valent state (97,98).

The oxides of lanthanum, praseodymium or neodymium were sifted into concentrated hydrochloric acid. Ten per cent excess acid was used to insure complete reaction. If concentrated acid is poured onto the solid oxides, a glassy cake is formed on the surface of the solids, and dissolution proceeds very slowly. When all of the oxide was added, the reaction mixture was heated to 80-90^{o} to effect complete solution.

The praseodymium oxide, Pr_6O_{11}, dissolves very slowly, but boiling of the mixture speeds up the dissolution.

The solutions of the chlorides were cooled to room temperature and crystallization occurred. After the initial crystallization was complete, the liquid was poured off and evaporated to approximately fifty per cent of the original volume. The concentrated solution was cooled to room temperature and another crop of crystals was obtained. The evaporation and crystallization processes were repeated to give maximum hydrate recovery. If the solution was evaporated to the point at which upon cooling the entire solution solidified, a small amount of water was added to the solid and the mixture heated to effect complete liquefaction. This was followed by cooling and crystallization. To rid the prepared hydrates of any excess hydrochloric acid, the crystals were washed three times with ethyl ether. The washed products were placed in desiccators, and ether removed by evacuation. The crystals were pulverized and any residual ether removed by additional evacuation.

The hydrated chlorides were placed in desiccators which contained sulfuric acid-water solutions exerting a vapor pressure of approximately 8.0 mm. The concentrations of these acid solutions were varied and those which provided the optimum humidity for the formation of free flowing hydrates were selected. Changes in the acid solution concentrations were made only after a thirty-six hour period to assure equilibrium

attainment. The concentrations for the sulfuric acid-water solutions found suitable for establishing constant humidity conditions for storing the prepared hydrates are given in Table I.

Table I. Sulfuric Acid Humidity Solutions

Hydrate	Analysis (Ln/H_2O)	Sulfuric Acid Concentration (per cent by weight)	Humidity (per cent)
$LaCl_3$	1/6.90	53.5	29.0
$PrCl_3$	1/6.84	51.5	33.0
$NdCl_3$	1/6.10	53.6	29.0

When the crystals appeared to be dry and free flowing, the water content was determined by the Karl Fischer method. Since the reactivity of all water of hydration of the lanthanon chlorides is not as rapid as with other hydrated compounds, several minutes were allowed for the true end point to be obtained. The hydrated salts had sat in their respective controlled humidities for twenty-five days at the time of analysis.

D. The Preparation of the Tetramethanolates of Lanthanum, Praseodymium and Neodymium Chlorides

For the preparation of the lanthanon chloride methanolates of lanthanum, praseodymium and neodymium the following procedure results in consistently reproducible products.

The compounds formed have the general composition $LnCl_3.nCH_3OH$, where n is found to range from 3.89 to 3.96. This variation of n is due largely to the instability of these compounds in the presence of water.

This process, based on the reaction of the lanthanon chloride hydrates with an easily hydrolyzable compound, employs 2,2-dimethoxypropane. The nature of this reaction has been discussed in an earlier section.

The 2,2-dimethoxypropane was supplied by the Dow Chemical Company, for which the analysis was given as ninety-eight per cent, with the major impurities as methanol and acetone.

The process for converting lanthanon chloride hydrates to the methanolates by reaction with 2,2-dimethoxypropane proceeds, in general, as follows:

Four grams of finely divided lanthanon chloride hydrate was added to 65 milliliters of a solution containing 50 milliliters of 2,2-dimethoxypropane and 15 milliliters of methanol. The mixture was placed on a steam bath and the temperature raised until steady boiling occurred. Application of heat to the mixture caused the hydrate to dissolve much more rapidly than at room temperature. The resulting solution was evaporated until the volume had reached approximately thirty per cent of the original volume, and then allowed to cool to room temperature. Whenever clouding of the solution was noted, heating was discontinued. After the reaction mixture had cooled to room temperature, 20 milliliters of 2,2-dimethoxypropane was added to the solution, which caused a separation

into two layers. The mixture of layers was allowed to sit for ten minutes. It was found that the product crystallizes from the lower layer, with disappearance of the viscous lower layer as the crystallization was effectively complete. Although crystallization did occur occasionally without it, seeding was necessary most of the time to effect crystallization of the product. Seeding crystals were obtained by dissolving 0.1 to 0.2 grams of the appropriate hydrated chloride in 20 milliliters of a 2,2-dimethoxypropane-methanol solution, of the same concentration as with the methanolate preparation, evaporating nearly to dryness, cooling and allowing to solidify. These solids were shown by analysis to be lanthanon chloride methanolate hydrates of the general composition $LnCl_3(H_2O)_x(CH_3OH)_y$. The seeding crystals, an impurity in the product, were removed mechanically, as completely as possible, after crystallization was complete.

The product crystals, in all handling operations, were protected from atmospheric moisture as much as possible. Since a dry box was not available, water contaminated products resulted. The crystals, covered with 2,2-dimethoxypropane, were caked and had to be broken away from the bottom of the preparative glassware. The mixture of crystals and mother liquor was quickly transferred to a mortar and pulverized to insure complete removal of 2,2-dimethoxypropane, acetone and unbound methanol by subsequent drying of the product under reduced pressure. The mother liquor was poured off as

completely as possible without undue exposure of the crystals to the air. The crystals, damp with mother liquor, were placed immediately in a desiccator. The desiccator was evacuated to approximately 90 mm and allowed to equilibrate. This process was repeated until the crystals appeared 'visually' dry. The crystals were spread in a thin layer before the drying operation to insure as uniform a product as possible.

Analytical results of the tetramethanolates are given in Table II.

E. Attempted Conversion of the Hydrated to the Anhydrous Chlorides by Toluene Distillation

Water may be removed from some compounds by refluxing the materials with toluene in a distilling system containing a water trap (100). In an effort to learn if the hydrated chloride of lanthanum could be so treated to produce the anhydrous salt, eighteen grams of the hydrate were mixed with 100 milliliters of toluene and refluxed for two hours. The amount of water which was separated in a trap was 0.25 milliliters. Based on the heptahydrate composition to the amount of hydrate used in the refluxing process, for the removal of each molecule of water 0.87 milliliters of water would have to have been collected. To form the anhydrous chloride would have necessitated the removal of 6.1 milliliters of water. To ascertain if the water collected in the hydrate distillation was originally present in the toluene, 100 milliliters of

Table II. Analytical Results of the Prepared Methanolates of Lanthanum, Praseodymium and Neodymium Chlorides

Metal Chloride	Molar Ratio		Per Cent Metal		Per Cent Chloride*		Per Cent MeOH		Formula
	Ln/Cl	Ln/MeOH	Found	Theo.	Found	Theo.	Found	Theo.	
$LaCl_3$	1/2.98	1/3.94	37.03 36.94 37.09	37.19	28.34	28.49	33.69 33.39 33.06	34.32	$LaCl_3.4CH_3OH$
$PrCl_3$	1/3.01	1/3.96	36.97 36.98	37.53	28.12	28.34	33.19 33.24	34.13	$PrCl_3.4CH_3OH$
$NdCl_3$	1/2.98	1/3.89	38.42 37.91 37.80	38.08	28.16	28.09	33.11 32.92 33.07	33.83	$NdCl_3.4CH_3OH$

Lanthanon determined by oxalate method; chloride determined by silver chloride method; methanol determined by dichromate oxidation.

*In all studies, the lanthanon to chloride ratio was consistently found to be 1/3.

toluene were refluxed in the same manner without the hydrate. After the toluene had refluxed for two hours, no water was collected in the trap. The water collected in the hydrate distillation came over very quickly then stopped. The water collected was probably due to a 'damp' hydrate. Results of this study obviate this as a means of preparing the anhydrous chlorides.

F. Reaction of the Hydrated Chlorides with Acetyl Chloride

Since this study was concerned with the reaction of easily hydrolyzable compounds with the hydrated chlorides of the lanthanons, it was decided to investigate whether the use of acetyl chloride could be employed to prepare the anhydrous chlorides. The fundamental reaction has already been cited. Prior to the investigation, it was realized that the reaction of acetyl chloride with the hydrated chlorides of the lanthanons could result in the formation of one of several compounds, or a mixture of two or more of them. Some considered possibilities were; anhydrous chlorides, anhydrous acetates, acetate chlorides, acetate complexes or various hydrates of chlorides, acetates or acetate chlorides. Taylor (48) has also reported that the anhydrous chlorides can not be prepared by this process.

Several experiments were performed in which lanthanum chloride heptahydrate was refluxed with acetyl chloride.

In all cases a partial conversion to a white flocculent substance occurred. This product was mechanically separated from the granular hydrate and thoroughly washed with ethyl ether to remove any acetyl chloride present. Qualitative tests showed the presence of acetate in the product. Because of the acetate in the product, further studies were not made.

G. Attempted Conversion of Lanthanon Oxychlorides to the Anhydrous Chlorides

It was decided to learn if the oxychlorides of lanthanum and neodymium could be converted to the anhydrous chlorides by treating them in a stream of chlorine at elevated temperatures. It has been reported that the oxychloride of praseodymium can be prepared by treating the sesquioxide with a stream of chlorine at 400° (101). The possibility of complete chlorination of the oxychloride was investigated.

Lanthanum chloride heptahydrate was heated at 800° to effect conversion of the chloride to the oxychloride. Chlorine was passed through the system continually to flush the water away from the formed oxychloride. The resultant oxychloride was heated in a stream of chlorine at 800° for one and one-half hours. The substance remaining after the chlorination process was tested for the presence of some anhydrous chloride. It is known that the anhydrous lanthanon chlorides are very soluble in water and that the oxychlorides are very insoluble in water. Hence a positive test for lanthanon ions in a water

solution obtained by treatment of the product with water would indicate some anhydrous chloride formation. The treated material was placed in hot water and stirred. The resultant mixture was filtered and the filtrate treated with saturated oxalic acid solution. No precipitate formed, indicating the absence of lanthanum in the solution. Treatment of the hexahydrated neodymium chloride in similar fashion gave similar results. This phase of the study was terminated since it showed no promise of easily producing the anhydrous chlorides.

IV. DISCUSSION

A. The Lanthanon Chloride Hydrates

In the preparation of crystals of the hydrates, if the solution of the hydrate is evaporated until complete solidification occurs upon cooling, water must be added to the solid such that, upon reheating the mixture and again cooling it, complete solidification does not occur. If the solution is permitted to solidify completely, the composition of the formed hydrates may be lower and more variable than the maximum hydration desired due to a deficiency of the amount of water necessary to form the higher hydrates. If such lower hydrates are placed in an atmosphere of regulated humidity there is a tendency to absorb water to form the higher hydrates, thus depleting the water content of the solution used for maintaining constant humidity. It is more efficient and satisfactory to redissolve the solid mass in a very small amount of water and to recrystallize the higher hydrate than to permit the lower hydrate to cause a disruption of the controlled humidity by absorbing water from the constant humidity solution.

