Quantitative conversion to the alkoxycarbonyl species Pt(SCN)($COOCH_3$)L_2 was also carried out as in (ii) below.

(ii) For X = NO_3 and C_6H_5, [Pt(X)(CO)L_2][BF_4] was shaken in neat methanol for 12 hr at 25° in an evacuated Pyrex Carius tube. The off-white precipitate was filtered, washed with water and methanol, and then recrystallized as above, affording pure Pt(NO_3)($COOCH_3$)L_2 ($\nu_{C=O}$ 1642 cm^{-1}, ν_{NO_3} 1520, 1350 cm^{-1}) and Pt(C_6H_5)($COOCH_3$)L_2 ($\nu_{C=O}$ 1646 cm^{-1}).

Solubility properties were identical with those of the analogs for X = Cl, Br, and I,[3] while ir assignments and pmr absorptions were qualitatively similar (Table IV).

(iii) As above, for X = CF_3, Pt(CF_3)($COOCH_3$)L_2 was isolated as an off-white solid, which decomposed in solution; $\nu_{C=O}$ 1645 cm^{-1}.

(iv) For X = H, [PtH(CO)L_2][BF_4] in CH_2Cl_2 (1 ml) was stirred with neat methanol for 1 hr at 25°. An insoluble orange-red solid was filtered, washed with water and methanol, and then dried under vacuum; $\nu_{C=O}$ 1800 cm^{-1} (b). Although there was no evidence for the formation of an alkoxycarbonyl derivative, the product could well contain a bridging carbonyl group.[23]

(v) For X = CH_3, [Pt(CH_3)(CO)L_2][BF] was stirred in neat methanol for 12 hr at 25°. There was no evidence for formation of the alkoxycarbonyl species.

(c) **For L = As(C_6H_5)$_3$ (Attempted).**—Conditions similar to (bi) applied to [Pt_2(SCN)$_2L_4$][BF_4]$_2$ resulted in pronounced decomposition.

5. **Attempted Preparation of [PtH(X)L_2].** (a) **For L = P(C_2H_5)$_3$.**—(i) For X = CH_3, [Pt(X)(CO)L_2][BF_4] was shaken with 20 ml of water–methanol (10:1) solution for 15 hr at 90° in an evacuated Pyrex Carius tube. No evidence for hydride formation was found. A similar reaction conducted at 100° gave pronounced decomposition.

(ii) For X = C_6H_5, identical reactions at 90 and 110° proceeded with less decomposition, yet no hydride was detected in the reaction products.

(iii) As above, reactions were unsuccessful for X = C_6H_5, H, and SCN.

(b) **For L = P(C_6H_5)$_3$.**—(i) For X = SCN, Pt(X)($COOCH_3$)L_2 was heated with saturated aqueous sodium thiocyanate solution (5 ml) at 110° for 12 hr in an evacuated Pyrex tube. Carbon dioxide and methanol could not be detected in the volatile products. Extraction of the residue with methylene chloride afforded unreacted starting material. No evidence for hydride formation was found.

(ii) For X = NO_3, Pt(X)($COOCH_3$)L_2 heated with saturated aqueous potassium nitrate gave similar results.

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Hydrothermal Equilibria and Crystal Growth of Rare Earth Oxides, Hydroxides, Hydroxynitrates, and Hydroxycarbonates

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The equilibria of praseodymium, neodymium, and terbium oxides with water have been examined at temperatures up to 900° and pressures of 1360 atm by hydrothermal techniques. In the trivalent Pr and Nd systems, only hexagonal trihydroxide and oxyhydroxide were observed with the phase boundary near 800°. In the presence of oxygen or oxidizing agent, fcc PrO_2 was found as a product after reaction at temperatures above 600°; under similar conditions diphasic mixtures of rhombohedral $TbO_{1.714}$ and monoclinic $TbO_{1.818}$ were obtained. The equilibria of praseodymium hydroxynitrate and hydroxycarbonate systems have been explored, and monoclinic $Pr(OH)_2NO_3$, hexagonal $Pr_2(OH)_5NO_3$, hexagonal $PrOHCO_3$, and hexagonal $Pr_2O_2CO_3$ have been characterized. Single crystals of trihydroxide, hydroxynitrate, and hydroxycarbonate phases have been prepared and examined by Weissenberg techniques; small crystals of the higher oxides have also been obtained. The use of nitrate ion as an oxidizing agent under high-temperature conditions and as an effective mineralizer at lower temperatures is described and discussed. Tga data for the hydroxy anion phases are presented, and discrepancies between the present hydrothermal results and those of previous reports are discussed.

Introduction

A detailed structural investigation of the intermediate oxides of praseodymium and terbium has been hindered by their unavailability as single crystals. The preparation of hexagonal A-type[1] and monoclinic B-type sesquioxide[2,3] crystals has been achieved by high-temperature techniques, but the oxidation of such samples to the fluorite-related intermediate phases appears to proceed with the loss of crystal integrity.[4] Attempts to employ the lower temperature procedures of chemical transport and flux techniques in this laboratory were unsuccessful. The results of Shafer and Roy,[5] who reported that the oxides of several trivalent rare earths were stable under the hydrothermal conditions, suggested that hydrothermal growth would be the most feasible method for preparing pure oxide crystals in a cubic-related crystallographic form suitable for structural analysis and the investigation of defect chemistry. Since oxygen pressures greater than 10^3 atm are necessary for the preparation of PrO_2 even at 500°[6] and since C-type Nd_2O_3 has been reported to be stable in water under appropriate temperature and pressure conditions, attempts to prepare C-type Pr_2O_3 by hydrothermal techniques were initiated.

After preliminary results for the Pr_2O_3–H_2O system

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were found inconsistent with previous reports[5,7] for other rare earth oxide–water systems, extensive examination of the praseodymia–water and neodymia–water systems was begun. These studies were subsequently extended to the terbia–water system. Indication of contamination by foreign anions in both the present and previous experiments led to an investigation of oxide–nitrate–water and oxide–carbonate–water systems.

