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Trichloroacetates of Lanthanum, Neodymium, and Dysprosium

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Lanthanum, neodymium, and dysprosium trichloroacetates have been prepared and characterized. Vacuum pyrolysis of the anhydrous salts yields anhydrous metal chlorides.

Introduction

Reported studies of rare earth metal trichloroacetates[2-5] have been mainly concerned with fractional separations. Wolff[4] observed the hydrolysis of the cerium(III) salt in aqueous solution to form the carbonate. None of these reports described the salts themselves. The present study was undertaken to characterize these salts more completely and to permit comparison with the recently reported trifluoroacetates.[6] The dysprosium salt was included to ascertain that the properties observed were not specific for the cerium group metals.

Experimental

Materials.—Lanthanum and neodymium oxides had been shown to be 99.99% pure by spectrography. A small sample of dysprosium oxide known to be 99.9% pure was used without further test. Other materials were of Analytical Reagent grade.

Analytical Methods.—Rare earth metals were determined by precipitation with oxalic acid and weighing the ignited oxide. Chlorine was determined by decomposition of the salt in a micro Paar bomb, followed by weighing silver chloride. Water of hydration was determined by loss of weight when the hydrated material was heated to constant weight at 60°.

Preparation of Trichloroacetates.—The general reaction

$$M_2O_3 + 6HC_2Cl_3O_2 \longrightarrow 2M(C_2Cl_3O_2)_3 + 3H_2O$$

was used. Five-gram portions of freshly ignited oxide were mixed with insufficient 50% aqueous trichloroacetic acid to dissolve the oxide. After a few hours standing at room temperature, the excess oxide was filtered off, the water was evaporated, and the product was recrystallized from water at room temperature. The trihydrate separated but lost water on heating at 60° (higher temperatures caused hydrolysis) or on storage in a vacuum desiccator over Anhydrone or phosphorus(V) oxide for 48 hr. to yield the pure anhydrous salts.

Anal. Calcd. for $La(Cl_3C_2O_2)_3$: La, 22.19; Cl, 50.97. Found: La, 22.20; Cl, 51.0. Calcd. for $Nd(Cl_3C_2O_2)_3$: Nd, 26.68; Cl, 50.60. Found: Nd, 26.66; Cl, 50.6. Calcd. for $Dy(Cl_3C_2O_2)_3$: Dy, 25.01. Found: Dy, 24.9.

Properties of the Salts.—A vapor pressure–composition diagram for the system $M(Cl_3C_2O_2)_3$–H_2O (Fig. 1) indicated that the trihydrate is the solid phase in equilibrium with saturated solution at 25° and that the lanthanum salt is distinctly more soluble than the neodymium salt. A more accurate estimate of solubility by direct analysis of the saturated solution yielded the values of 174 g. of lanthanum salt and 106 g. of neodymium salt per 100 ml. of water, respectively. Furthermore, the serial order of solubility of the cerium group metal salts was established by fractional crystallization, the separation being followed by average atomic weight and by spectrophotometric measurements. Solubilities of the salts of the elements lanthanum through neodymium are inversely related to atomic number.

Qualitatively, the salts are quite soluble in methanol, ethanol, dioxane, toluene, acetone, and carbon tetrachloride. They are practically insoluble in chlorobenzene, iodobenzene, and mineral oil.

Densities, determined pycnometrically by displacement of chlorobenzene, were 2.24 g./ml.; no difference was detected.

Crystallography.—The rare earth metal trichloroacetate trihydrates are monoclinic, optically negative, and of the same general habit (Fig. 2). By Mallard's method, $2V$ was estimated to be 50°, a value well in accord with that calculated from the refractive indices: α is 1.58, β is 1.68, and γ is 1.71. Arrowhead twinning was characteristic of the lanthanum salt but was not observed for the other salts. The extinction angle between γ and the c axis is 6°, which is sufficiently small that the twinned crystals sometimes appear to show parallel extinction.

Powder X-ray diffraction patterns, obtained with $CuK\alpha$ radiation in a standard Norelco unit with a Phillips 114-mm. camera, are given in Table I. Intensities were estimated visually.