Analytical data from the analyses of the prepared hydrates of the lanthanon chlorides show the lanthanum and praseodymium chlorides are close to the heptahydrate

composition, while the neodymium chloride is close to that of the hexahydrate. Data are given in Table III. The data in Tables I and III indicate the constant humidity conditions for storing the prepared hydrates.

Table III. Water Analysis of Hydrates of the Lanthanons

Sample	Weight (grams)	SO_2 Solution (mls)	I_2 Solution (mls)	Ln/H_2O
Blank	.....	25.0	2.50	.....
Standard	0.0610	25.0	14.85	.....
$LaCl_3$ hydrate	0.1430	25.0	12.10	1/6.90
$PrCl_3$ hydrate	0.0607	25.0	6.45	1/6.84
$NdCl_3$ hydrate	0.0679	25.0	6.60	1/6.10

Twenty-five milliliters of ethanol were used as a solvent in each determination.

Infra-red Spectral Studies

A problem involved in the preparation of both the hydrates and the methanolates was concerned with the presence of water. Accordingly, infra-red spectral studies were made to determine whether or not the absorption bands due to the H-OH bending frequencies were observed for the products made in this study. Bands for these bending vibrations should appear at about 1600-1650 cm^{-1}. Spectra obtained for the prepared hydrated chlorides were found to exhibit bands in the region from 1630-1635 cm^{-1} (Figure 1 and Table IV).

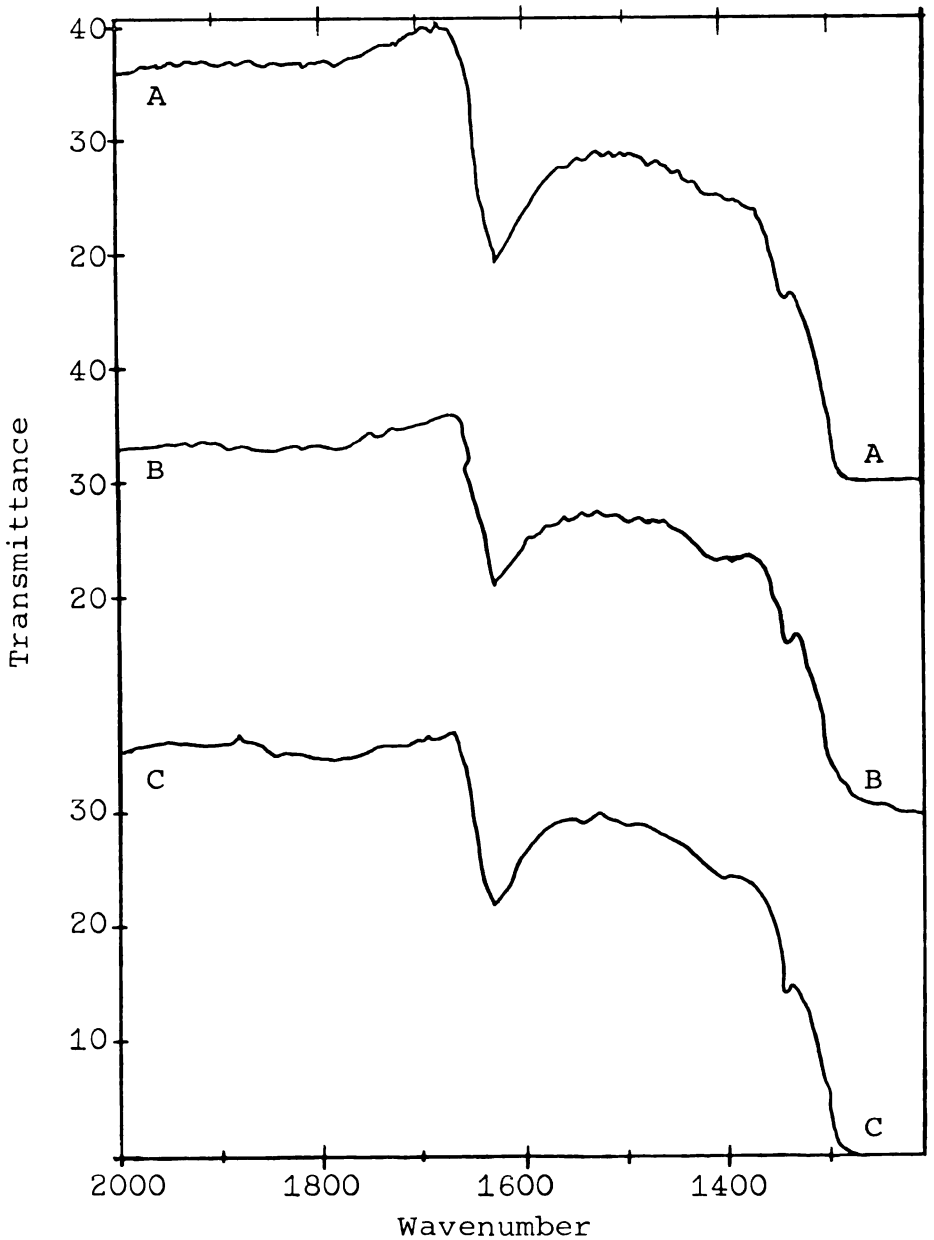


Figure 1. Infrared spectra of the hydrates of:
A Lanthanum Chloride
B Praseodymium Chloride
C Neodymium Chloride

Table IV. H-OH Bending Frequencies of Some Lanthanon Chloride Hydrates

Sample	Band (cm^{-1})	Figure 3, spectrum
$LaCl_3 . 6.90 H_2O$	1630	A
$PrCl_3 . 6.84 H_2O$	1630	B
$NdCl_3 . 6.10 H_2O$	1635	C

Dehydration Studies

Another problem in arriving at an understanding of the composition of the hydrated chlorides was approached by dehydration studies of these compounds with Anhydrone (magnesium perchlorate, anhydrous) and with sulfuric acid (96 per cent).

The desiccation of the hydrates by Anhydrone was carried out for approximately two hundred days, while that of the sulfuric acid was discontinued after one hundred and fourteen days when it was noted that the inside of the desiccator had become coated with water.

Results of the dehydration study were in general agreement with data regarding the efficiency of Anhydrone and sulfuric acid as drying agents. Based upon equal desiccating times of approximately one hundred and ten days, the Anhydrone removed seventy-four and seventy-eight per cent as much water from the neodymium and lanthanum hydrates, respectively, as was removed by the sulfuric acid.

From the data given in Tables VII and VIII, and from the curves in Figures 2 and 3, the dehydration of the salts by sulfuric acid was not complete. At the time of the discontinuance of this study the slopes of the curves for both the neodymium and lanthanum salts were still changing noticeably, but extensive dehydration of the salts had occurred (Table V). Analytical data, obtained by Karl Fischer method, show the following:

Table V. Dehydration of Lanthanon Chloride Hydrate with Sulfuric Acid

Hydrate	Time (days)	Ln/H_2O	Time (days)	Ln/H_2O*
$LaCl_3$	0	1/7.08	111	1/1.53
$NdCl_3$	0	1/6.50	114	1/1.60

*Lanthanon to water ratios of the hydrates at the termination of this study were based on weight losses.

It is interesting to note from the data represented by the curves in Figures 2 and 3 (taken from Tables 7 and 8) that the different desiccants have dissimilar effects on the hydrates. It can be seen, in the case of the Anhydrone study, that both the lanthanum and neodymium salts are dehydrated rather rapidly but reach a rather sharp leveling off of water removal at points which are indicative of hydrates whose composition approaches that of the trihydrates. The percentage

weight losses required, corresponding to the trihydrates, are as follows: neodymium chloride 17.1, lanthanum chloride 20.0. The sulfuric acid desiccation begins to level off in the area corresponding to the trihydrate compositions, but is slightly higher in its percentage of water removal from the salts than Anhydrone.

Data from the Anhydrone desiccation indicates that the compositions are approaching those of the dihydrates. Extrapolation of the data from the Anhydrone studies seems to indicate that both the neodymium and lanthanum chlorides would very nearly approach the dihydrate composition in approximately four hundred days, dependent on the continued drying efficiency of the Anhydrone.

Water analyses at the termination of the Anhydrone study by the Karl Fischer method and the weight loss data for both the lanthanum and neodymium salts were in very good agreement (Table VI).

Table VI. Dehydration of Lanthanon Chloride Hydrate with Anhydrone

Hydrate	Time (days)	Ln/H_2O	Time (days)	Ln/H_2O	
				Karl Fischer	Weight Loss
$LnCl_3$	0	1/7.08	199	1/2.54	1/2.50
$NdCl_3$	0	1/6.50	201	1/2.74	1/2.75

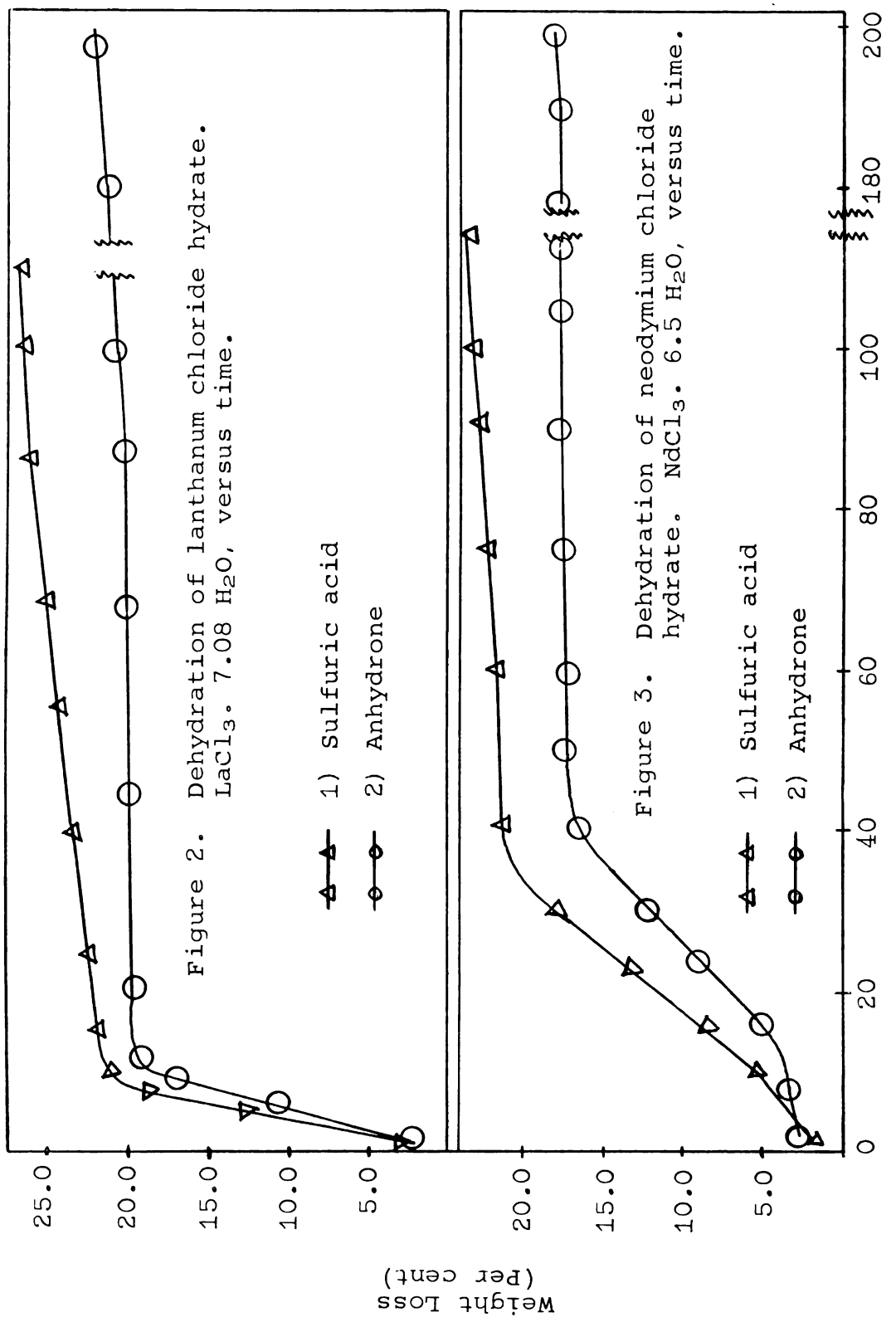


Figure 2. Dehydration of lanthanum chloride hydrate. $LaCl_3 \cdot 7.08\ H_2O$, versus time.