Experimental Section

Phase equilibration and crystal growth experiments were effected with a hydrothermal unit constructed for 4000-atm service. Four externally heated Stellite cold-seal reactors (Tem-Pres Research, State College, Pa.) were employed for the purposes described previously;[8] however, the system was arranged in an inverted configuration, *i.e.*, cone closures downward, with connection to a manifold providing outlets to a Bourdon gauge (Astra Products, Willow Grove, Pa.), safety disks, and a gas-driven water intensifier (S. C. Hydrolic Engineering Corp., Los Angeles, Calif.). This design minimized thermal loss from water convection and allowed for continuous measurement and control of pressure. External reactor temperatures were measured in a thermocouple well and internal temperatures and profiles were calibrated in separate runs with an Inconel-sheathed thermocouple mounted inside the pressure vessel. The estimated uncertainties in the measured temperatures and pressures are ±25° and ±34 atm, respectively.

Sample containers (2.5–4.0 cm in length) were fashioned of thin-walled gold tubing (5.0-mm o.d., 4.5-mm i.d.). End closures were made by crimping with a three-jaw chuck and then sealing by welding with a dc arc, or in some instances one end was not welded allowing communication with the reactor interior. The use of platinum and of 70% silver–30% palladium vessels was also investigated. The quantity of distilled water or mineralizer solution (0.08–0.25 g) which was combined with a substrate (0.2–0.6 g) before welding was calculated for the desired temperature and pressure conditions by using specific volume data for water.[9] Leaks in welded capsules were detected by weight loss on extended heating at 100°. All experiments were conducted isobarically by applying and maintaining the desired pressure during the heating cycle (3 days–3 weeks at temperatures up to 900°) and during quenching. Quenching was achieved with an air- and water-cooled jacket in 15–30 min for small reactors (32-mm o.d., 6.3-mm i.d.) and 30–45 min for larger reactors (50-mm o.d., 12.7-mm. i.d.).

Phase studies were effected with praseodymium, neodymium, and terbium oxides. Specifically, the equilibria in the systems A-type Pr_2O_3–H_2O, $PrO_{1.833}$–H_2O, A-type Pr_2O_3–H_2O–oxidizing agents, A-type Pr_2O_3–$Pr(NO_3)_3$–H_2O, amorphous $Pr(OH)_3$–H_2O (all amorphous $Pr(OH)_3$ used in these experiments contained substantial nitrate impurity as discussed below), A-type Pr_2O_3–$Pr_2(CO_3)_3$–H_2O, A-type Pr_2O_3–$Pr(NO_3)_3$–$Pr_2(CO_3)_3$–H_2O, A-type Nd_2O_3–H_2O, $TbO_{1.818}$–H_2O, and C-type Tb_2O_3–$Tb(NO_3)_3$–H_2O were investigated. Substrate materials were prepared from calcined 99.9% praseodymia, 99.999% terbia (American Potash and Chemical Corp., Lindsay Division, Chicago, Ill.), and 99.9% neodymia (Michigan Chemical Corp., Chicago, Ill.). Samples of A-type Pr_2O_3 and C-type Tb_2O_3 were prepared by reduction of the intermediate oxides at 800–900° under 1 atm of hydrogen, while PrO_2 was prepared by heating $PrO_{1.833}$ at 400° in a pressure vessel under 200 atm of oxygen. Hydrated praseodymium and terbium nitrates were prepared by digesting excess oxide with nitric acid, condensing the filtrate, and drying at 100° in air. Amorphous praseodymium trihydroxide, which was precipitated with ammonium hydroxide from a solution of the nitrate, was washed repeatedly and centrifuged before being dried at 120° under inert-gas flow or under vacuum to prevent carbonate contamination. Praseodymium sesquicarbonate octahydrate was prepared by homogeneous precipitation with trichloroacetic acid.[10]

For the equilibration of Pr_2O_3, $PrO_{1.833}$, amorphous $Pr(OH)_3$, Nd_2O_3, or $TbO_{1.818}$ with *excess* water, the samples were allowed to react at selected temperatures and pressures in the regions 300–900° and 340–1360 atm. The Pr_2O_3–H_2O equilibrium was investigated in the presence of two oxidizing agents, 30% hydrogen peroxide and nitrate ion. Nitrate oxidizing media included 1 *M* solutions of HNO_3 or NH_4NO_3 and praseodymium sesquioxide–praseodymium trinitrate–water mixtures in which the praseodymium ion:nitrate ion molar ratio was varied from 2:1 to 3:1. Although welded capsules were generally used, crimped closures were employed in some instances since they avoided the crushing of the capsule during the isobaric cycle. Similar oxidation experiments were conducted with terbium sesquioxide–terbium trinitrate mixtures with metal:nitrate ratios of 3:1 to 4:1.

The effects of temperature, pressure, and composition variations were investigated for the praseodymium–hydroxide–anion phases. Oxide–nitrate mixtures which varied from pure Pr_2O_3 to pure $Pr(NO_3)_3\cdot(2.2 \pm 0.1)H_2O$ (composition based on metal analysis) were equilibrated with water in the ranges 350–500° and 680–1040 atm. Since the larger reactors accommodated up to four capsules simultaneously, several compositions were equilibrated under identical conditions of temperature and pressure. Analogous experiments were conducted for terium sesquioxide–terbium trinitrate mixtures over a limited composition and temperature–pressure range. Mixtures of Pr_2O_3 and $Pr_2(CO_3)_3\cdot 8H_2O$ were also allowed to react over the entire composition range but in a temperature range which extended up to 800°. Praseodymium sesquioxide–praseodymium trinitrate–praseodymium sesquicarbonate mixtures and amorphous trihydroxide samples which were contaminated with occluded nitrate and with carbonate from extended exposure to air were also equilibrated with water in the regions 300–800° and 680–1040 atm.

The growth of single crystals of oxide, hydroxide, and hydroxy anion phases was examined for a variety of conditions. The effectiveness of potential mineralizers (1 *M* solutions of NaOH, Na_2CO_3, NH_4NO_3, $Pr(NO_3)_3$, HNO_3, H_3BO_3, $(NH_4)_2CO_3$, $LiClO_4$, and $NaBF_4$) on $PrO_{1.833}$ and PrO_2 substrates were tested with welded capsules at 800° and 1190 atm. The mineralizing effects of 1 *M* NH_4NO_3 and $Pr(NO_3)_3$ on Pr_2O_3 and $Pr_2(CO_3)_3$ substrates were also observed in the ranges 300–500° and 680–1040 atm.

