

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MASSACHUSETTS, AMHERST, MASS.]

Lanthanum and Neodymium Salts of Trifluoroacetic Acid

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Lanthanum and neodymium trifluoroacetates have been prepared and characterized by analysis, crystallography, density and solubility. When heated, these compounds decompose to form quantitative yields of metal fluoride, carbon monoxide, carbon dioxide and trifluoroacetyl fluoride.

Trifluoroacetates of some of the lanthanides have been prepared by earlier workers.¹ These preparations, however, were not characterized fully as to extent of hydration, physical properties other than solubility or chemical reactions. The present investigation was undertaken to characterize these compounds to permit ready comparison with other more familiar compounds of these elements.

Experimental

Preparation.—Pure freshly ignited lanthanum or neodymium oxide was added in slight excess to trifluoroacetic acid. Reaction occurred immediately with the evolution of heat. The mixture was allowed to stand overnight, the excess oxide filtered off and the filtrate evaporated on the steam-bath. Recrystallization from water yielded crystals approximating the trihydrate in composition but retaining some occluded water. Dehydration in vacuum followed by rehydration in a hydrostat over deliquescent sodium bromide (58% relative humidity) yielded pure trihydrate. The products were analyzed by precipitation of the rare earth as oxalate and by ignition to oxide.

Anal. Calcd. for $\text{La}(\text{CF}_3\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$: La, 26.11. Found: La, 26.21. Calcd. for $\text{Nd}(\text{CF}_3\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$: Nd, 26.85. Found: Na, 26.84.

Dehydration.—When stored in vacuum over anhydrous, the trihydrated neodymium salt crystals disintegrated to a fine, very hygroscopic powder. Analysis showed it to be anhydrous.

Anal. Calcd. for $\text{Nd}(\text{CF}_3\text{CO}_2)_3$: Nd, 28.78. Found: 28.97.

The lanthanum salt behaved in an exactly similar manner. **Crystallography.**—Although the trihydrates are very soluble in water, they could be crystallized readily on a microscope slide. $\text{Nd}(\text{CF}_3\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$ crystallized in biaxial, optically negative monoclinic plates predominantly lying on the 010 face. Acute angle β was $64^\circ 48'$. The angle of extinction with the *c* direction was $11^\circ 21'$. Birefringence was small and pleochroism was not observed. Refractive indices for white light at room temperature were found to be: $\alpha = 1.40$, $\beta = 1.42$, $\gamma = 1.43$. $2V$ was estimated to be 80° . Differences which must exist between the lanthanum and neodymium salt could not be observed, such differences being below the limit of sensitivity of these methods. Details are shown in Fig. 1. In a micro sublimation chamber on a hot stage, the trihydrate was observed to "melt" at 195 – 198° . At 215° , growth of fine crystals within the liquid drops began and continued to complete solidification at 290° . The melting was probably dissolution in the water of crystallization and the second solid phase was rare earth fluoride as shown in the subsequent experiments on thermal decomposition.

Density.—Densities of the trihydrated salts were determined in tared 25 ml. Gay-Lussac pycnometers at 25° . Chlorobenzene was used as immersion liquid and the pycnometers were calibrated with water. Found for $\text{La}(\text{CF}_3\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$: 2.25 g./ml.; found for $\text{Nd}(\text{CF}_3\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$: 2.27 g./ml.

Solubility.—The water solubility of the salts was determined by equilibrating salt and water in rotated tubes in a constant temperature bath at 25.0° , followed by analysis of

the saturated solution. For each compound, a solubility of 1.21 g. anhydrous salt per ml. of solution was found. The solid phase in equilibrium was the trihydrate in both cases. Densities of the saturated solutions were 1.77 g./ml. for the lanthanum salt and 1.79 g./ml. for the neodymium salt.

To obtain an indication of the relative solubilities of the trifluoroacetates of the cerium end of the rare earth series, a mixture of monazite oxides, from which the bulk of the cerium had been removed, was converted to trifluoroacetates and fractionally crystallized from water. Five fractions were obtained and were analyzed by determination of average atomic weight.² Values of 142.8, 143.4, 141.6, 141.7 and 140.1 resulted, the first being the crystal end, the last the solution end. Apparently, therefore, lanthanum trifluoroacetate is slightly more soluble than neodymium trifluoroacetate, though the difference is small. This is analogous to the simple acetates for which solubility decreases with increasing atomic number.