Figure 3. Dehydration of neodymium chloride hydrate. $NdCl_3 \cdot 6.5\ H_2O$, versus time.

Table VII. Dehydration of Lanthanum Chloride Hydrate versus Time

Desiccant: Sulfuric Acid		Desiccant: Anhydrone	
Time (days)	Weight Loss (per cent)	Time (days)	Weight Loss (per cent)
1	3.13	1	2.59
2	5.31	3	6.56
3	8.10	4	8.53
4	10.80	7	13.68
5	13.51	8	15.49
6	15.70	9	17.78
10	21.45	10	19.02
11	21.68	14	19.71
13	21.75	18	19.75
16	22.06	21	19.75
18	22.16	25	19.80
19	22.16	31	19.84
23	22.47	33	19.90
25	22.67	36	19.90
27	22.88	39	19.90
29	23.29	45	20.00
37	23.76	50	20.11
51	24.58	52	20.18
65	25.36	53	20.18
74	25.80	57	20.20
84	26.11	59	20.27
111	26.79	61	20.30
		65	20.37
		72	20.40
		86	20.56
		100	20.80
		109	21.00
		119	21.10
		147	21.40
		159	21.40
		199	22.15

Analysis of hydrates made immediately prior to start of dehydration study: La/H_2O 1/7.08.

Table VIII. Dehydration of Neodymium Chloride Hydrate versus Time

Desiccant: Sulfuric Acid		Desiccant: Anhydrone	
Time (days)	Weight Loss (per cent)	Time (days)	Weight Loss (per cent)
1	1.50	1	2.04
2	1.84	2	2.20
3	2.51	5	2.99
4	2.79	6	3.12
5	3.13	8	3.30
6	3.49	9	3.45
11	5.73	12	3.69
12	6.40	13	3.79
13	7.02	14	3.99
14	7.69	15	4.35
17	9.69	19	6.58
19	11.04	23	8.55
20	11.62	26	10.19
24	14.41	30	12.39
26	15.82	36	15.19
28	17.10	38	16.09
32	19.23	41	16.92
40	21.10	44	17.22
54	21.55	48	17.22
68	21.55	49	17.23
77	22.56	54	17.27
87	22.97	56	17.27
114	23.94	57	17.27
		61	17.27
		63	17.27
		65	17.60
		69	17.60
		77	17.60
		91	17.60
		104	17.67
		113	17.71
		123	17.73
		151	17.90
		154	17.94
		201	18.40

Analysis of hydrate made immediately prior to start of dehydration study: Nd/H_2O 1/6.5.

B. The Lanthanon Chloride Tetramethanolates

The 2,2-dimethoxypropane, selected as the 'dehydrating' agent, hydrolyzes slowly at room temperature. The presence of mineral acids causes cracking and polymerization, both of which are enhanced by increased temperatures. The presence of an acid catalyst, exclusive of the mineral acids, increases the rate of reaction proportionally to the acidity of the reaction medium (102). A basic medium impedes the hydrolysis reaction.

2,2-Dimethoxypropane is the reacting substance with the bound water of the hydrated lanthanon chlorides. However, it appears that only through the presence of an amount of methanol sufficient to dissolve the hydrates can a clean reaction product be obtained. At room temperature, when only 2,2-dimethoxypropane is mixed with the hydrated chlorides, the reaction appears dormant. When the lanthanon chloride hydrate-dimethoxypropane mixture is being heated apparent polymerization occurs before a complete conversion of the hydrate into a viscous layer. The "polymerization" exhibits itself by an initial yellowing of the solid phase, ultimately changing to a brown color. The neodymium chloride hydrate is extensively converted into the viscous layer before the yellowing begins. The praseodymium chloride hydrate undergoes slight conversion while the lanthanum salt appears to be unreactive. Apparent polymerization takes place regardless of

the amount or intensity of heat applied to the reaction mixture; it is much more rapid and extensive at increased temperatures.

When limited polymerization was allowed to occur, analyses of the products gave the following data for the neodymium compounds:

Nd (per cent)	Cl (per cent)	CH_3OH (per cent)	H_2O (per cent)
31.01	22.90	23.60	6.35
29.01	21.44	27.45	5.98
32.18	23.76	24.70	4.57

Total analyses of these reaction products, based on neodymium, chloride, methanol and water range from 83.86 to 85.21 per cent. These analyses indicate the possible presence of a polymeric substance, based on the known tendency of 2,2-dimethoxypropane to polymerize. In addition, they do not correspond to any specific methanolates or methanolate hydrates. The praseodymium chloride hydrate gave similar results when treated the same way. The lanthanum hydrate was not studied, as it apparently does not react under these conditions.

As lanthanum chloride hydrate did not react to give the viscous layer, the possibility of how to initiate a reaction was considered. A few drops of water were placed on the crystals of the hydrate prior to addition of the 2,2-dimethoxypropane. After the mixture was heated on a steam bath, a viscous layer formed quite readily; upon analyses

the product was found to be an alcoholate hydrate. The nitrochromic acid test for methanol and a qualitative Karl Fischer test for water were both positive. When the experiments were repeated with longer heating, the viscous layer became brown colored, indicative of polymerization.

When initial attempts to obtain a complete and uniform reaction by means of a solid-liquid reaction were without success, a means was sought to create a homogeneous reaction medium. Since the hydrated chlorides of the lanthanons are quite soluble in methanol, which itself is very soluble in dimethoxypropane, the possibility of dissolving the hydrates in a methanol-dimethoxypropane solution was considered. A suitable solution consisting of thirty per cent methanol and seventy per cent dimethoxypropane proved effective in the dissolution of the hydrates, with subsequent preparation of consistently reproducible products. Although the amount of methanol was in excess, an amount of this solvent necessary to dissolve the hydrate completely must be present, and due to the dispersion of the methanol in the dimethoxypropane an excessive amount was needed.

After solution of the lanthanon chloride hydrate in the methanol-dimethoxypropane solution, which was aided by heating, no formation of separate layers occurred. As heat was applied to the solution the temperature rose to 56-58^{o}, at which steady boiling occurred. Condensate collected from this boiling gave a positive iodoform test, indicative of

acetone. Acetone, a product in the hydrolysis reaction, boils at 56.5° at 760 mm. After evaporation of a portion of the solution, the temperature rose to approximately 60-62°, approaching the boiling point of methanol, 64.1°. However, the azeotropic relationships for acetone, methanol and dimethoxypropane are useful in explaining the difference in boiling points of the mixtures from those of the pure substances. Tollens test for the presence of methanol in the condensate obtained from the 60-62° boiling action was positive. The temperature remained between 60 and 63° for the remainder of the evaporation process because methanol and dimethoxypropane form a binary azeotrope of forty-five per cent methanol at 62° (102). The evaporation cannot be too extensive, for if only the methanol layer containing the product is left, non uniform products will form; too much evaporation can decrease the amount of methanol below that required for the methanolate formation. Without the 2,2-dimethoxypropane as a protective layer moisture can attack the product layer and result in products containing hydrated methanolates in addition to the desired methanolates.

At first, when crystals failed to separate from either layer of the solution mixture, seeding with crystals of the hydrated chloride was tried without success. The reason for the attempt was that if new solvates with acetone or methanol were formed, they might be isomorphous with the hydrates. Since the two layer mixture contained essentially only

methanol, acetone, dimethoxypropane and the lanthanon material, it was decided to learn if crystals could be obtained by evaporation of methanol-dimethoxypropane solutions to which hydrated lanthanon chloride had been added. The first mixture, evaporated to near dryness, gave a glassy residue on cooling. Some of this solid was used to seed another solution which had not been evaporated down as far as the first. Crystallization occurred. Analysis of the seeding crystals gave the general composition of $LnCl_3(H_2O)_x(CH_3OH)_y$. Since subsequent analysis of crystals formed in the careful synthesis showed the products to be tetramethanolates, and since the crystals formed in the crystallization process contained a larger amount of methanol, there is sufficient similarity in composition and form of $LnCl_3(H_2O)_x(CH_3OH)_y$ to start crystallization. This last concept applies to all three series of preparations since the lanthanum crystals could be used to seed either the praseodymium or neodymium mixtures, or vice versa. It was found that a solution of 6 milliliters of methanol and 14 milliliters of 2,2-dimethoxypropane to which 0.1 to 0.2 grams of the appropriate lanthanon chloride hydrate had been added, when boiled down to near dryness, cooled, and allowed to solidify, good crystals of the general composition $LnCl_3(H_2O)_x(CH_3OH)_y$ were obtained.

All three lanthanon compounds crystallized in the same general form; short needle-like shafts, approximately two to three millimeters in length. Crystallization was effectively

complete with the disappearance of the lower, viscous layer. With the exception of the viscous layer of the lanthanum product, which took on a water-like appearance in going from the hydrate composition to that of the methanolate, the viscous layers of the praseodymium and neodymium products retained their characteristic green and violet appearances, respectively.

The preparation of samples for analytical studies was critical. The product must be entirely free of mother liquor. Initially, the products were dried by evaporation under reduced pressure. The drying was carried out only until the product appeared 'visually' dry. The product was not pulverized prior to drying. Regardless of the consistent treatment of the product for analytical studies, the analytical results for methanol content were erratic, varying as much as three per cent. The presence of the lone electron pair in oxygen present in the acetone made this substance a possible coordinating species in the product. Infra-red studies of the products were inconclusive (Figure 5), but positive iodoform tests were obtained, indicative of the presence of acetone. However, no consistency in obtaining positive iodoform tests with various preparations of the methanolates was found. Studies showed that acetone, a product in the hydrolysis reaction, became 'trapped' in the caking of the product which accompanied the crystallization process. It was found that by pulverizing the product crystals prior to drying under reduced pressure, the acetone was no longer detected.