In addition to oxidation reactions of praseodymium sesquioxide by nitrate in sealed capsules containing seed crystals (approximately 0.005 mm on an edge) of hydrothermally grown praseodymium dioxide, an attempt was made to exploit the transport potential of nitrate oxidation. Seed crystals of dioxide were placed in a perforated platinum foil cup near the welded end of a gold capsule. A substrate mixture of praseodymium sesquioxide and praseodymium trinitrate was maintained by a crimped closure at the other end of the tube. An isobaric heating cycle of 3 weeks at 1190 atm was employed with the seeded sealed end at 750–800° and the nutrient at 650–700°.

Substrates and products of the phase studies and crystal growth procedures were characterized by several techniques. Powder X-ray diffraction data were collected with a Guinier–Hägg forward-focusing camera using Cu Kα (λ 1.5418 Å) radiation and ThO_2 (a_0 = 5.59625 Å) or KCl (a_0 = 6.29300 Å) internal standards; single-crystal data were obtained by equiinclination Weissenberg techniques. Refined lattice constants were calculated from the Guinier data with the computer program of Appleman, *et al.*[11]

Starting materials and products were examined for foreign rare earth contamination and for container reaction by scanning the X-ray fluorescence spectra in the Lα and Lβ regions of the rare earths and gold with a Norelco spectrometer. Cation analyses were obtained by ignition to the stable oxide in air, while anion analyses of hydroxide and hydroxycarbonate phases were effected microgravimetrically by combustion in oxygen and the collection of water and carbon dioxide on anhydrous magnesium perchlorate and Ascarite, respectively. Although attempts were made to remove nitrogen dioxide by reaction with lead dioxide at 180°, reproducible water analyses of hydroxynitrate phases could not be obtained. Nitrate-containing phases were analyzed qualitatively with the $FeNO^{2+}$ brown ring test and semiquantitatively at the ppm level with a Leco Nitrox apparatus. Data in the 3–10 wt % nitrogen range were obtained by linear extrapolation of the ppm calibration values.

Thermal decomposition data were collected with a Cahn RG-10

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microbalance as described previously.[12] Samples were heated to a maximum of 840° under 10^{-8} Torr initial vacuum with heating rates which varied from 0.75 to 1.0°/min. Infrared spectra of hydroxy anion phases were measured with a Beckman IR-12 spectrometer using KBr matrices. Products were also subjected to microscopic examination up to 600× and single crystals were examined under cross-polarized light at magnifications up to 50×.

Hydrothermally prepared praseodymium dioxide samples were analyzed for both metal and oxygen content. Trace contamination by praseodymium trihydroxide was removed by leaching the samples in 0.1–0.2 *M* HNO_3 for up to 24 hr and then washing thoroughly with distilled water. Leached materials were examined by powder X-ray diffraction and then reduced to Pr_2O_3 under hydrogen at 800–900° for gravimetric oxygen determination. The sesquioxide was dissolved in dilute HNO_3 and filtered for the determination of solid contaminants (*e.g.*, small chips of gold introduced by capsule welding and opening) before the filtrate was condensed and ignited to $PrO_{1.833}$ for gravimetric metal analysis.

Results and Discussion

Pr_2O_3–H_2O Equilibria.—The equilibration of A-type Pr_2O_3 with water in the range 400–850° and 340–1190 atm produced only light green polycrystalline samples of praseodymium trihydroxide. The X-ray reflections, indexed on hexagonal symmetry ($a = 6.454 \pm 0.002$ Å, $c = 3.772 \pm 0.001$ Å), were in agreement with previous reports.[13] Chemical analysis for metal and water gave the composition $Pr(OH)_{3.04\pm0.02}$. By analogy to the neodymium and lanthanum systems[5] "dense trihydroxide" was anticipated below 550°, while oxyhydroxide and oxide phases were expected above 550 and 650°, respectively. However, no evidence was found for any of these phases. Although the use of isobaric cycles with slow quenching procedures might result in the rehydration of oxide phases which were stable at high temperatures, additional data suggest that such reactions do not occur. Results which were obtained in this laboratory[14] with a more rapid quenching procedure also indicated that trihydroxide was stable up to 700°. Evidence that rehydration does not occur was obtained from the equilibration of A-type Pr_2O_3 with 1 *M* solutions of NaOH and Na_2CO_3 at 800° and 1190 atm. X-Ray analysis of the products from these experiments showed them to be mixtures of $Pr(OH)_3$ and PrOOH. All reflections not assignable to hexagonal $Pr(OH)_3$ were indexed with monoclinic cell parameters ($a = 6.287 \pm 0.003$ Å, $b = 3.861 \pm 0.002$ Å, $c = 4.397 \pm 0.002$ Å, $\beta = 107.81 \pm 0.09°$) consistent with those reported for NdOOH.[15] For verification of the PrOOH diffraction data, a sample of crystallographically pure PrOOH was prepared by the reaction of a stoichiometric mixture of $Pr(OH)_3$ and Pr_2O_3 in an evacuated quartz ampoule heated at 550–600° for 1 week. If rehydration of the oxide occurred during quenching, only the trihydroxide would have been observed; there is no reason for expecting hydration to stop at the oxyhydroxide intermediate. Since no oxyhydroxide was observed in water, its appearance in basic media is somewhat surprising; however, as Ballman and Laudise have noted,[16] the addition of an acidic or alkaline mineralizer in even low concentrations often shifts the equilibrium temperature of a phase transition by as much as 50°. The present results suggest that hexagonal $Pr(OH)_3$ is the only stable phase in water up to 800° and that the $Pr(OH)_3$–PrOOH phase boundary lies near but slightly above this temperature.

$PrO_{1.833}$–H_2O Equilibria.—Representative results obtained from the equilibration of $PrO_{1.833}$ with excess water in welded gold capsules over a 500° temperature range are listed in Table I. At temperatures below 600° the products were pure $Pr(OH)_3$ plus oxygen gas, but at temperatures above 600°, a black phase, which became an increasingly larger fraction of the products with increasing temperature, was present with smaller quantities of trihydroxide and oxygen. X-Ray diffraction showed the presence of the hexagonal trihydroxide and an fcc phase with $a_0 = 5.393 \pm 0.002$ Å, a value which agrees exactly with that of praseodymium dioxide.[17] Since different reaction times gave identical results and since no $PrO_{1.833}$ remained, the equilibria do not appear to be kinetically limited.

