J. Inorg. Nucl. Chem., 1959, Vol. 9, pp. 222 to 231. Pergamon Press Ltd. Printed in Northern Ireland

PREPARATION OF SOME BASIC AND ANHYDROUS RARE EARTH ACETATES. THEIR PROPERTIES AND REACTIONS IN ACETIC ACID AS SOLVENT

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(*Received* 6 *August* 1958)

Abstract—Solutions of rare earth oxides in anhydrous acetic acid represent metastable systems from which hydroxo-acetates, $Ln_2(OH)_3(OAc)_3 \cdot 2HOAc$, gradually precipitate. Presence of equivalent amounts of acetic anhydride causes formation of so-called basic acetates which are best represented as binuclear oxo- complexes with the type formula, $Ln_2O(OAc)_4 \cdot 2HOAc$ (where Ln = La, Nd, Sm). The anhydrous acetates were prepared by refluxing the oxides with acetic anhydride. The solubility of neodymium acetate in acetic acid increases markedly in the presence of potassium acetate to form a negatively charged complex ion, suggesting that the anhydrous rare earth acetates exhibit amphoteric characteristics in acetic acid. Conductometric titrations of solutions of the oxo- and anhydrous acetates in acetic acid with various acids show complete neutralization only with perchloric acid; with sulphuric and oxalic acids, minima correspond to formation of insoluble 1 : 1 compounds (moles acid per mole rare earth); with phosphoric and citric acids, maxima suggest formation of soluble 1 : 1 compounds, followed by minima corresponding to insoluble compounds with 3 : 2 and 2 : 1 mole ratios, respectively.

THE marked solubility of neodymium oxide in anhydrous acetic acid, (HOAc), led to the hope that such solutions might find use for the preparation of anhydrous neodymium compounds. It was soon discovered that minor variations in the nature of the solvent produce a rather marked effect on the stabilities of such solutions. The pertinent observations may be summarized as follows:

(a) Solutions of the oxide in 98% HOAc (2% H_2O) are stable for many months, whereas solutions prepared using the anhydrous solvent gradually yield on standing at room temperature a precipitate whose composition can be represented by the formula, $Nd_2(OH)_3(OAc)_3 \cdot 2HOAc$.(I)

(b) Solutions of the oxide in 100% HOAc containing an amount of acetic anhydride, Ac_2O, stoicheiometrically equivalent to, or in excess of that required for removal of water presumably formed as the result of the solution process possess variable stability. If such systems are initially refluxed for several hours, formation of a crystalline precipitate begins to take place after several days. If the solutions have not been heated, precipitation will be delayed for a matter of weeks or even months. In both instances precipitation continues until only a small amount of neodymium remains in solution. These phenomena cannot be ascribed to supersaturation since seeding with crystals of the precipitated phase do not hasten formation of additional product. The precipitated compound, is found to correspond in composition to a hemihydrate, $Nd(OAc)_3 \cdot \frac{1}{2}H_2O$. For reasons given below and substantiated by the results of a study of the conductometric behaviour of such solutions and products, this compound is believed to be an oxo-acetate, $Nd_2O(OAc)_4 \cdot 2HOAc$(II). Similar binuclear oxo-acetates were obtained for La, Sm, Yt.

To further characterize the unusual nature of the products obtained from acetic acid–acetic anhydride solutions, it became necessary to prepare the anhydrous normal acetates. These were obtained by the interaction of acetic anhydride with the corresponding oxides (except for yttrium oxide, which was found to be non-reactive with Ac_2O). The anhydrous acetates were found to differ from the oxo-acetate(II) on the basis of:

(i) qualitative solubility differences in 100% HOAc,
(ii) their analytical compositions,
(iii) their X-ray diffraction patterns and
(iv) their reactions with various acidic solutions in 100% HOAc as solvent.