As noted in Figure 5, the spectra of the dried methanolates exhibit no absorption bands in the region from 1650-1750$^{cm^{-1}}$ which would indicate the presence of acetone by their presence in the spectra (Carbonyl stretch).

Attempts were made to determine the extent to which the mother liquor had been removed by drying the crystals under reduced pressure. Boiling point-pressure relationships of methanol, acetone and 2,2-dimethoxypropane were reviewed (Figure 4). At the pressure used for drying of the product, 90 mm at 25°, the temperatures of vaporization are as follows: 2,2-dimethoxypropane 23°, methanol 16° and acetone 6°. The work of Howard, Lorette and Brown (99) has shown that the azeotropes of these three compounds increase in the percentage of acetone and methanol as the temperature decreases; at 62° the azeotrope consists of forty-five per cent methanol and fifty-five per cent dimethoxypropane, at 56° the azeotrope consists of seventy-five per cent acetone, twenty per cent methanol and only five per cent dimethoxypropane. These data would indicate that a removal of the dimethoxypropane from the product would be accompanied by removal of the acetone and unbound methanol.

Infra-red Spectral Studies of Dried Tetramethanolates

Infra-red studies were made to determine the extent to which the dimethoxypropane was removed from the product crystals by drying under reduced pressure (Figures 5 and 6).

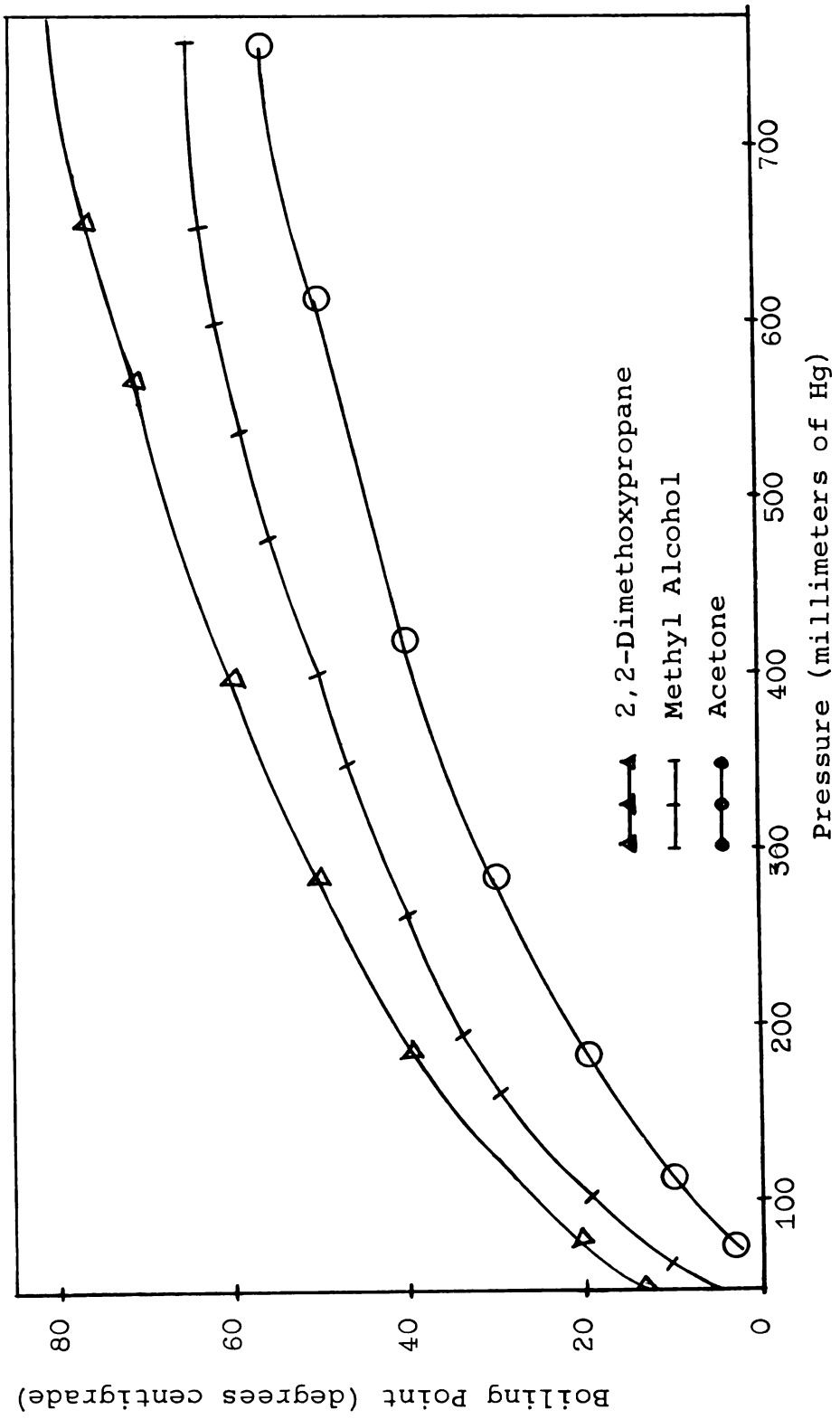


Figure 4. Boiling point-pressure relationships.

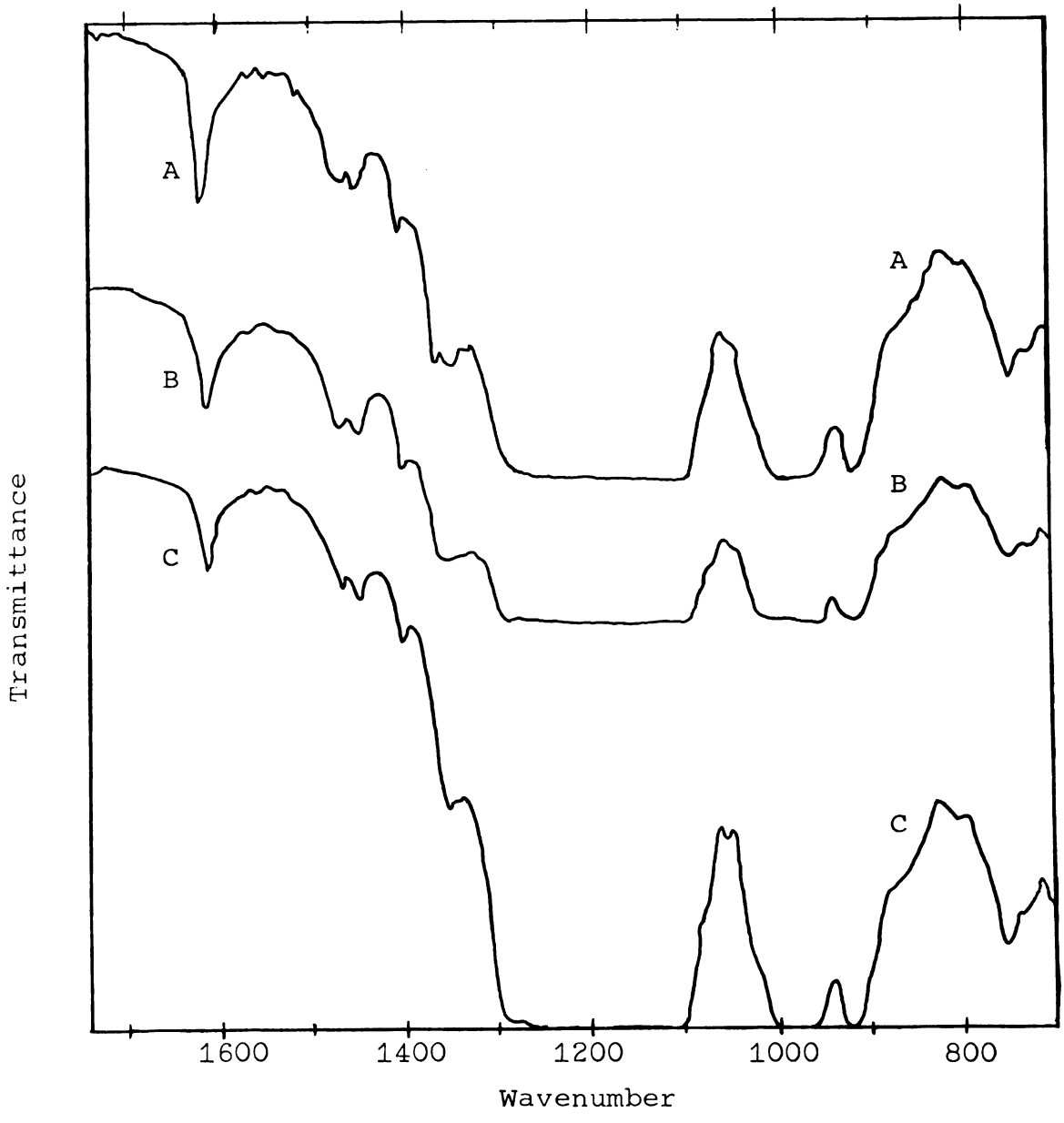


Figure 5. Infra-red spectra of dried tetramethanolates of:
A. Lanthanum Chloride
B. Praseodymium Chloride
C. Neodymium Chloride