TABLE I

PHASES OBSERVED WHEN $PrO_{1.833}$ AND WATER ARE EQUILIBRATED AT VARIOUS TEMPERATURES AND PRESSURES

Temp, °C	*P*, atm	Products
300	680	$Pr(OH)_3(s) + O_2(g)$
500	680	$Pr(OH)_3(s) + O_2(g)$
500	1040	$Pr(OH)_3(s) + O_2(g)$
600	1040	$Pr(OH)_3(s) + PrO_2(s)(trace) + O_2(g)$
700	680	$Pr(OH)_3(s) + PrO_2(s)(minor) + O_2(g)$
700	1040	$Pr(OH)_3(s) + PrO_2(s)(minor) + O_2(g)$
800	1190	$PrO_2(s) + Pr(OH)_3(s)$
800	1360	$PrO_2(s) + Pr(OH)_3(s)$

The appearance of PrO_2 with $Pr(OH)_3$ is explained as resulting from oxidation of an intermediate oxide upon cooling. A consideration of the relative stabilities of the possible products in pressure–temperature–free energy space indicates that these results are plausible. The height of the free energy surface of $Pr(OH)_3$ apparently increases with temperature such that at some point, in the presence of oxygen, it intersects the oxide surface. Obviously the remaining unanswered question is why the higher oxide surface is lower than that of sesquioxide. Although ΔPV contributions to the free energy are small at low pressures, the pressure effect of hydrothermal conditions appears to be an important factor. If molar volumes, $\bar{V}$, are calculated from crystallographic data[17] for the most dense trivalent oxide A-type $PrO_{1.5}$ and for $PrO_{2.00}$, for example, almost identical values are obtained (0.0233 and 0.0235 l./mol, respectively). The difference in molar volumes of A-type $PrO_{1.5}(s) + 0.25O_2(g)$ and $PrO_2(s)$ obviously favors the formation of dioxide. At 1190 atm and 800°, where $\bar{V}$ of O_2 is 0.085 l./mol[18] and compressibilities of the solid phases are assumed equal, the molar volume of the dioxide is approximately half that of the sesquioxide plus 0.25 mol of oxygen. Because of the complexity of the PrO_x–$Pr(OH)_3$–H_2O system, which is at least trivariant, no attempt has been made to construct a phase diagram.

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Pr_2O_3–H_2O–Oxidizing Agent Equilibria.—The oxidation of trivalent praseodymium under hydrothermal conditions has been achieved with two oxidizing agents, hydrogen peroxide and nitrate ion. The equilibration of A-type Pr_2O_3 with 30% H_2O_2 at 800° in the pressure range 1040–1360 atm produced mixtures of dioxide and trihydroxide. Because of the difficulties encountered with surface-catalyzed and thermally induced peroxide decomposition during capsule welding, this system was not studied extensively; however, the stability fields at the proper oxygen fugacity should be identical with those observed for $PrO_{1.833}$–H_2O equilibria.

Although the equilibration of A-type Pr_2O_3 with water at 800° yielded only trihydroxide, similar experiments with 1 *M* solutions of HNO_3 and NH_4NO_3 produced samples containing black products which were identified by X-ray diffraction as praseodymium dioxide (a_0 = 5.393 ± 0.002 Å). Identical results were observed with water and amorphous $Pr(OH)_3$ substrates in which the presence of occluded nitrate could not be eliminated. Subsequent experiments in which praseodymium sesquioxide–praseodymium trinitrate mixtures were equilibrated with water produced dioxide in the regions 700–900° and 680–1230 atm. Although only trace amounts of dioxide were present with trihydroxide at 700°, it constituted the major product above 800°. After reaction cycles were complete, capsules were distended and contained a relatively high pressure of noncondensable gas in addition to solid products and water. Attempts to equilibrate mixtures with large nitrate to metal ratios resulted in capsule rupture and sample contamination. Confirmation of the dioxide composition for the acid-leached black products was obtained by metal and oxygen analyses, which yielded $PrO_{1.98\pm0.04}$. No indication of capsule interaction was observed either by visual examination or by X-ray fluorescence analysis for gold, but both platinum and palladium–silver capsules reacted noticeably with the substrate at 800°.

The data obtained with nitrate ion as an oxidizing agent suggests that oxidation probably proceeds *via* thermal decomposition of a nitrate, $M(NO_3)_n$, according to reaction 1. This reaction not only provides a source

$$M(NO_3)_n + (n/2)H_2O \longrightarrow M(OH)_n + nNO_2(g) + (n/4)O_2(g) \quad (1)$$

of oxygen, but it also produces a strong oxidizing agent, NO_2, which gives rise to noncondensable gases according to reaction 2. Experimental verification of nitrate

$$NO_2(g) \longrightarrow 0.5N_2(g) + O_2(g) \quad (2)$$

decomposition according to this general scheme was obtained from results with the different cations (M^{n+} = Pr^{3+}, H^+, and NH_4^+, respectively). As would be predicted, praseodymium trihydroxide was produced in the first case and a neutral solution resulted in the case of nitric acid. The ammonium nitrate solution yielded a PrO_2–$Pr(OH)_3$–PrOOH mixture, which is consistent with the production of ammonium hydroxide according to reaction 1 and the effects of basic media on the $Pr(OH)_3$–PrOOH phase boundary. Although gas analyses were not obtained, no evidence for nitrogen dioxide was observed. Thermal decomposition might proceed by a one-step process, but reaction 2 does indicate one substantial driving force for nitrate oxidation. The free energy change for this reaction at 800° is approximately −24 kcal/mol.[19] Although nitrate ion above 700° may serve only as a source of oxygen for equilibria similar to those of the $PrO_{1.833}$–H_2O and Pr_2O_3–H_2O_2–H_2O systems, the oxidizing capacity of nitrate melts[20] and nitrogen dioxide gas[21,22] in the formation of PrO_2 from the lower oxides under anhydrous conditions has been observed previously. Of course, the high pressures would tend to reduce the decomposition of NO_2.