DISCUSSION OF RESULTS

Reaction of the rare earth oxides with solvent acetic acid

It is evident that the solutions of neodymium oxide in acetic acid are relatively metastable systems from which the hydroxo-, or the oxo-acetates, (I) and (II) slowly precipitate. The attack of the solvent upon the polymeric oxide structure can most certainly be regarded as a stepwise process entailing progressive cleavage of Nd–O–Nd linkages. Reactants in such systems include not only the *solvent*, but also *water*, which may have been present originally or formed during the solution or the subsequent stabilization processes. Where specified, *acetic anhydride* may also be considered to be a reactant. From a purely formalistic point of view, the following solvation reactions may be assumed to occur:

$$Nd_2O_3 + HOAc \rightarrow Nd_2O_2(OH)(OAc) \quad (A) \qquad (1)$$

$$A + HOAc \rightarrow Nd_2O(OH)_2(OAc)_2 \quad (B) \qquad (2)$$

$$B + HOAc \rightarrow Nd_2(OH)_3(OAc)_3 \quad (C) \qquad (3)$$

The solvolytic action of acetic acid upon any one of these hypothetical intermediates entailing replacement of hydroxo groups by acetato groups could also be important:

$$Nd_2O_{3-n}(OH)_n(OAc)_n + mHOAc \rightarrow Nd_2O_{3-n}(OH)_{n-m}(OAc)_{n+m} + mH_2O \qquad (4)$$

where $$n,\ m = <3$$

Equation (4) suggests that the presence of either water or of acetic anhydride could influence the nature of the species present in acetic acid or obtainable by precipitation from such systems. In any case such a picture leads to the conclusion that a binuclear complex may constitute the simplest structural unit obtainable as the intermediate or end product of the solution process. In the absence of acetic anhydride, a product represented by the general formula $Nd_2O_{3-n}(OH)_n(OAc)_n$ might therefore result from the solvation of neodymium oxide. A compound which may be represented by the formula for which $n = 3$ was actually isolated as a 2-acetic acid solvate (I). The presence of a small amount of water either retards formation of this substance or greatly increases its solubility as no crystalline products were obtained from a solution of Nd_2O_3 in 98 per cent acetic acid.

Attack of the intermediate hydroxo-compounds by the solvent acetic acid, entailing replacement of hydroxo-groups by acetato-groups should be favoured by the presence of acetic anhydride. The latter could serve not only to remove water formed during the solvolytic process, but might also conceivably convert the hydroxo-bridged species into oxo-bridged complexes by a mechanism amounting to oxolation. It is our opinion that the processes of solvolysis (eqn. 5) and of oxolation (eqn. 6) represent the slow temperature-dependent reactions which lead eventually to the precipitation of the binuclear oxo-acetate(II) as the 2-acetic acid solvate.

$$Nd_2(OH)_3(OAc)_3 + HOAc \rightarrow Nd_2(OH)_2(OAc)_4 + H_2O \qquad (5)$$

$$Nd_2(OH)_2(OAc)_4 + Ac_2O \rightarrow Nd_2O(OAc)_4 + 2HOAc \qquad (6)$$

Even though the oxo-acetate(II) could be represented as a hemi-hydrate,

$$Nd(OAc)_3 \cdot \tfrac{1}{2}H_2O,$$

the dimeric structure with an oxo bridge is believed to be more reasonable, both on the basis of the mechanism outlined above, as well as the behaviour of this substance in acetic acid. The "basic" acetates of titanium⁽¹⁾ and of boron⁽²⁾ are represented by similar structures. Basic acetates of chromium⁽³⁾ have been assigned structures containing both oxo and acetato groups as bridging units.

The oxo-acetates(II) of neodymium, lanthanum, samarium, and yttrium were prepared, analysed and characterized during present investigation.