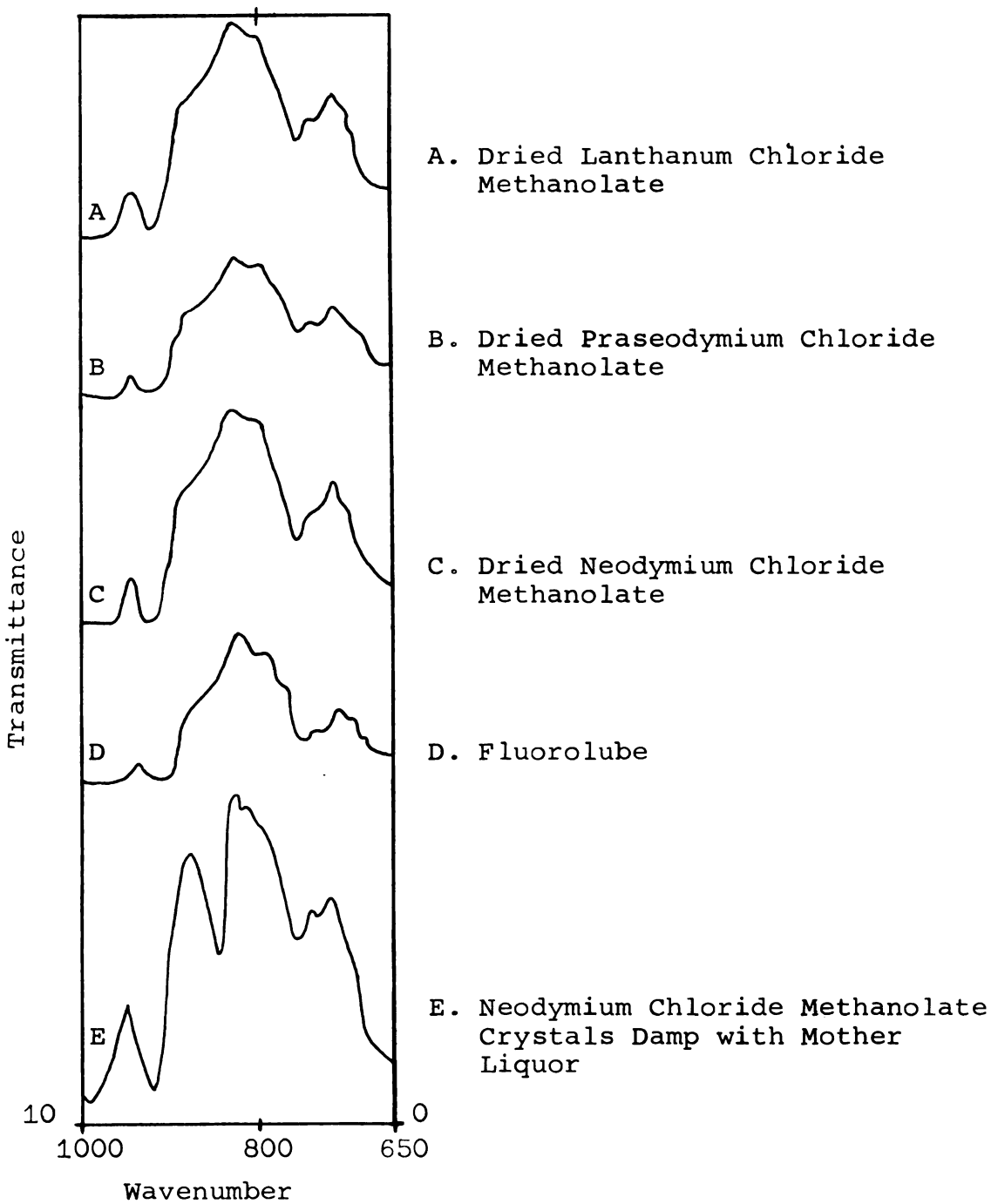


Figure 6. Infra-red spectral region including the region for O-C-O asymmetric stretch ($840^{cm^{-1}}$).

The spectra shown in Figure 6 for the region from 650 to $1000^{cm^{-1}}$ includes the region for the absorption band due to O-C-O asymmetric stretching, at $840^{cm^{-1}}$. In the dimethoxypropane there is an O-C-O linkage, which exhibits a very strong band. This band was useful in indicating the presence or absence of the substance in the dried products, as well as indicating the drying efficiency of the method employed in this study. Figure 6 contains spectra of the following; A) dried lanthanum chloride methanolate, B) dried praseodymium chloride methanolate, C) dried neodymium chloride methanolate, D) Fluorolube and E) neodymium chloride methanolate damp with mother liquor. In spectra A-D, it is noted that the $840^{cm^{-1}}$ band is absent, as it is present in spectrum E. Since the $840^{cm^{-1}}$ band is due to the O-C-O linkage of dimethoxypropane, spectra A-D indicate no dimethoxypropane present in these samples, whereas it is present in the substance for spectrum E.

Data obtained from boiling point-pressure relationships, the azeotropic relationships of the three substances present in the mother liquor and the infra-red spectral studies would indicate the complete removal of the mother liquor from the dried products.

Methanol Loss via Reduced Pressure

Vacuum treatment of the tetramethanolate of neodymium chloride at approximately 25 millimeters pressure indicates an instability of the salt; the composition of the material

appeared to approach that of the trimethanolate, based on periodic methanol analyses (Figure 7 and Table IX).

The tetramethanolate of neodymium chloride was placed in a desiccator under reduced pressure (25 millimeters of Hg) and taken to the first 'visual' dryness, at which point a methanol determination of the dried product was made. The dried material was then subjected to continual treatment under the same conditions, with periodic methanol analyses.

Table IX. Tetramethanolate Methanol Loss versus Time (at 25 mm Hg)

Elapsed Time	Analysis	
	CH_3OH (per cent)	H_2O (per cent)
1) First 'visual' dryness	32.14	0.30
2) One hour	31.03	
3) Three hours	28.35	
4) Five hours	27.95	0.90

The theoretical value for methanol in the trimethanolate of neodymium chloride is 27.72 per cent. Karl Fischer water analyses indicated a very low water content; if the product were to contain one molecule of water the percentage would need to be greater than 4.5. Also, drying under reduced pressure must be done carefully if the tetramethanolate is to be retained. In this study a pressure of approximately 90 millimeters at 25° was employed, which theoretically is low

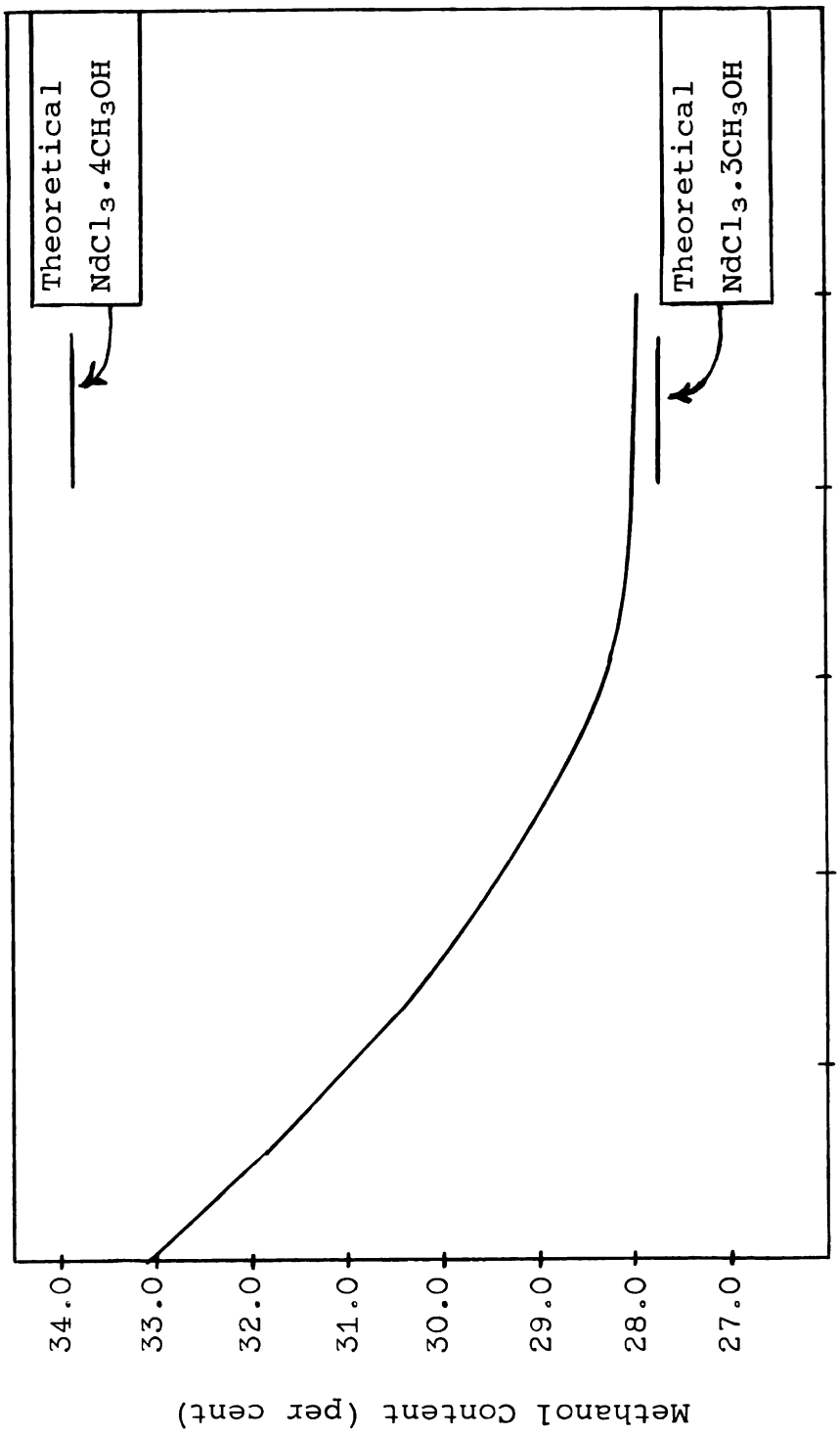


Figure 7. Methanol loss versus time from $NdCl_3 \cdot nCH_3OH$ at 25 mm of Hg.

enough to remove the mother liquor in the drying of the product for analytical studies (Figure 4), although the dried products were not allowed to remain under reduced pressure after the first 'visual' dryness.

Reactivity Towards Water

1. Composition Change on Exposure to Moisture

The instability of the tetramethanolates in the presence of water, may be due in part to water displacement of the co-ordinated methanol. To check this concept, the neodymium product was placed in a desiccator containing water. A nitro-chromic acid test for methanol on the product prior to place-ment in the desiccator was positive. After twenty-four hours, the watch glass on which the crystals had been placed contained a liquid. A subsequent nitrochromic acid test was very weak compared to that obtained on the original crystals, indicating a displacement of the methanol from the product.

Since the starting material was the hexahydrated chloride, the coordination attributed to neodymium would be six; on the other hand, product analysis would indicate a coordination of four for the tetramethanolates. Possibili-ties of changing structures are; the displacement of methanol by water with addition of water to that position or another position, or replacement of methanol by water accompanied by addition of water to other positions. The former pos-sibility would result in an increase in the neodymium percentage because of the relatively low molecular

weight of water compared to that of methanol. However, analysis of products which have been exposed to moisture show a decrease in the neodymium percentage, indicating the latter possibility. For the prepared methanolates, the total lanthanon, chloride and methanol analyses are consistently less than 100 per cent (Table II).

Lanthanum chloride methanolate	99.06
Praseodymium chloride methanolate	98.28
Neodymium chloride methanolate	99.69

Water analyses of the methanolates varied, but were consistently near one per cent. These water analyses were appreciably lower than the 4-5 percentages of water required for the monohydrate tetramethanolates of the lanthanon chlorides.

This study has shown that the methanolates take up water quite readily, but the rate of water take-up decreases after water content reaches approximately five per cent, indicative of formation of a monohydrate methanolate. Water analyses were made on the neodymium product after exposure to the air for varying lengths of time. To check on the extent of hydration of the methanolates which occurs as a result of their contact with moisture in the atmosphere for an extended period of time, crystals of neodymium chloride tetramethanolate were placed in an open container at room temperature for approximately forty-six hours. The results of this study are presented in Table X and in Figure 8.

Table X. Methanol-Water Reactivity versus Time

Sample	Time Exposed to Atmosphere (Hours)	Water Content (Per cent)
$NdCl_3.4CH_3OH$	minimal	0.51
$NdCl_3.4CH_3OH$	0.3	4.61
$NdCl_3.4CH_3OH$	0.5	5.23
$NdCl_3.4CH_3OH$	46.0	28.55

Minimal time indicates the time of exposure as a result of normal handling of the sample by drying and weighing for analysis.