Pr_2O_3–$Pr(NO_3)_3$–H_2O Equilibria.—Although oxidation occurs in sesquioxide–trinitrate mixtures at temperatures above 700°, the nitrate ion is stable at lower temperatures and hydroxynitrates are the equilibrium phases. X-Ray diffraction data showed the existence of three two-phased regions in the composition range between pure oxide and pure nitrate; a trihydroxide–hydroxynitrate region was found between pure Pr_2O_3 and the $3Pr_2O_3$–$Pr(NO_3)_3$ (6:1 OH^-–NO_3^-) composition, while a hydroxynitrate–hydroxynitrate region was observed between the $3Pr_2O_3$–$Pr(NO_3)_3$ and Pr_2O_3–$Pr(NO_3)_3$ (2:1 OH^-–NO_3^-) compositions. Since aqueous solutions of $Pr(NO_3)_3$ did not hydrolyze under these conditions, the second hydroxynitrate was the only solid phase present between the Pr_2O_3–$Pr(NO_3)_3$ composition and pure $Pr(NO_3)_3$. Because of the hygroscopic nature of the trinitrate, accurate stoichiometric combination could not be employed for precise determination of hydroxynitrate compositions. Metal analyses of the phases yielded 59.14 ± 0.10 and 66.1 ± 0.6 wt % Pr, values which correspond with the compositions $Pr(OH)_2NO_3$ (59.08 % Pr) and $Pr_2(OH)_5NO_3$ (65.59 % Pr), respectively. The discrepancy and large uncertainty in the pentahydroxynitrate value arises because samples of this phase generally contained small amounts of trihydroxide contamination. Nitrogen analyses of $Pr(OH)_2NO_3$ and $Pr_2(OH)_5NO_3$ showed 10.1 ± 1.8 and 3.8 ± 0.3 wt % N, respectively, and are not in good agreement with the theoretical values of 5.91 and 3.28%. The quantitative reliability of these data are questionable because of the long extrapolation employed in their determination. The absence of waters of hydration in these phases was evidenced by their low solubility in water, by their ir spectra which showed only one sharp hydroxide frequency like that $Pr(OH)_3$ (3590 cm^{-1}) with no evidence for broad water bands (3400 cm^{-1}) characteristic of hydrated anion phases, and by the thermogravimetric data (Figure 1) which indicated no sample decomposition under vacuum until approximately 250°. Because of the analytical uncertainty, $Pr_3(OH)_8NO_3$ (67.98 wt % Pr) was considered as an alternative for the more hydroxide-rich phase with poorer agreement.

Hydroxynitrate products were highly crystalline green phases. The crystal habit of the dihydroxynitrate was large polyhedra and irregular platelets (0.05–3-mm edges), while that of the pentahydroxynitrate was long thin needles (0.005–0.01 mm × 3–5 mm) which tended to layer parallel to the needle axis. Weissenberg data for $Pr(OH)_2NO_3$ showed monoclinic symmetry (a = 6.442 ± 0.002 Å, b = 3.874 ± 0.002 Å, c = 7.742 ± 0.003 Å, β = 98.75 ± 0.13°) with the possible space groups $P2_1$ or $P2_1/m$ ($0k0$, $k = 2n + 1$ ex-

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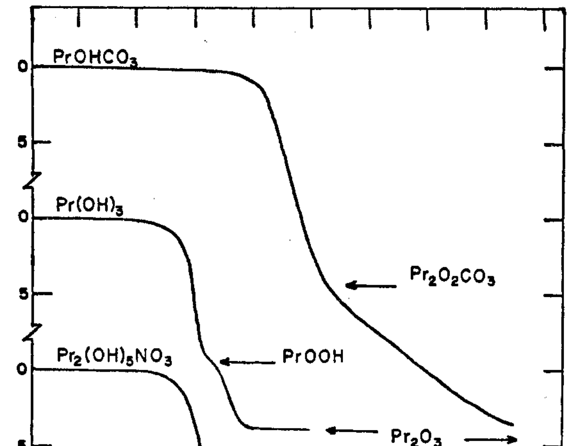

Figure 1.—Thermogravimetric analysis curves for praseodymium hydroxide and certain hydroxycarbonates and nitrates.

tinct). For $Pr_2(OH)_5NO_3$, a hexagonal symmetry (a = 18.410 ± 0.002 Å, c = 3.804 ± 0.001 Å, needle axis collinear with c) was observed, and systematic extinctions ($00l$, $l = 2n + 1$ absent) indicate that the possible space groups are $P6_3$ and $P6_3/m$. The space group $P6_322$ is excluded by Laue symmetry considerations. The systematically high intensities of $h0l$ reflections with $h = 3n$ suggests that the subcell is related to a hexagonal pseudocell in which $A = a/3 = 6.205$ Å and $C = c$. An interesting lattice parameter relationship which exists among $Pr(OH)_3$, $Pr_2(OH)_5NO_3$, and $Pr(OH)_2NO_3$ is indicated in Table II. The close correspondence between the a and c parameters suggests that a structural similarity such as layering is present in these phases. A complete structure determination for the hydroxynitrate phases would be of interest. The analytical and crystallographic data suggest that these hydroxynitrate phases are two members (n = 1, 2) of an ionic substitution series with the general formula $Pr_2(OH)_{6-n}(NO_3)_n$ based on $Pr(OH)_3$ as the terminal (n = 0) member. Careful phase studies in the lower temperature and pressure regions might be successful in producing additional members of this series.

TABLE II
X-RAY DATA FOR PRASEODYMIUM TRIHYDROXIDE AND HYDROXYNITRATES

Phase	a, Å	b, Å	c, Å
$Pr(OH)_3$	6.287	...	3.861
$Pr_2(OH)_5NO_3$	6.205[a]	...	3.804
$Pr(OH)_2NO_3$	6.442	7.742[b]	3.874[b]

[a] Pseudocell: $A = a/3$, $V = V_{\text{true}}/9$, $Z = Z_{\text{true}}/9$. [b] First setting (c axis unique) for monoclinic cell.

Amorphous $Pr(OH)_3$–H_2O Equilibria.—Equilibration of amorphous trihydroxide and water at temperatures below 700° produced essentially pure samples of $Pr_2(OH)_5NO_3$, while at higher temperatures the products were dioxide, trihydroxide, and noncondensable gas. The presence of nitrate in both the substrate materials and the low-temperature products was confirmed by qualitative nitrate tests. Since the products from several different trihydroxide preparations showed only $Pr_2(OH)_5NO_3$ plus small amounts of $Pr(OH)_3$, it appears that precipitation of praseodymium nitrate solutions with concentrated ammonium hydroxide actually produces the amorphous pentahydroxynitrate. Simple occlusion of exactly the proper nitrate ion concentration by several different precipitation and washing procedures seems somewhat unlikely.