Interaction of rare earth compounds with acetic anhydride

Two procedures are given in the literature for the preparation of the anhydrous rare earth acetates: (a) the reaction of the rare earth nitrate 6-hydrate with acetic anhydride⁽⁴,⁵⁾ and (b) the solution of the rare earth oxide in fused ammonium acetate.⁽⁶⁾ Since the latter reaction is reported to give an impure product it was not further investigated. A critical evaluation of published results covering the first of these methods reveals that the analytical data correspond more satisfactorily with those rquired for the oxo-acetates. Analytical results for the La_2O_3 content of a so-called anhydrous lanthanum acetate bear out this contention (Found: 49·7 and 49·5. Calc. for $La(OAc)_3$; 51·6 and for $La_2O(OAc)_4 \cdot 2HOAc$, 50·2%). Investigators⁽⁴,⁵⁾ who have most recently used this method did not perform elemental analyses.

Attempts in this laboratory to prepare the anhydrous acetates by refluxing the nitrates or the precipitated hydroxides with acetic anhydride gave only the oxo-acetates(II). Their formation was verified both by analsyis and by X-ray diffraction patterns. However, small samples of the oxo-acetates were found to undergo conversion into the anhydrous acetates when refluxed for approximately 16 hr with acetic anhydride. This suggests that reaction of the hydroxides or nitrates with acetic anhydride can lead to the formation of the anhydrous acetates if the reflux time is sufficiently long.

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(2) R. G. HAYTER, A. W. LAUBENGAYER and P. G. THOMPSON, *J. Amer. Chem. Soc.* **79**, 4243 (1957).

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Reaction of rare earth oxides with acetic anhydride

Reaction of neodymium oxide (and of La_2O_3 and Sm_2O_3) with boiling acetic anhydride yields the anhydrous acetate. A hydroxo compound cannot possibly be formed under these conditions. Here again the solvolysis of neodymium oxide may be regarded as entailing the stepwise destruction of the polymeric oxide structure. No solution appears to take place. Rupture of Nd–O–Nd linkages by simultaneous addition of the acetyl and acetate ions(7) presumably characterizing the reactive species formed by self-ionization of the solvent: $(CH_3CO)_2O \rightleftharpoons CH_3CO^+ + CH_3COO^-$ may constitute the principle mode of attack. Obviously incomplete reaction could result in the occlusion of oxide, or of the partially solvolysed material containing Nd–O–Nd units. The mechanism of the process can be represented formalistically in the following fashion:

$$[\text{O–Nd–O–Nd–O}]_n \xrightarrow{2n\text{AcOAc}} [(\text{AcO})_2\text{Nd–O–Nd(OAc)}_2]_n \xrightarrow{n\text{AcOAc}} [\text{Nd(OAc)}_3]_n$$

Properties of the oxo- and anhydrous rare earth acetates

Both classes of acetates are soluble in water. The anhydrous acetates were more soluble in 100% HOAc than the basic acetates. The two classes of compounds were also found to differ with respect to their X-ray diffraction patterns and their I.R. spectra.

The visible and ultra-violet absorption spectra of the neodymium acetate in water and acetic acid, and of the metastable solutions of the oxide in acetic acid were found to reveal no significant differences. In general, the molar absorptivities of such solutions were found to be slightly lower in acetic acid than in water. The molar absorptivities of the three solutions at the 523 mμ absorption peak are given in Table 1. The observed value of 3·91 for neodymium acetate in water compares favourably with the figure given in the literature, 3·80.(8) The results of this spectrophotometric study verify the near constancy of the absorption spectra of the neodymium compounds. Slight differences have been observed in different solvents and with different anions, but no marked changes in absorption spectra have been observed except in the case of very strong complexing action.

TABLE 1.—ABSORPTION OF VARIOUS NEODYMIUM ACETATE SOLUTIONS AT ca. 523 mμ

Compound	Solvent	Molar absorptivity
$Nd(OAc)_3$	Water	3·91
$Nd(OAc)_3$	Acetic acid	3·61
Nd_2O_3–HOAc solution	Acetic acid	3·53

Amphoterism of neodymium acetate. The solubility of anhydrous neodymium acetate in acetic acid was found to increase upon the addition of potassium acetate. Data are given in Table 2. Migration experiments showed that the coloured solutions move toward the positive electrode indicating the formation of a negatively charged

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ionic species containing an acetato-neodymiate(III) complex. These observations may be interpreted by the following general equation:

$$Nd(OAc)_3 + nKOAc \rightarrow K_n[Nd(OAc)_{3+n}]$$

Neodymium acetate may thus be added to the list of inorganic acetates that exhibit amphoteric behaviour in acetic acid. It seems most likely that other rare earth acetates will show similar behaviour.