Since absorption bands in the 1400 to 1500 cm^{-1} region, indicative of methanol, were not observed in an infra-red spectrum taken at the end of the forty-six hour exposure period (Figure 8), the nearly complete or complete removal of methanol from the material must be assumed.

The exposed material contained 28.55 per cent water content, by Karl Fischer analysis, compared to the theoretical value of 30.14 per cent for the hexahydrated neodymium chloride. That the water content was not closer to the theoretical value of the hexahydrated salt may have been due to an insufficient time for complete water take-up, or to too low humidity in the laboratory.

These data indicate that upon contact with moist air the tetramethanolate tends to convert to the hexahydrate.

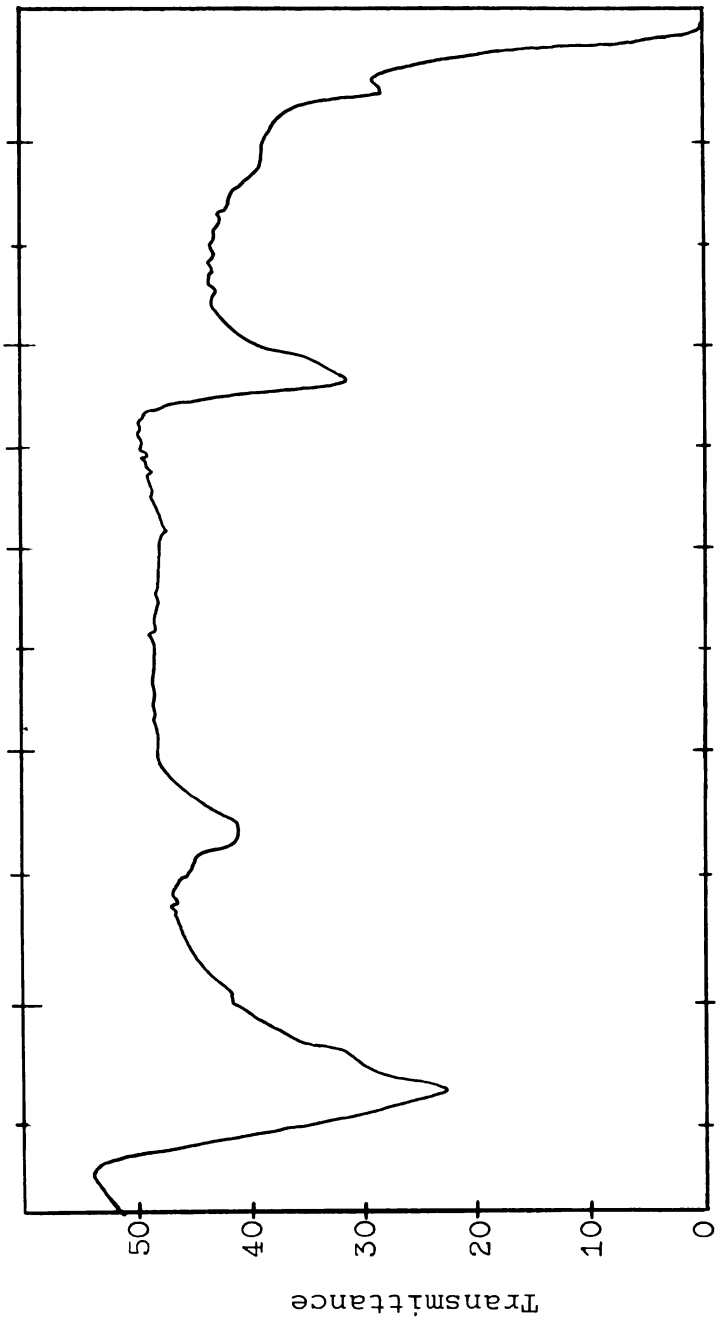


Figure 8. Infra-red spectrum of neodymium chloride tetramethanolate after exposure to atmospheric moisture for forty-six hours.

2. Infra-red Spectral Studies

Infra-red spectra of the dried products (Figure 5) show strong absorption bands at approximately $1620^{cm^{-1}}$ for the lanthanum, praseodymium and neodymium products. In Figure 1 the H-OH bending frequencies of the normal hydrates of the three lanthanon chlorides exhibit bands at approximately $1630^{cm^{-1}}$. In the drying studies of the hydrates with Anhydrone, discussed earlier in this report, an infra-red spectrum was made of the partially dehydrated neodymium chloride hydrate at the termination of that study (Figure 9, spectrum A). Comparison of the spectrum of the hexahydrated salt, spectrum B, and the spectrum of the partially dehydrated salt, spectrum A, shows that the water band of the latter has an absorption maximum which is spread out and 'forked', peaks were noted at approximately 1620 and $1635^{cm^{-1}}$. It was noted that the water band of the normal neodymium hydrate is exhibited at approximately $1635^{cm^{-1}}$ (spectrum B) and the water band of the neodymium chloride methanolate which has some water contamination (spectrum D) is located at approximately $1620^{cm^{-1}}$.

From the data, Figure 9, there appears to be a shifting of the bands due to H-OH bending frequencies, in the 1620-$1635^{cm^{-1}}$ region, to lower wave numbers as the degree of hydration decreases, and a shifting to higher wave numbers as the degree of hydration increases. This shifting trend is seen in the data in Table XI.

Table XI. Extent of Hydration via Infra-red Studies

Spectrum	Figure	Nd/H_2O	Position of Band (cm^{-1})
Hexahydrate	9 B	1/6.1	1635
Partially dehydrated salt	9 A	1/2.7	1620, 1635
Dried product -water contaminated	9 D	1/1.0	1620
Dried product plus absorbed water	9 C	1/>1.0	1635

The product used for this study was dried in the usual manner under reduced pressure and allowed to sit in the atmosphere for twenty minutes. Upon analysis, the water was found to be 4.61 per cent, which could indicate a monohydrate had formed. The addition of water to the dried product was accomplished by placing the dried product in a desiccator containing water and allowing it to absorb for one hour. As is noted in Figure 9 spectrum C, addition of water to the dried methanolate by absorption in a moist atmosphere, shows a shifting of the band maxima at $1620^{cm^{-1}}$ to approximately $1635^{cm^{-1}}$, which could indicate a condition in which two types of bonding are associated with the waters of hydration in these hydrates.

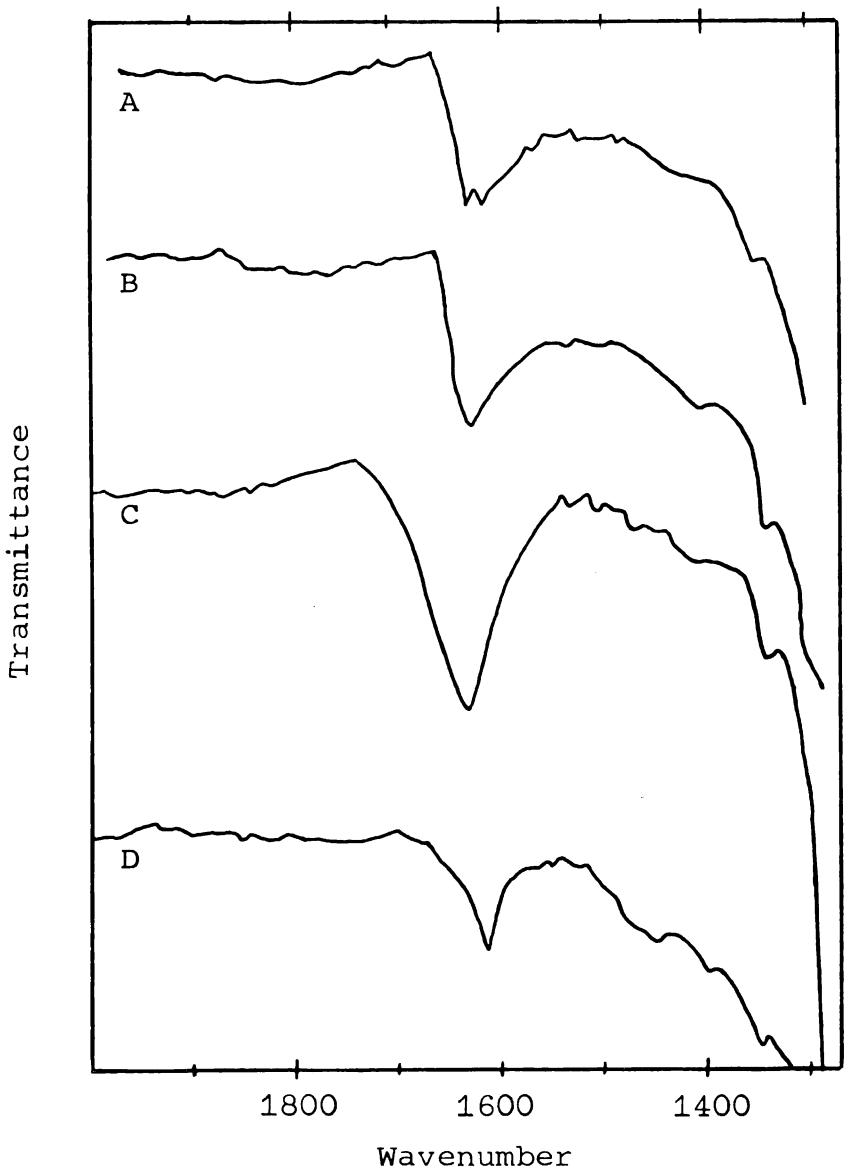


Figure 9. Infra-red spectra showing effect on water band position with increasing water content.

A. Nd/H_2O 1/2.74 ($NdCl_3$. hydrate)
B. Nd/H_2O 1/6.1 ($NdCl_3$. hydrate)
C. Nd/H_2O 1/>1.0 ($NdCl_3.4CH_3OH$ plus absorbed water)
D. Nd/H_2O 1/1.0 ($NdCl_3.4CH_3OH$ dried product, water contaminated)

The inability to completely dehydrate the hydrated lanthanon chlorides by thermal decomposition in air is well-known. At temperatures near 110^{o}, most of the water is removed readily, but dehydration reaches a limit with the formation of the monohydrate, and heating at 110^{o} for long periods of time or at higher temperatures does not result in the formation of the anhydrous chloride but rather of a chloride-oxychloride mixture. This behavior seems to indicate that a strong binding force coordinates this one water molecule to the lanthanon. It is difficult to say if this behavior could be the result of one of the following; the bound water in the monohydrate is bound more strongly due to the absence of other water molecules which allows the central ion to exert a greater electrostatic attraction on the lone water molecule, or if one of the water molecules entering into coordination with the central ion occupies a position associated with a different degree or type of bonding.

Since water was indicated to be present in the dried methanolates by the presence of the bands at approximately $1620^{cm^{-1}}$ in the infra-red spectrum (Figure 5), and also by positive Karl Fischer tests, it was decided to ascertain if this water was present as a result of product contact with the atmosphere or if it were inherent in the product. The possibility of incomplete dehydration in the reaction of the hydrates with the dimethoxypropane was considered. Failure to dehydrate the monohydrate was ruled out because water

analyses of the products showed a water content of 0.3 to 0.5 per cent, compared to the 4.5 per cent required for a monohydrate methanolate.