In contrast to the trichloroacetates,³ aqueous solutions of the trifluoroacetates can be boiled for long periods without any apparent decomposition or precipitation.

Preliminary results of a phase rule study at 25° of the system $\text{Nd}(\text{CF}_3\text{CO}_2)_3$ – KCF_3CO_2 – H_2O shows the non-existence of complexes or double salts in this system.

Qualitatively, lanthanum and neodymium trifluoroacetates are very soluble in methyl, ethyl and amyl alcohols, nitromethane, acetone, dioxane and diethyl ether but practically insoluble in chlorobenzene, chloroform and carbon tetrachloride. Hara and Cady¹ found the solubility of $\text{La}(\text{Ce, Pr, Nd})(\text{CF}_3\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$ in trifluoroacetic acid to be very small.

Thermal Decomposition.—Hydrated lanthanum and neodymium trifluoroacetates both could be heated in air at 110° for short periods to produce anhydrous material. Prolonged heating, however, invariably produced material which gave a cloudy solution in water. The insoluble material was rare earth fluoride. Above 110° , the decomposition was accelerated and became very rapid between 250 and 300° , anhydrous fluoride being the final product. Above 700° , heating in air caused a further small weight loss, oxyfluoride, LaOF or NdOF being the final product. Confirmation of quantitative production of anhydrous metal fluoride was found by the weight ratio of residue after heating to initial trihydrate. Calcd. for $\text{NdF}_3/\text{Nd}(\text{CF}_3\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$: 37.45%. Found: 37.43 and 37.47%. This residue had a Nd content of 71.57, 71.53%. Calcd. for NdF_3 , 71.68%.

This decomposition was also observed in a thermobalance. The data show (Fig. 2) that NdF_3 is produced quantitatively at 300° , and on further heating in air produces NdOF . Furthermore, the curve about 110° is not quite horizontal, indicating a slow decomposition even at this temperature.

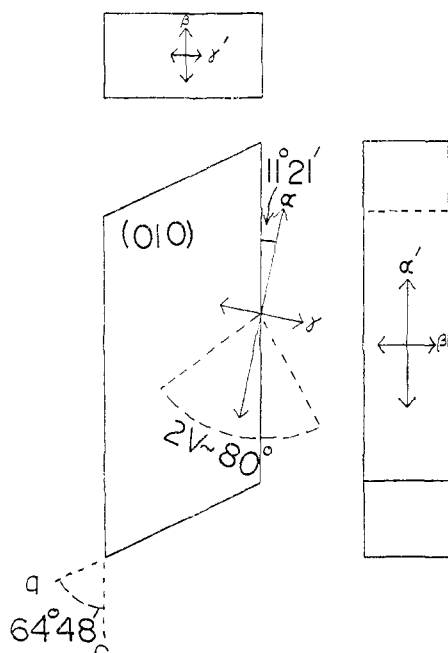
To identify the other products of the thermal decomposition, anhydrous neodymium trifluoroacetate was heated in a vacuum system. At approximately 300° , the salt suddenly began to swell and gases were evolved. Once started, this decomposition proceeded unaided, almost as if the compound were burning. The gases were passed through a Dry Ice trap, then to the line for molecular weight determination. A value of 36.6 was found which indicated an equimolar mixture of CO and CO_2 . Insertion of an Ascarite absorption tube after the Dry Ice trap removed CO_2 and the effluent gas was found to have a molecular weight of 27.8, compared to the calculated value of 28 for CO. The Dry Ice trap was found to contain a volatile liquid of molecular weight 115.5; the value calculated for trifluoroacetyl fluoride is 116.

Further evidence for the nature of these products was obtained by absorbing the acid fluoride in water, the carbon

(2) W. C. Fernelius, editor, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 58.

(3) L. I. Quill and M. L. Salutsky, *Anal. Chem.*, **24**, 1453 (1952).

(1) R. Hara and G. Cady, *THIS JOURNAL*, **76**, 4285 (1954).