Pr_2O_3–$Pr_2(CO_3)_3$–H_2O Equilibria.—The equilibration of all compositions of sesquioxide and sesquicarbonate produced large quantities of carbon dioxide and two solids, $Pr(OH)_3$ and a second phase which was obtained pure from the equilibration of sesquicarbonate with water. Metal, water, and carbon dioxide analyses of the light green phase indicated the monohydroxycarbonate composition $Pr(OH)_{1.02\pm0.02}(CO_3)_{1.00\pm0.01}$. Although samples were generally prepared at 500°, the phase was also obtained at temperatures up to 800° and consequently appears to have a large stability field. No evidence for other hydroxycarbonates was observed. Although the products were generally fine powders, small single crystals were obtained from praseodymium nitrate mineralizer solutions. Weissenberg data indicated that the hydroxycarbonate is hexagonal (a = 4.146 ± 0.001 Å, c = 4.986 ± 0.001 Å) with no observed systematic extinctions. These results are consistent with the conclusions of Sawyer,[23] who proposed the existence of rare earth monohydroxycarbonates analogous to bastnaesite, $RFCO_3$, and suggested that the high-pressure lanthanum trihydroxide reported by Shafer and Roy[5] is actually hexagonal $LaOHCO_3$ (a = 4.214 Å, c = 5.041 Å). A comparison of the diffraction data, which are given for the lanthanum and praseodymium phases in Table III, indicates that the phases are isostructural and that traces of extraneous material(s) may be present in the lanthanum sample. These results suggest that the lanthanum trihydroxide substrates of Shafer and Roy were contaminated with substantial quantities of carbonate, which presumably resulted from exposure of the trihydroxide to atmospheric carbon dioxide.

Pr_2O_3–$Pr(NO_3)_3$–$Pr_2(CO_3)_3$–H_2O Equilibria.—Since neither the hydroxynitrates nor the hydroxycarbonate could account for the high-pressure form of $Nd(OH)_3$,[5] the possibility of a quaternary metal–hydroxide–nitrate–carbonate phase was investigated. Several mixtures containing these components showed that at

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(23) J. O. Sawyer in Technical Progress Report COO-1109-59, DTIE, U. S. Atomic Energy Commission Contract AT(11-1)-1109, July 1971.

TABLE III

COMPARISON OF X-RAY DATA FOR "HIGH-PRESSURE RARE EARTH TRIHYDROXIDES"[5] WITH THOSE OF HYDROXYCARBONATE AND DIOXYCARBONATE

d, Å			
$PrOHCO_3$	High-pressure $La(OH)_3$[6]	$Nd_2O_2CO_3$-II[23]	High-pressure $Nd(OH)_3$[5]
4.980	5.067	7.80	7.885
3.592	3.662	3.897	3.930
...	3.068	3.445	3.456
2.912	2.962	3.365	3.375
2.493	2.518	3.155	3.160
2.072	2.110	2.875	2.970
2.047	2.071	2.600	2.614
1.914	1.945	2.077	2.084
1.794	1.827	1.994	1.993
1.662	1.717	1.931	1.906
1.593	1.616	1.871	1.876
1.508	1.523	1.774	1.774

temperatures up to 500°, the products, which varied with nitrate content, were mixtures of either $Pr(OH)_3$, $Pr_2(OH)_5NO_3$, and $PrOHCO_3$ or $Pr_2(OH)_5NO_3$, $Pr(OH)_2NO_3$, and $PrOHCO_3$. At higher temperatures a new phase (X) was observed in some instances. Between 500 and 600°, amorphous trihydroxide samples contaminated with both nitrate and carbonate produced a mixture of $Pr(OH)_3$ and X; at 800°, sesquioxide–trinitrate–sesquicarbonate gave mixtures of PrO_2, $Pr(OH)_3$, and X. Although noticeable variations were observed in the X-ray diffraction patterns of X prepared at the two temperatures, the data showed a close correspondence to those of high-pressure $Nd(OH)_3$;[5] all of the patterns were indexible on hexagonal symmetry with lattice constants corresponding closely to those of type-II $Pr_2O_2CO_3$ ($a = 4.012$ Å, $c = 15.693$ Å).[23] Refinement of the lattice parameters for the phase prepared hydrothermally at 550 and 800° yielded $a = 4.011 \pm 0.001$ Å, $c = 15.715 \pm 0.008$ Å and $a = 3.986 \pm 0.001$ Å, $c = 15.910 \pm 0.004$ Å, respectively. Since large quantities of the pure phase were not available, analytical data were not collected; however, acidification tests indicated the presence of carbonate and the ir spectra were identical with that reported for type-II $Pr_2O_2CO_3$.[24] The variations in lattice parameters of the $Pr_2O_2CO_3$ samples indicate a sizable composition variation as a function of the temperature and the partial pressures of CO_2 and O_2.

Nd_2O_3–H_2O Equilibria.—The equilibration of A-type Nd_2O_3 with H_2O produced hexagonal $Nd(OH)_3$ ($a = 6.425 \pm 0.001$ Å, $c = 3.739 \pm 0.001$ Å) at temperatures up to 750° and a mixture of $Nd(OH)_3$ and monoclinic NdOOH ($a = 6.242 \pm 0.008$ Å, $b = 3.809 \pm 0.005$ Å, $c = 4.391 \pm 0.004$ Å, $\beta = 108.18 \pm 0.27°$) at 800°. Consequently, the oxide–water phase diagram for neodymium is very similar to that observed for praseodymium. Evidence was not found for the high-pressure $Nd(OH)_3$, NdOOH, and Nd_2O_3 phase fields as had been reported previously[5] although NdOOH is observed at higher temperatures. A comparison of the X-ray diffraction data (Table III) for high-pressure $Nd(OH)_3$[5] and type-II $Nd_2O_2CO_3$ suggests that the phase observed by Shafer and Roy is actually the dioxymonocarbonate. Refinement of their X-ray data on hexagonal symmetry yielded $a = 3.987 \pm 0.008$ Å and $c = 15.69 \pm 0.09$ Å, which are in good agreement with those of type-II $Nd_2O_2CO_3$ ($a = 3.986$ Å, $c = 15.59$ Å).[23]

Analysis of the diffraction data for high-pressure $Sm(OH)_3$[5] suggests that type-II $Sm_2O_2CO_3$ is probably present along with another phase or phases. As in the case of lanthanum, significant carbonate contamination of the neodymium and samarium substrate materials is evident.