A spectrum of the viscous layer, which forms during the preparation of the tetramethanolate of neodymium chloride, indicates the absence of water at this stage of the preparation (Figure 10). This spectrum exhibits bands at approximately 830 to 1700 cm^{-1}, indicating the presence of dimethoxypropane (O-C-O structure) and acetone (carbonyl structure), respectively. A spectrum of the neodymium product crystals, damp with mother liquor, was made to determine if water were present in the dimethoxypropane added to the viscous material to effect layer separation and to serve as a protective covering from the atmosphere (Figure 11). This spectrum does not indicate the presence of water. However, the water band appears at 1620 cm^{-1} in the spectra of the dried methanolates (Figure 5). Thus, it must be concluded that water present results from contact of the product with the atmosphere during its preparation for analysis.

Figure 12 presents the spectra of the methanolates of lanthanum, praseodymium and neodymium chlorides dried by different methods. In this figure, spectra A-1, B-1 and C-1 are of methanolates which were dried in the following manner. Product crystals were removed from the mother liquor, transferred to an open weighing bottle, and dried in a vacuum disiccator under reduced pressure. At the first visual dryness,

air was admitted to the desiccator, and the weighing bottle was capped. The weighing bottle was opened to the atmosphere for approximately five to ten seconds, the average time of exposure in the weighing of a sample, followed by making a Fluorolube mull of the dried product for infra-red studies. The effect of contact with the atmosphere for this short period can be seen by the absorption bands at approximately $1620^{cm^{-1}}$, indicating the presence of water in the material. A Karl Fischer water test on the neodymium material was positive.

Spectra A-2, B-2 and C-2, are of crystals of the methanolates which were dried by placing the crystal-mother liquor mixture in a desiccator and evacuating to the first visual dryness. A drying tube, filled with Anhydrone, was connected to the evacuating stem of the desiccator. Air was then admitted to the desiccator very slowly. Removal of the desiccator lid was followed by immediately covering the dried salt with Fluorolube in order to have minimal contact of the product with the atmosphere. As indicated by the spectra of these methanolates, there is an indication of slight contamination of the product by water by the rather broad bend in the spectra in the region near $1600^{cm^{-1}}$. A Karl Fischer test on the neodymium product was negative.

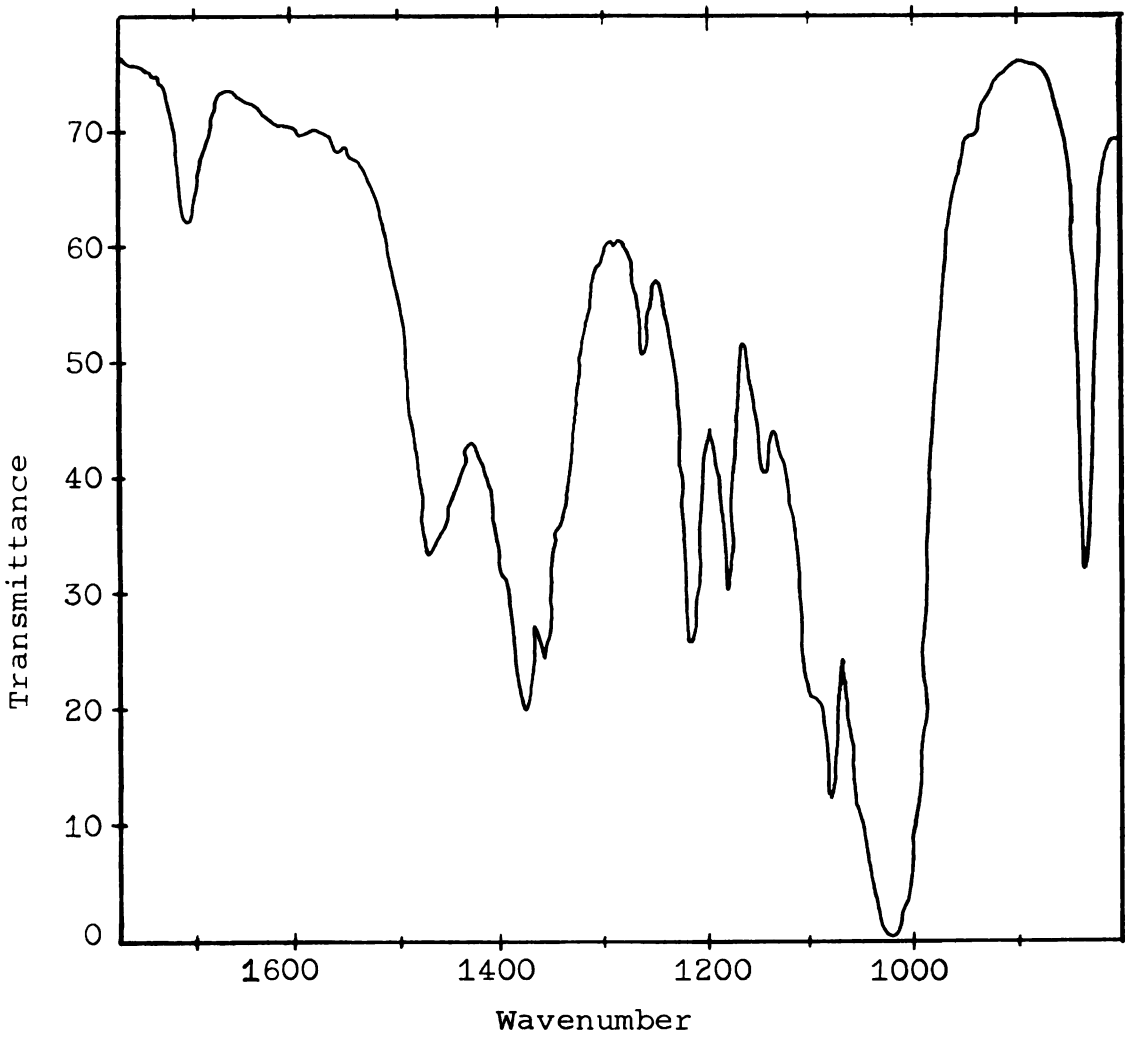


Figure 10. Infra-red spectrum of viscous neodymium chloride alcoholate layer.

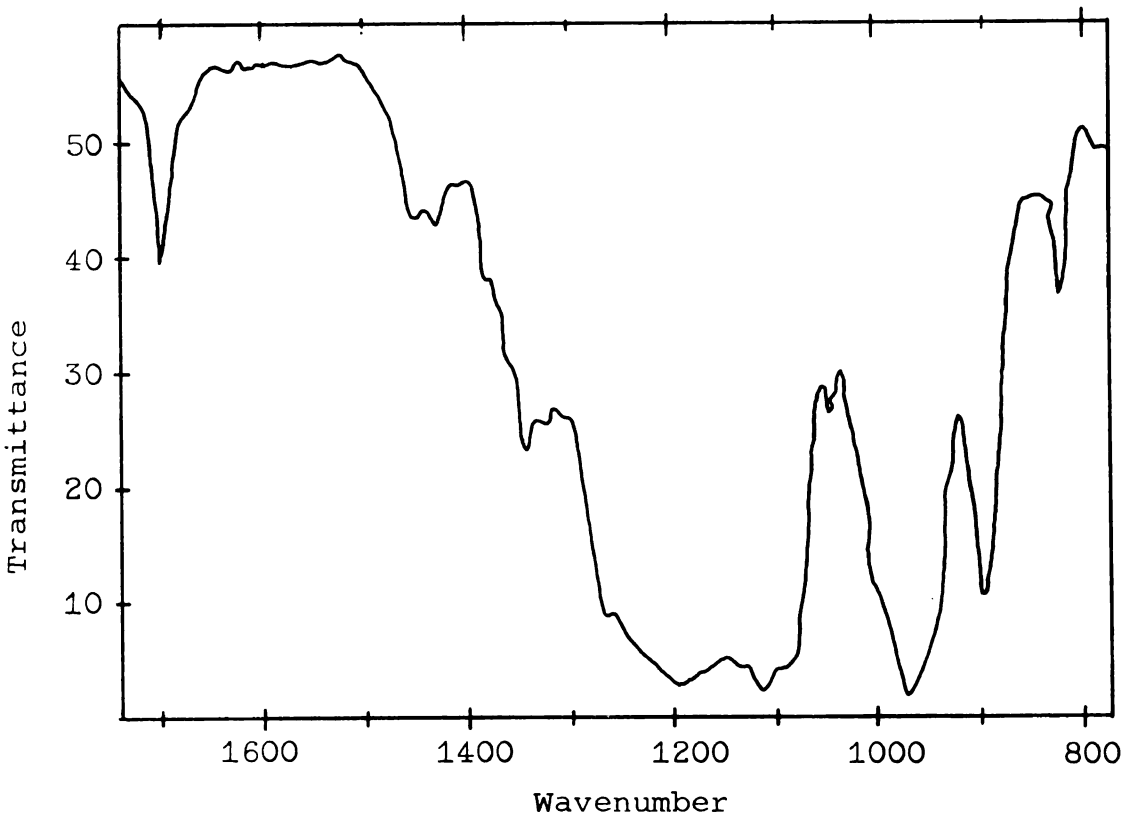


Figure 11. Spectrum of neodymium chloride methanolate-mother liquor mixture.