Fig. 1.— $\text{Nd}(\text{CF}_3\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$.

dioxide on Ascarite, passing the residual gas over hot copper oxide and again absorbing it on Ascarite. The water solution of the acid fluoride was titrated with standard base. 2.60 mmoles of $\text{Nd}(\text{CF}_3\text{CO}_2)_3$ yielded 4.04 mmoles of CF_3COF , 3.84 mmoles of CO_2 and 3.83 mmoles of CO . The

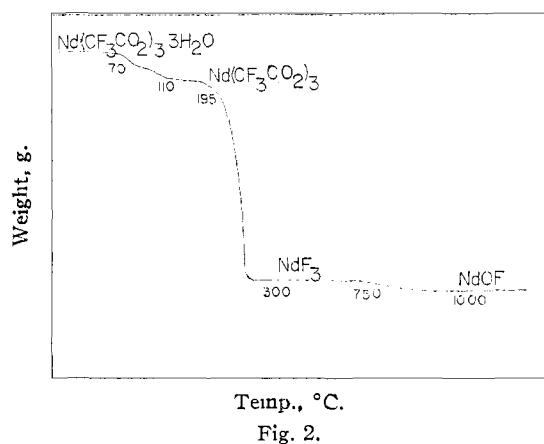
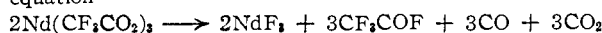


Fig. 2.

thermal decomposition is therefore represented by the equation



This is entirely analogous to the thermal decomposition of sodium trifluoroacetate as found by Swarts.⁴ The lanthanum salt behaved in exactly the same manner.

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(4) Swarts, *Bull. Classe Sci., Acad. Roy. Belg.*, **8**, 343 (1922).

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Compounds of Heptavalent Rhenium with the Perovskite Structure

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The compounds $\text{Ba}(\text{Na}_{0.5}\text{Re}_{0.5})\text{O}_3$ and $\text{Ba}(\text{Li}_{0.5}\text{Re}_{0.5})\text{O}_3$ have been prepared by interaction of rhenium metal with barium and alkali carbonates at 900°. They form a continuous series of solid solutions. The structure is shown to be of the ordered perovskite type in which the alkali metal ions and the rhenium(VII) ion are in sixfold coordination with oxygen.

Introduction

The recognition that multiple substitution of the B cations can be brought about in perovskite-type compounds (ABO_3) has led to the preparation of a multitude of phases.¹⁻⁴

When the A cation was barium or strontium, the B cations could be combinations of hexavalent and divalent cations—a typical example of which is $\text{Ba}(\text{Zn}_{0.5}\text{W}_{0.5})\text{O}_3$ (2) or combinations of pentavalent and trivalent cations leading to such compounds as $\text{Ba}(\text{Fe}_{0.5}\text{III}\text{Ta}_{0.5})\text{O}_3$ (1). Both of these compounds have structures of the cubic perovskite type. In the latter, the arrangement of the iron and tantalum ions is random in the B-sites of the perovskite cell. The former, on the contrary, presents an ordered arrangement of the zinc and tungsten ions leading

to a unit cell whose edge is twice that of the simple perovskite unit. The arrangement of the B cations is thus face-centered cubic, each being surrounded by oxygen octahedra in which each oxygen is shared by the two different B cations. It appears that the tendency toward ordering is favored by the larger charge difference between the two types of B cations.

It therefore seemed possible that similar compounds could be prepared containing a combination of a heptavalent and a univalent cation except that octahedral coordination with oxygen has not been reported for heptavalent metal ions. This paper describes the preparation and properties of compounds of this type having the composition $\text{Ba}(\text{Na}_{0.5}\text{Re}_{0.5})\text{O}_3$ and $\text{Ba}(\text{Li}_{0.5}\text{Re}_{0.5})\text{O}_3$.

Experimental

Reagents.—The carbonates of lithium, sodium, strontium and barium were C.P. or reagent grade. Rhenium metal (99.99%) was procured from the Chase Brass and Copper

(1) Francis Galasso, Lewis Katz and Roland Ward, *THIS JOURNAL*, **81**, 820 (1959).

(2) E. J. Frescia, Lewis Katz and Roland Ward, *ibid.*, **81**, 4783 (1959).

(3) L. H. Brixner, *ibid.*, **80**, 3214 (1958).

(4) L. H. Brixner, *J. Phys. Chem.*, **64**, 165 (1960).