TABLE 2.—SOLUBILITY OF NEODYMIUM ACETATE IN ACETIC ACID AS A FUNCTION OF ACETATE CONCENTRATION (temp. 30°C)

Solubility g $Nd(OAc)_3$/100 g HOAc	KOAc concentration molarity
1·94	0·00
2·00	0·10
4·25	0·50
7·26	1·00

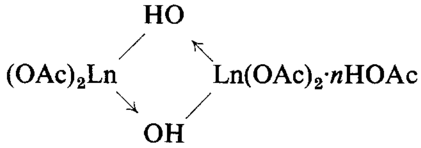
Reactions of rare earth oxide solutions in acetic acid with various acids. The present investigation was undertaken in order to study the practicability of preparing anhydrous rare earth compounds from solutions of the oxides in acetic acid. Analytical results for products obtained by the addition of various acids to the rare earth oxide–acetic acid solutions were found to be difficult to interpret. Conductometric titrations were therefore carried out to gain a clearer insight into the nature of these reactions. Surprisingly, the titation curves for solutions of the oxides and of the anhydrous acetates in acetic acid were found to reveal no significant differences in form or shape. The titration curves are plotted schematically in Fig. 1 in terms of moles acid per mole Nd. Similar curves were obtained for solutions of the corresponding lanthanum and samarium compounds.

The complete "neutralization" of the rare earth species with perchloric acid is indicated by a break in the titration curve at a molar ratio of 3 : 1 for $HClO_4$: Nd. For H_2SO_4, $H_2C_2O_4$, citric acid and phosphoric acid 1 : 1 compounds are suggested. The 1 : 1 reaction products with sulphuric and oxalic acid are precipitated completely, whereas those formed with citric acid and phosphoric acid appear to be appreciably soluble. However, precipitation of a citrate with a 2 : 1 molar ratio (citric acid : Nd) begins beyond the maximum of the conductance curve and of a 3 : 2 compound with phosphoric acid begins to occur just before the maximum is reached. Since all titration curves show initial increases in conductance whether precipitation takes place or not, there is some question whether the pronounced maxima at the 1 : 1 ratios, obtained when solutions of citric and phosphoric acids were used as titrants, represent soluble compounds corresponding to this ratio.

Only when perchloric acid, one of the strongest acids known to exist in acetic acid, was used as the titrant does the conductometric evidence suggest complete reaction. Results obtained for the other acids suggest that only two of the three acetate groups per neodymium atom in the oxo- and anhydrous acetates, when formulated as $Nd(OAc)_3 \cdot \frac{1}{2}H_2O$ and $Nd(OAc)_3$, respectively, participate in the reaction.

The conductometric evidence together with the analytical data for the oxo- and anhydrous acetates therefore demonstrate

(a) that solutions of the oxides in acetic acid can be represented in their simplest form as binuclear hydroxo-acetates:

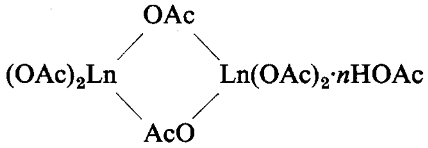


(b) that the oxo-acetates formed by gradual crystallization from such solutions containing acetic anhydride can be considered as oxolated complexes:

$$(OAc)_2Ln\text{–}O\text{–}Ln(OAc)_2\cdot nHOAc$$

and

(c) that even the anhydrous acetates behave in acetic acid as polymeric species in which acetato-groups constitute bridging units, as follows:



For purposes of comparison conductometric titrations were also carried out using solutions of potassium acid phthalate with the same acids. Solvolysis of potassium acid phthalate to give potassium acetate and the non-electrolyte, phthalic acid, makes it possible to use the phthalate as a base standard in HOAc.(9) The titration data are plotted schematically in Fig. 2 and show

(a) that perchloric acid and phosphoric acid serve as mono-basic acids to form $KClO_4$ and KH_2PO_4, respectively,

(b) that sulphuric acid yields both the normal as well as the hydrogen sulphates, K_2SO_4 and $KHSO_4$, and

(c) that oxalic and citric acids are non-electrolytes in acetic acid.

EXPERIMENTAL

Materials and methods

(a) *Anhydrous acetic acid.* Preparation of the anhydrous solvent from glacial acetic acid was effected by two procedures:

(1) by refluxing the 99·7 per cent acid with CrO_3 to remove oxidizable impurities followed by treatment with "boron acetate" to effect removal of water(10) and

(2) by dehydration with acetic anhydride.(11) Refluxing of the acid with the anhydride (500 ml CH_3COOH plus 15 ml $(CH_3CO)_2O$) for 3 hr is reported to effect quantitative reaction between the anhydride and water present in acetic acid. Final purification was accomplished in both instances by fractional distillation.

(b) *Rare earth materials.* The neodymium oxide used in this investigation was material of 99·9 per cent purity taken from the University of Illinois stock. The yttrium, samarium and lanthanum

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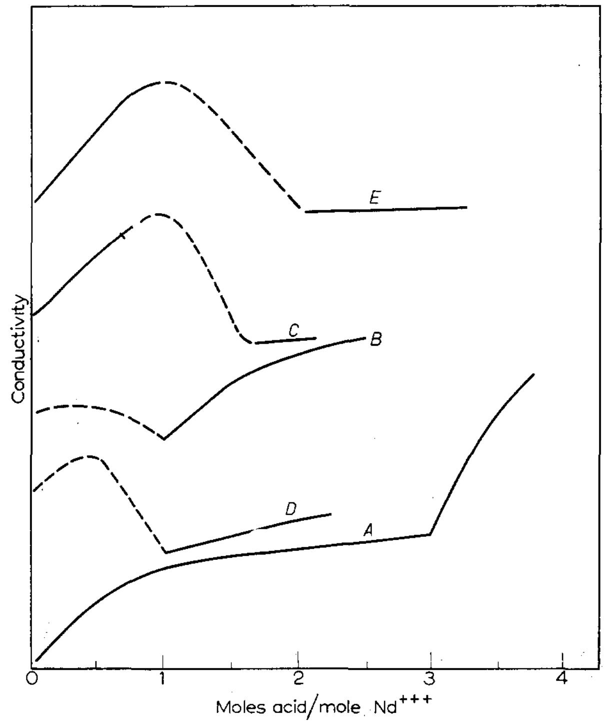

FIG. 1.—Conductometric titration curves representing addition of various acids to solutions of neodymium oxide (or of the acetate or oxo-acetate) in 100% HOAc. Broken lines indicate formation of precipitates. Titrants: *A*, 0·1 M/$HClO_4$; *B*, 0·05 M/H_2SO_4; *C*, 0·4 M/H_3PO_4; *D*, 0·1 M/$H_2C_2O_4$; *E*, 0·1 M citric acid. [Nd^{3+}] = ~0·01 M.