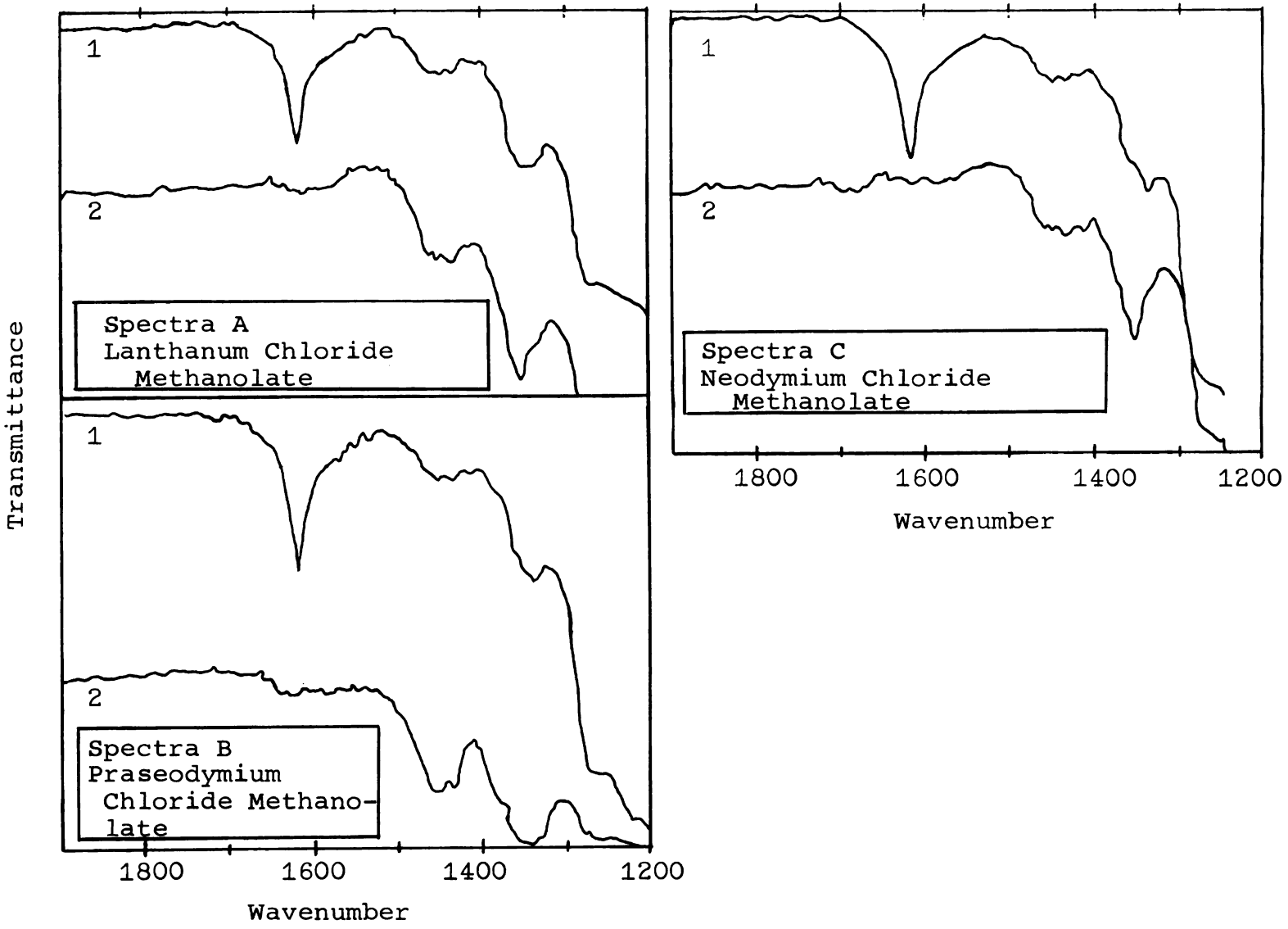


Figure 12. Infra-red spectra of dried methanolates.
Spectra 1 - Normal drying procedure
Spectra 2 - Drying with minimal contact with atmosphere.

Analytical

In the determination of methanol by oxidation with potassium dichromate, stoichiometric results could not be obtained by reacting the sample with the oxidant at room temperature. Of the several difficulties encountered, the most important one was that the oxidation of methanol does not terminate with the formation of formic acid, but is oxidized further to carbon dioxide (Reactions 1, 2, 3).

$$3CH_3OH + Cr_2O_7^{=} + 8H^{+} \longrightarrow 3HCHO + 2Cr^{+3} + 7H_2O \quad (1)$$

$$3HCHO + Cr_2O_7^{=} + 8H^{+} \longrightarrow 3HCOOH + 2Cr^{+3} + 4H_2O \quad (2)$$

$$3HCOOH + Cr_2O_7^{=} + 8H^{+} \longrightarrow 3CO_2 + 2Cr^{+3} + 7H_2O \quad (3)$$

$$CH_3OH + Cr_2O_7^{=} + 8H^{+} \longrightarrow CO_2 + 2Cr^{+3} + 6H_2O$$

A measured excess of standard potassium dichromate solution in a reflux flask was acidified with sulfuric acid. The solution was cooled to room temperature before addition of the sample. The addition of sulfuric acid to the dichromate solution causes a considerable rise in the temperature of the solution. Addition of a methanol sample to the acidic solution at increased temperatures results in low consumption of dichromate, giving low results for the amount of methanol present. This lower consumption is probably due to partial oxidation of methanol by the sulfuric acid at higher temperatures. The weighed sample to be analyzed was immediately dissolved in water to prevent any loss from the sample of methanol by water displacement through contact with the air.

The aqueous solution containing the sample was mixed with the oxidizing solution at room temperature; the resultant solution was allowed to remain at room temperature for two hours, to effect complete conversion of the methanol to formic acid (reactions 1,2). The solution was then refluxed for ten minutes to complete the oxidation of formic acid to carbon dioxide (reaction 3). Although some of the formic acid was oxidized to carbon dioxide at room temperature, the conversion is quite slow. A study of this conversion with measured amounts of reagent grade formic acid showed that with a twofold excess of dichromate, a nine per cent conversion of formic acid to carbon dioxide resulted after two hours. The same proportions of these reactants resulted in a 99.93 per cent conversion when refluxed for ten minutes. The partial oxidation of the methanol by sulfuric acid is indicated by the low dichromate consumption when the sample was mixed with the oxidizing solution without first cooling the latter to room temperature. When the sample was placed in the oxidizing solution without first cooling it to room temperature, followed by setting for two hours with subsequent ten minute reflux results in 93.66 per cent consumption of the dichromate, based on results obtained from those which were first cooled to room temperature before addition of the sample. One determination for a sample refluxed for ten minutes without first cooling the oxidant to room temperature and not allowing the sample-oxidizer solution to set for two

hours resulted in a consumption of dichromate of only 87.54 per cent.

After the refluxed solution was cooled to room temperature, a measured excess of standard ferrous ammonium sulfate solution was added to the flask. Care was taken to insure an excess of this reagent, since the first color change of the sample solution to green upon addition of the ferrous solution was substantially short of that necessary for complete reduction of the excess dichromate in the refluxed solution.

The method, tested in three trials with known amounts of methanol, gave an average level of reaction of 99.66 per cent, based on the reaction of one mole of dichromate per mole of methanol. For these tests, the deviation was 3.4 parts per thousand.

Consideration of Possible Structure

Conductance measurements made by Mehrotra et al. (89), have indicated that at low concentrations of lanthanum and cerium(III) chlorides in methyl and ethyl alcohols the chlorides are not completely ionized and thus exhibit the typical behavior of a weak electrolyte. The conductance is lower in the ethanol than in the methanol.

Mehrotra et al., prepared the trialcoholates and dialcoholate monohydrates. One or two points should be commented upon about the structure of these materials. In general, it is accepted that the lanthanon ions are

hexacoordinated. Mehrotra and co-workers make the comment "that the presumably hexacoordinated $LaCl_3.3ROH$ and $CeCl_3.3ROH$ compounds result directly in the above reactions." From the composition of these compounds, and from known lanthanon complexes such as higher hydrates, acetylacetonates, etc., it would appear that hexacoordination is not achieved for these alcoholates. For the tetramethanolates prepared in this study, one could assume either a square planar, dsp^2, or a tetrahedral arrangement, sp^3. Further work is needed to prove whether the lanthanon ions are four coordinated (e.g., $[Ln(CH_3OH)_4]^{+3}$) or six coordinated (e.g., $[Ln(CH_3OH)_4Cl_2]^{+1}$).

It should be noted that this present study has afforded data which indicates the relatively greater stability of the trimethanolates as compared to that of the tetramethanolates, based on studies of the prepared materials under reduced pressure.

V. SUGGESTED ADDITIONAL STUDIES

After a procedure for reproducibly preparing a new compound has been established, investigations into physico-chemical properties of the compound are necessary in order to characterize the substance. Since certain phases of the present study were hampered because of water contamination of the tetramethanolates, future studies should be carried out under 'dry box' conditions. Contaminated substances are of little use in physico-chemical studies.

Preparation of the tetramethanolates of the heavier lanthanons by the reaction of the hydrated chlorides with methanol-dimethoxypropane solutions should be studied. Since this investigation has indicated the relatively low stability of the tetramethanolates, it would be interesting to determine if the same type of compounds could be prepared with the less basic ions of the heavier lanthanons. If the compounds could be made, their stabilities should be compared with the results in this study, and their other properties should be observed.

The establishment of a procedure for preparing the trimethanolates from the tetramethanolates by intensive drying under reduced pressure should be attempted.

The preparation of the tri- or tetra-ethanolates of the lanthanon chlorides should be attempted by reacting the hydrated chlorides with the ethyl analog, 2,2-diethoxypropane.

Molecular weight determinations of the tetramethanolates are of interest, primarily to determine if these compounds are monomolecular or associated. However, the decision as to a suitable solvent may pose a problem. The tetramethanolates are decomposed by water. There may well be a degree of dissociation in methanol, and alcohol exchange by interreaction of the alcoholates with higher alcohols is known.

Conductivity studies of the tetramethanolates and of other possible alcoholates would be helpful in providing information about the type of bonding of the complexes. The choice of solvent would be a problem because of decomposition of the product by water and of alcohol interchange with other alcohols.

More detailed infra-red studies of the hydrated chlorides of the lanthanons should be made in order to determine the position of other absorption bands due to water in addition to those for the H-OH bonding frequencies, which were determined approximately in this study.

Infra-red studies of the tetramethanolates could be made to determine the extent of band shifting from the methanol due to polarization of this species in its coordination to the lanthanons. Similar spectral studies should be made on other alcoholates, if possible.

VI. SUMMARY

Lanthanum, praseodymium and neodymium chloride hydrates were prepared by reacting the appropriate oxide with concentrated hydrochloric acid, concentrating the solution by evaporation until the salt crystallized. Hydrates with a constant composition were maintained in desiccators containing appropriate sulfuric acid-water solutions to give constant humidity. The lanthanum and praseodymium salts were very nearly the heptahydrates and the neodymium salt the hexahydrate. Infra-red spectra of the hydrated chlorides of lanthanum, praseodymium and neodymium were very similar; the water bands occurred in the same spectral region for all three hydrates; namely, at 1630, 1630 and 1635 cm^{-1}, respectively. These data for the hydrated lanthanon chlorides have probably been recorded for the first time.

Dehydration studies of lanthanum and neodymium chloride hydrates with Anhydrone and with sulfuric acid indicated the hydrates were approaching the compositions of the dihydrates while in proximity with either dessicant, although sulfuric acid proved to be the more efficient, based on the length of the study.

Crystalline tetramethanolates of lanthanum, praseodymium and neodymium chlorides were prepared by reacting the

appropriate lanthanon chloride hydrate with a 2,2-dimethoxypropane-methanol solution.

Excess solvent was removed from the tetramethanolates by an evacuation process. Extended evacuation resulted in the loss of some methanol with a trend toward formation of the trimethanolates.

Infra-red spectral studies of the hydrates and the tetramethanolates showed each series of salts to be very similar. The tetramethanolates are very reactive toward water, as shown by both infra-red studies and Karl Fischer water analyses. The tetramethanolates tend to form the normal hydrates upon extended exposure to moist air.

Attempts to produce the anhydrous chlorides of lanthanum and neodymium by refluxing the hydrated chlorides with acetyl chloride resulted in the formation of acetate chloride mixtures.

Refluxing of the hydrated chloride of lanthanum with toluene in equipment containing a water trap did not yield the anhydrous chloride.

Preparation of the anhydrous chlorides of lanthanum and neodymium by passing a stream of chlorine over the oxychlorides at 800° was not successful.

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