Tb_2O_3–$Tb(NO_3)_3$–H_2O Equilibria.—Nitrate oxidation with terbium sesquioxide–terbium trinitrate mixtures also produced higher oxides at 800°; however, in this case, intermediate oxides were obtained instead of the dioxide. X-Ray diffraction data showed that the products were diphasic mixtures of rhombohedral $TbO_{1.714}$ ($a = 6.507 \pm 0.001$ Å, $\alpha = 99.37 \pm 0.02°$) and monoclinic $TbO_{1.818}$ ($a = b = c = 5.285 \pm 0.004$ Å, $\alpha = \beta = 89.5 \pm 0.01°$, $\gamma = 90.00 \pm 0.09°$). These lattice constants are in good agreement with those reported previously.[17] Although the relative quantities of the two oxides appeared to vary with nitrate composition, no evidence for hydrated trivalent phases was detected. This latter observation is consistent with the results obtained when samples of $TbO_{1.818}$ were heated at temperatures up to 800° for extended periods in water and found to be essentially inert to hydrolysis. (It may be remembered that minor quantities of PrOOH were observed after 1 week at 800°.) Such differences between terbium and praseodymium are to be anticipated as a result of increasing oxide acidity with increasing atomic number. In the lower temperature regions, terbium hydroxynitrate phases were observed, but preliminary X-ray data indicate that they are not isostructural with the praseodymium phases.

Crystal Growth and Mineralizer Effects.—Nitrate ion was found to be an effective mineralizer for several praseodymium phases in the temperature range below its decomposition point. In the presence of $Pr(NO_3)_3$ and NH_4NO_3, large single crystals of $Pr(OH)_3$ were obtained at 500° and 680 atm. In crimped capsules which provided large growth volumes, the products of oxide–nitrate compositions between $Pr(OH)_3$ and $Pr_2(OH)_5NO_3$ contained needleshaped trihydroxide crystals ($0.5 \times 0.5 \times 10$–20 mm). After 72 hr, the product from mineralization of A-type Pr_2O_3 with 1 *M* NH_4NO_3 was essentially uniform trihydroxide crystals ($0.05 \times 0.05 \times 1$ mm). Weissenberg data and optical extinction properties indicated that the needle axis was collinear with the hexagonal *c* axis. Small needleshaped crystals ($0.01 \times 0.01 \times 0.5$ mm) of $PrOHCO_3$ were also obtained with $Pr(NO_3)_3$ mineralizer under similar conditions after 3 weeks; some coarsening was also observed with 1 *M* NH_4NO_3 after 72 hr. Again the needle and sixfold crystallographic axes were collinear. The rapid growth of hydroxynitrate crystals is also indicative of the mineralizing effects of nitrate ion.

Investigation of the effects of various mineralizers on praseodymium dioxide showed that under the conditions employed, none appeared to enhance crystal growth. However, the stability of the dioxide was found to vary markedly as a function of mineralizer acidity. Although dioxide was stable in acidic media (H_3BO_3, HNO_3), basic solutions (NaOH, Na_2CO_3) yielded mixtures of $Pr(OH)_3$ and PrOOH. The products from neutral media ($LiClO_4$, $(NH_4)_2CO_3$, $NaBF_4$) were generally mixtures of $Pr(OH)_3$, PrO_2, and unknown phases indicative of reaction between substrate and mineralizer.

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(24) R. P. Turcotte, J. O. Sawyer, and L. Eyring, *Inorg. Chem.*, **8**, 238 (1969).

Small crystals of praseodymium dioxide and intermediate terbium oxides were obtained at 800° and 1190 atm by sealed-capsule equilibration of oxide–nitrate mixtures and hydroxynitrate substrates with water. Dioxide samples with the largest particle sizes were obtained from $Pr_2(OH)_5NO_3$ substrates and exhibited well-defined triangular faces 0.005–0.010 mm on an edge. Simultaneous nucleation apparently began at a large number of sites, and the growth of large crystals was hindered. The invariance of particle size with length of equilibration suggests that crystal growth occurred during a rapid oxidation process and was not achieved or enhanced by mineralization effects. Attempts to employ crimped capsules with large free volumes resulted in nitrate diffusion out of the capsule, reaction with the pressure vessel, and contamination of the sample. Sealed-capsule experiments with Tb_2O_3–$Tb(NO_3)_3$ mixtures yielded $TbO_{1.714}$–$TbO_{1.818}$ products with triangular faces 0.02–0.05 mm on an edge and some indication of octahedral geometry. Oscillation data collected for a small unaligned terbium oxide crystal indicated that the particle was either a single crystal or contained large crystallites. Again, particle size was apparently unaffected by length of heating cycle.

Initial attempts to grow dioxide crystals by transport to and nitrate oxidation at a seed crystal surface have been unsuccessful. Although praseodymium was transported to the sample cup, the product was principally trihydroxide with small quantities of dioxide; no enhancement of crystal size was evident. During the course of this lengthy experiment, extensive nitrate migration through the crimped closure resulted in the growth of large square platelets of an uncharacterized brown phase in the 500–600° region of the reactor. Successful application of this technique will probably necessitate the use of sealed capsules for prevention of nitrate depletion and sample contamination and the control of such parameters as temperature gradients, concentration, and convection.

Thermogravimetric Analysis.—Tga data for the various trivalent praseodymium phases are presented in Figure 1. The observed weight loss percentages agree well with the theoretical values for decomposition to Pr_2O_3. Only in the cases of $PrOHCO_3$, for which decomposition appeared to be incomplete at 840°, and of $Pr_2(OH)_5NO_3$, which apparently contained some trihydroxide contamination, were discrepancies of approximately 1% evident. The trihydroxide and hydroxynitrates all began to decompose at approximately 245°, but only in the case of $Pr(OH)_3$ was an intermediate hydroxide, PrOOH, observed. The oxyhydroxide, which had a transitory existence in the 300–310° range, decomposed to the sesquioxide at 375°. An intermediate phase which agreed well with the $PrO_{1.714}$ composition was observed for $Pr(OH)_2NO_3$ on both the heating and cooling cycles. Although the system was continuously pumped, residual nitrogen dioxide apparently stabilized the intermediate oxide and resulted in reoxidation on cooling. An analogous plateau was observed for $Pr_2(OH)_5NO_3$ but not for $Pr(OH)_3$. The onset of $PrOHCO_3$ decomposition was not observed until approximately 350°. Weight loss was slow, but a noticeable inflection point at 525° is assignable to $Pr_2O_2CO_3$ which gradually decayed to the sesquioxide.