Pyrolysis of the Salts.—When anhydrous neodymium trichloroacetate was heated slowly under vacuum, decomposition occurred at 240° with much swelling of the solid and evolution of gas.

$$2Nd(Cl_3C_2O_2)_3 \xrightarrow{240°} 2NdCl_3 + 3CCl_3COCl + 3CO_2 + 3CO$$

Once started, the decomposition proceeded unaided though less vigorously and rapidly than in the case of the trifluoroacetates.[6] The gaseous products were identified by passage through a trap cooled with Dry Ice, then to an Ascarite bulb, and finally to a gas density bulb. The uncondensed and unabsorbed gas had a molecular weight of 29.1 (calculated for CO: 28) and readily produced a black precipitate with aqueous ammoniacal silver nitrate, thus identifying carbon monoxide. The Ascarite bulb showed a gain in weight corresponding to 1.535 moles of CO_2 per mole of anhydrous neodymium trichloroacetate. Fractionation of the condensate in the cooled trap yielded a major fraction of molecular weight 181–182 (calculated for trichloroacetyl chloride: 181.85) with traces of phosgene. A 0.0353-g. portion of this material was hydrolyzed and the solution titrated with base, then with silver nitrate. *Anal.* Calcd. for trichloroacetyl chloride: 0.389 mequiv. of acid, 0.195 mequiv. of chloride. Found: 0.386 mequiv. of acid, 0.195 mequiv. of chloride. The boiling point of this fraction was 116–118° (Emich's method) compared to 118° reported for trichloroacetyl chloride.[7]

The fluffy solid residue from the thermal decomposition was completely soluble in water and had a Cl:Nd atom ratio of 2.99, 3.00, 3.00 for successive reactions, thus identifying $NdCl_3$. The product tended to absorb the other decomposition products

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[1] Taken in part from the M.S. Thesis of George P. Tilley, University of Massachusetts, 1950.

[2] G. Urbain, *Ann. Chim. Phys.*, **19**, 184 (1900).

[3] A. Mandl, *Z. anorg. allgem. Chem.*, **37**, 252 (1903).

[4] H. Wolff, *ibid.*, **45**, 89 (1905).

[5] L. L. Quill and M. L. Salutsky, *J. Am. Chem. Soc.*, **72**, 3306 (1950); *Anal. Chem.*, **24**, 1453 (1952).

[6] J. E. Roberts, *J. Am. Chem. Soc.*, **83**, 1087 (1961).

[7] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 680.

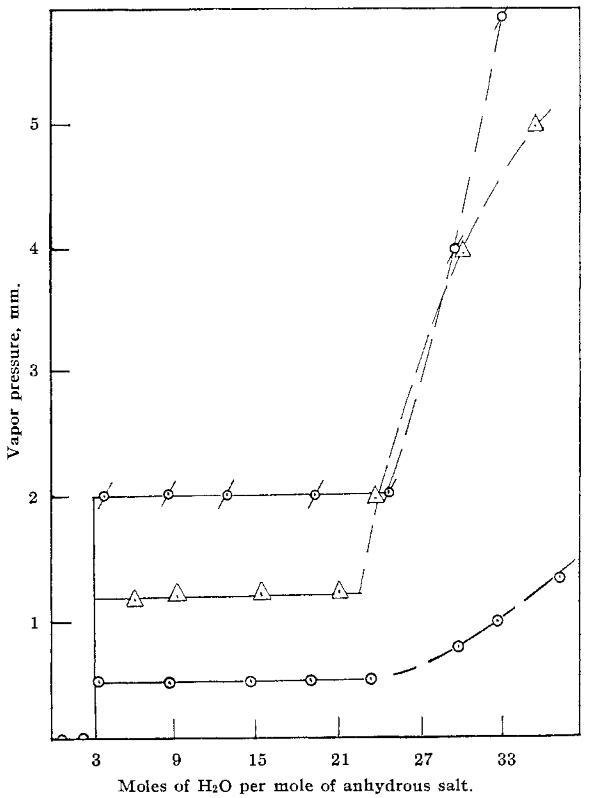

Fig. 1.—Vapor pressures of hydrated trichloroacetates of lanthanum (⊙), neodymium (△), and dysprosium (⌀) at 25°.