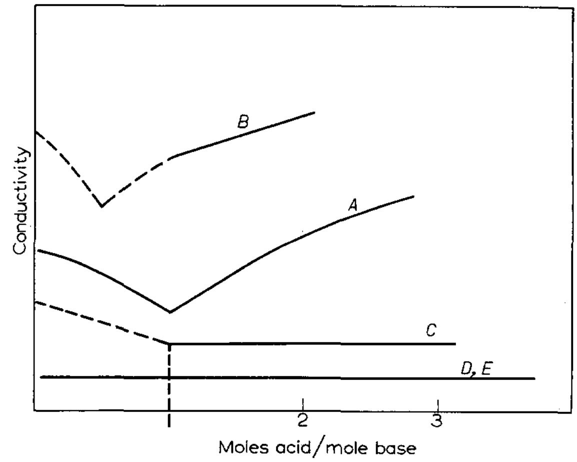

FIG. 2.—Schematic presentation of conductometric titration curves of potassium hydrogen phthalate as base standard in 100% HOAc using various acids. Solutions contained about 0·2 g KHPhth per 150 ml HOAc as solvent. Titrants: *A*, 0·1 M/$HClO_4$; *B*, 0·05 M/H_2SO_4; *C*, 0·4 M/H_3PO_4; *D* and *E*, $H_2C_2O_4$ and citric acid. Broken lines indicate precipitate formation ($KHSO_4$, K_2SO_4, KH_2PO_4). Solutions of oxalic and citric acids are essentially non-acidic in 100% HOAc.

oxides (purity "99 per cent plus") were obtained from the Lindsay Chemical Company. The oxides were ignited at 800–900° before use.

The hydrated neodymium and yttrium hydroxides were prepared by the addition of ammonium hydroxide to solutions containing their respective nitrates. The hydroxides were washed with water, ethanol and ether, and dried for 6 hr at 106°C.

(c) *Experimental techniques.* Conductometric titrations were carried out utilizing a Leeds and Northrup bridge, Model 4866. The electrodes consisted of 1 cm^2 platinum sheets separated from each other by a distance of 2 mm. Titrations were carried out at 25–26° and at 30°.

Spectrophotometric measurements in the ultra-violet and visible regions were determined by use of a Cary Model 14 M recording spectrophotometer. A Perkin–Elmer Model 21 instrument was employed for the infra-red studies. One centimeter quartz cells were used with the Cary spectrophotometer; nujol mulls were prepared for use with the Perkin–Elmer instrument. The infra-red spectra were used only for purposes of comparison.

X-ray powder patterns were obtained by use of a Hull-Debye-Scherrer X-ray diffraction apparatus equipped with a copper target and utilizing a nickel filter. The samples were sealed in Lindeman glass tubes. The X-ray diffraction patterns were employed only for purposes of comparison and identification.

(d) *Analytical methods.* The carbon and hydrogen contents of the various rare earth compounds were determined by standard microanalytical methods. Final ignition of microanalytical samples was accomplished by heating at 950°C for approximately 10 min. The resulting residues were also weighed to give values for the rare earth oxide contents of the samples. These values compared favourably with results obtained when macro samples were dissolved in nitric acid and treated with oxalic acid solution to precipitate the rare earth oxalates. The oxalates were subsequently ignited to the oxides.

(e) *Standard solutions in* 100% CH_3COOH. The titres of solutions were checked conductometrically against potassium acid phthalate which serves as a primary base standard in acetic acid.

Standard solutions of sulphuric acid (0·05 M) and of phosphoric acid (0·4 N) were prepared from 95 to 98% H_2SO_4 and 85% H_3PO_4, respectively, by dissolving weighed quantities of each in acetic. acid, adding the calculated quantity of acetic anhydride to remove water introduced with the acids refluxing briefly to effect reaction between the anhydride and water, and diluting to known volumes. Such solutions were allowed to stand for two days before use.

Solutions of oxalic acid in acetic acid prepared by dissolving the 2-hydrate were found to decompose rapidly with gas evolution when acetic anhydride was added to effect removal of water. It was therefore necessary to prepare standard solutions from anhydrous oxalic acid (furnished by the Victor Chemical Works). Solutions containing approximately 0·1 mole oxalic acid per litre were prepared by dissolving accurately weighed samples in acetic acid.

Tenth molar solutions of citric acid were prepared by dissolving accurately weighed samples of the 1-hydrate in anhydrous acetic acid containing the calculated amount of acetic anhydride to react with the water present. The solution was diluted to a known volume with anhydrous solvent and allowed to stand two days before use. Some evidence for decomposition was observed after standing for one week, based upon variable titrimetric results against standardized neodymium solutions.

Interaction of rare earth oxides with acetic acid

(a) *In the presence of acetic anhydride (formation of the oxo-acetates).* Solutions of rare earth oxides in acetic acid were prepared by dissolving weighed portions of the ignited oxides in acetic acid and refluxing the solutions for 3 hr with an amount of acetic anhydride calculated to remove the water formed on the assumption that the reaction would produce the anhydrous acetates. Yttrium oxide was found to be insoluble and unreactive. The solutions were cooled and diluted to known volumes with anhydrous acetic acid and the molarities of the solutions calculated with respect to the rare earth ion contents. Solutions in which as much as 4 g of the oxide were dissolved in 100 ml of acetic acid were prepared in this manner. Such solutions were used directly for conductometric studies and for the preparation of the oxo-acetates.

Neodymium solutions were found to yield precipitates after standing at room temperature for five days or longer (up to several months in those instances where the solutions had not been refluxed). Attempts to seed solutions with crystals of the precipitate were unsuccessful. Precipitation was observed to take place more rapidly from solutions of the samarium and the lanthanum oxides.

The precipitates were found to be the same whether a calculated or a two-fold excess of acetic anhydride had been added to react with the water assumed to be formed. The crystalline compounds were dried over calcium chloride and potassium hydroxide in a vacuum desiccator for ten days after which the odour of acetic acid was no longer evident and the compositions as determined by analysis had become constant. Compounds of the same composition were obtained by drying the crystalline substances for 24 hr in an Abderhalden apparatus at 100°C. Typical analyses for the compounds which are designated as *oxo-acetates* are given below:

Found: C, 22·00; H, 2·78; La, 42·75. Calc. for $La(OAc)_3\cdot\frac{1}{2}H_2O$: C, 22·17; H, 3·11; La, 42·73%. Found: C, 21·70; H, 3·06; Nd, 43·6. Calc. for $Nd(OAc)_3\cdot\frac{1}{2}H_2O$: C, 21·82; H, 3·05; Nd, 43·66%. Found: C, 21·60; H, 3·13; Sm, 45·5. Calc. for $Sm(OAc)_3\cdot\frac{1}{2}H_2O$: C, 21·47; H, 2·99; Sm, 44·7%.

The oxo-acetates were found to be soluble in water, but insoluble in ethanol, nitrobenzene, benzene, diethyl ether, and acetone. The oxo-acetates can be recrystallized from anhydrous acetic acid. These substances are believed to be binuclear oxo complexes, and may be represented by the type formula, $Ln_2O(OAc)_4\cdot 2HOAc$ (where Ln = lanthanon).

(b) *In the absence of acetic anhydride (formation of hydroxo-acetates).* One gramme of ignited neodymium oxide was dissolved by refluxing for 1 hr in 25 ml of anhydrous acetic acid. The precipitate which formed after approximately one week was dried for two days on a porous plate in a vacuum desiccator over potassium hydroxide and calcium chloride. The sample was then dried in an Abderhalden apparatus at 100°C for 24 hr. Found: C, 18·49; H, 2·85; Nd, 45·6. Calc. for $Nd_2(OH)_3(OAc)_3\cdot 2HOAc$: C, 18·85; H, 3·16; Nd, 45·32%).

Interaction of rare earth compounds with acetic anhydride

Anhydrous rare earth acetates were obtained when the oxides of lanthanum, neodymium and samarium were refluxed with acetic anhydride; the oxo-acetates were formed when neodymium and yttrium hydroxides and neodymium nitrate 6-hydrate were allowed to react with acetic anhydride.