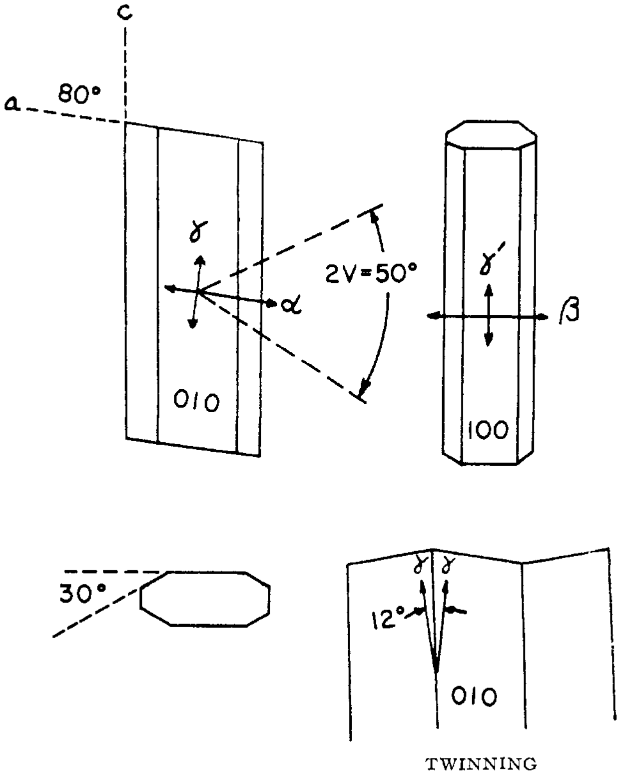

Fig. 2.—Crystallography of lanthanum trichloroacetatetrihydrate.

strongly, but by prolonged pumping a product of 99.4% purity was obtained.

Thermal decomposition in carefully dried air yielded the same products as under vacuum. When traces of moisture were present, NdOCl rather than $NdCl_3$ was formed, the other products being the same with a larger proportion of phosgene.

Table I

Powder X-Ray Diffraction Patterns for $Nd(Cl_3C_2O_2)_3$ and $La(Cl_3C_2O_2)_3$

$Nd(Cl_3C_2O_2)_3$		$La(Cl_3C_2O_2)_3$			
d, Å.	$10^2I/I_1$	d, Å.	$10^2I/I_1$	d, Å.	$10^2I/I_1$
11.0	70	10.8	30	2.34	5
9.6	40	9.0	50	2.28	5
8.8	100	8.5	30	2.22	5
6.4	10	8.0	70	2.16	20
5.8	30	6.9	60	2.14	10
5.2	20	6.5	90	2.08	5
4.8	20	5.4	5	2.05	5
4.5	40	5.2	10	1.99	5
4.3	60	4.41	10	1.96	10
4.04	70	4.30	40	1.93	5
3.75	50	3.90	90	1.86	10
3.69	50	3.70	20	1.81	5
3.39	10	3.60	20	1.78	5
2.93	5	3.48	5	1.74	5
2.80	10	3.28	5	1.70	5
2.71	20	3.08	5	1.59	5
2.57	30	3.01	5	1.45	5
2.42	30	2.81	40	1.42	5
2.15	5	2.77	60	1.40	5
2.10	5	2.66	100	1.38	5
1.91	5	2.53	10		
1.72	5	2.48	5		
1.60	5	2.38	5		

The latter was identified by molecular weight and by hydrolysis, the resulting solution having a milliequivalent ratio of acid to chloride of only 1.02. At the cool end of the reaction tube were a few well formed crystals. These were soluble in alcohol, ether, and carbon tetrachloride, could readily be sublimed, and were examined in the hot stage of a polarizing microscope. A phase change of 46° and a second phase change to isometric at 71° followed by sublimation at higher temperatures strongly indicated that the compound was hexachloroethane.[8]

Lanthanum and dysprosium salts behaved identically on pyrolysis. In all cases the chloride to metal atom ratio was 3.00 ± 0.08.

Discussion

Pyrolysis of rare earth metal trichloroacetates follows the same route as that of the trifluoroacetates with the added complication of further decomposition of one of the pyrolysis products. Both phosgene and hexachloroethane could result from decomposition of trichloroacetyl chloride[7]

$$2CCl_3COCl \longrightarrow C_2Cl_6 + COCl_2 + CO$$

Crystallographically, the trichloroacetates and trifluoroacetates are similar though the former show a distinctly greater birefringence. The lower decomposition temperature found for the trichloroacetates (as well as their easy hydrolysis) indicates lower stability compared to the trifluoroacetates.

As a preparative method, the thermal decomposition of the trichloroacetates is the most convenient method yet reported for the preparation of anhydrous rare earth metal chlorides. In the absence of evidence to the contrary and in view of the general similarity of rare earth metal compounds, it is quite reasonable to assume that this reaction which has been proved for lanthanum, neodymium, and dysprosium will apply equally well for the other members of the lanthanide series.

[8] A. N. Winchell, "The Optical Properties of Organic Compounds," Academic Press, New York, N. Y., 1954, p. 3.