(a) *Rare earth hydroxides.* Approximately 2·5 g of hydrated neodymium hydroxide was refluxed for 3 hr with 100 ml of acetic anhydride. No solution appeared to take place, but the product changed in appearance as refluxing was continued. The resulting compound was dried on a porous plate in a vacuum desiccator over potassium hydroxide and calcium chloride for two days and then dried for 24 hr in an Abderhalden apparatus at 100°C. The X-ray diffraction pattern revealed the compound to be the oxo-acetate.

Found: C, 21·64; H, 3·00; Nd, 43·7. Calc. for $Nd(OAc)_3\cdot\frac{1}{2}H_2O$: C, 21·82; H, 3·05; Nd 43·66%).

(b) *Rare earth nitrates.* Approximately 4 g of neodymium nitrate 6-hydrate was dissolved in 25 ml of acetic anhydride. The solution was heated gently until reaction occurred with the evolution of nitrogen dioxide and the concurrent formation of a very viscous substance. The product gradually hardened; heating was continued until no more nitrogen dioxide was evolved. The precipitate was crushed, washed with acetic anhydride, and dried on a porous plate in the vacuum desiccator over potassium hydroxide and calcium chloride for two days, followed by an additional 24 hr in an Abderhalden apparatus at 100°C. The diffraction pattern of this product was found to agree with that of the oxo-acetate.

Found: C, 20·77; H, 2·85; Nd, 43·2. Calc. for $Nd(OAc)_3\cdot\frac{1}{2}H_2O$: C, 21·82; H, 3·05; Nd, 43·66%).

(c) *Rare earth oxides.* Four grammes of ignited neodymium oxide was refluxed with 200 ml of acetic anhydride. A light blue suspension was formed which turned violet in colour upon applying heat. The suspension cleared when the refluxing became vigorous; the rare earth compound settled to the bottom of the flask as a viscous mass which quickly formed a hard cake. After 2 hr of refluxing, the solid mass was broken up thoroughly and refluxing continued for 4–8 hr. Samples of La_2O_3 and Sm_2O_3 were treated in a similar fashion. Yttrium oxide was found to be unreactive. Products after drying were found to give analytical results demonstrating that the anhydrous acetates had been formed.

Found: C, 22·63; H, 2·98; La, 44·4. Calc. for $La(OAc)_3$: C, 22·80; H, 2·87; La, 43·96%.
Found: C, 22·19; H, 2·98; Nd, 44·9. Calc. for $Nd(OAc)_3$; C, 22·42; H, 2·82; Nd, 44·89%.
Found: C, 21·59; H, 2·99; Sm, 46·0. Calc. for $Sm(OAc)_3$: C, 21·99; H, 2·77; Sm, 45·93%.

These compounds were found to be completely soluble in water and anhydrous acetic acid. The

X-ray diffraction patterns of these compounds were found to be different from those of the oxo-acetates. The anhydrous acetates are believed to be poly-nuclear (in acetic acid) with bridging acetato groups (see page 227).

(d) *Neodymium oxo-acetate*. One gramme of the oxo-acetate of neodymium was refluxed with 50 ml of acetic anhydride for approximately 16 hr. The sample was removed and dried first in a vacuum desiccator for two days over potassium hydroxide and calcium chloride and subsequently in the Abderhalden for 24 hrs at 100°C. The X-ray diffraction pattern of the product prepared in this manner was found to be identical with that of the anhydrous acetate:

Found: C, 22·31; H, 2·87; Nd, 44·8. Calc. for $Nd(OAc)_3$: C, 22·42; H, 2·82; Nd, 44·89%. The above experiment suggests that long refluxing of the oxo-acetates with acetic anhydride will effect their conversion to the anhydrous acetates.

Acknowledgements—The authors are indebted to the Atomic Energy Commission for a grant in support of this investigation (Contract No. AT(11-1)-67, Project No. 18). Some of the earlier exploratory work on this problem was carried out by MR. R. E. WHITNEY (B.S. Thesis, University of Illinois, 1955) whose efforts are acknowledged with gratitude. The authors are also grateful to MR. J. NEMETH for the microanalytical determinations and to PROFESSOR G. T. MOELLER for helpful suggestions.