Although the tga data reconfirm the analytical results for all the phases, the results for $PrOHCO_3$ are particularly interesting in that they provide a means for explaining the discrepancies between the present data for the Nd_2O_3–H_2O system and those of Shafer and Roy.[5] The previous report indicated that $Nd(OH)_3$, high-pressure $Nd(OH)_3$, NdOOH, C-type Nd_2O_3, and B-type Nd_2O_3 are stable in water below 1000° and 1360 atm, but in the present experiments, evidence could not be found for any phases other than $Nd(OH)_3$ and NdOOH, which appear to be in equilibrium near 800°. Our experiments have identified the high-pressure phase as $Nd_2O_2CO_3$, but the previously reported phase field and experimental conditions are not consistent with those of $Pr_2O_2CO_3$. The data in Figure 1 suggest that if $Nd_2O_2CO_3$ were produced by thermal decomposition of the hydroxycarbonate, it would be the major product between 400 and 600°, the stability region reported for the high-pressure trihydroxide. Neodymium hydroxycarbonate was presumably present in the $Nd(OH)_3$ phase field below that of the high-pressure phase, but since diffraction data for this region were not reported, its presence cannot be established. These observations imply that $Nd_2O_2CO_3$ and all the higher temperature phases observed by Shafer and Roy are products of thermal decomposition, not of hydrothermal equilibration.

Conclusions

The equilibria observed for rare earth oxide–water systems are not those which had been predicted on the basis of previous data and equilibrium oxygen pressures. The stabilities of praseodymium dioxide and the intermediate terbium oxides in water at elevated temperatures was unexpected and not well understood. Although PrO_2 has a low molar volume and is therefore favored over A-type Pr_2O_3 because of pressure effects, the sesquioxide appears to be particularly unstable in water. Since the trihydroxide–oxyhydroxide phase boundaries of praseodymium and neodymium are not observed until approximately 800°, the stability fields of the rare earth sesquioxides are probably much higher and beyond the range of the present apparatus. Because of the high temperatures and unfavorable pressures apparently necessary to stabilize the trivalent oxide, the hydrothermal preparation of C-type oxides of the basic rare earths is not anticipated. However, the heavier sesquioxides, which are more acidic and have C-type phases with greater thermal stability, might be attained by hydrothermal techniques.

The existence of hydroxynitrate and hydroxycarbonate phases under hydrothermal conditions is consistent with recent reports of rare earth hydroxychloride phases.[25] These results suggest that a wealth of chemistry similar to that of the rare earth–oxy anion phases, RO_nX_m, exists for the analogous hydroxy anion systems, $R(OH)_nX_m$.

The discrepancies between our results and those of Shafer and Roy[5] appear to arise from two sources, contamination and experimental procedure. The presence of carbonate contamination in their trihydroxide substrates is obvious; the presence of extraneous lines in the diffraction patterns of several phases suggests the involvement of materials from the reactor. Our experiments have demonstrated the necessity of using sealed

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[25] F. L. Carter and S. Levinson, *Inorg. Chem.*, **8**, 2788 (1969).

reaction capsules. The most important difference is in the quenching technique. The "leak quenching" procedure employed by Roy and coworkers[5,7] involves first venting the water pressure while the reactor is still at the equilibration temperature and then rapidly cooling the reactor. In relation to this procedure the statement is made that "the success of this method depends on the fact that the hydrates will not decompose rapidly at temperatures near their equilibrium dehydration temperatures in the presence of water." Although this rationale is valid near the dehydration point, it is not particularly relevant to cases in which a phase is at some temperature much higher than its dehydration point. Venting the water pressure under the latter conditions should rapidly produce the phase which is stable at the higher temperature and a water pressure of nominally 1 atm. This type of thermal decomposition accounts for the high-pressure trihydroxide and oxide phase fields observed by Shafer and Roy. It seems that the temperature–pressure diagrams reported by these investigators are incorrect because their pressure axis is a parameter which bears little or no relationship to the equilibration pressure. The essentially vertical equilibrium lines are only indicative of the decomposition temperatures of the various phases at 1 atm water pressure.

One of the most significant results of the present investigation is the characterization of nitrate ion as an oxidizing agent under the appropriate hydrothermal conditions. The *in situ* generation of gaseous reaction products from a solid substrate is a particularly powerful tool which allows convenient and accurate adjustment of oxygen to substrate ratios without elaborate or expensive equipment. Since reactions 1 and 2 proceed in the presence of a variety of cations (H^+, NH_4^+, Pr^{3+}), the method should be highly versatile. A particularly advantageous nitrate source is HNO_3, which generates only H_2O, O_2, and N_2. Although the nitrate decomposition process has not been completely characterized, it appears to be analogous to that of oxalic acid which has recently been employed for *in situ* generation of CO_2 atmospheres.[26]

A second important application of nitrate ion in the hydrothermal synthesis of ionic rare earth phases is its apparent effect as a mineralizer. Results of the present investigation suggest that nitrate might be generally applicable as a noninteracting complexing species for the rare earths at temperatures below 550°. Since essentially nothing is known about the mineralization and transport properties of nitrate, a careful examination of the conditions and limits of its application would be a worthwhile investigation.

The present investigation has resulted in a reexamination of the rare earth oxide–water phase systems and should provide a basis for the investigation of oxide crystal growth and hydroxy anion phase preparation by hydrothermal techniques.

Acknowledgment.—Katie Reimer obtained the ir spectra, Eric Miller analyzed several of the compounds and ran the tga curves, and Frederick M. Delles performed the nitrogen analysis. Their help is gratefully acknowledged. Many discussions with Dr. John Holloway were critical in the construction of the high-pressure apparatus and in obtaining the results. The support of the United States Atomic Energy Commission made these studies possible.

[26] J. R. Holloway, C. W. Burnham, and G. L. Millhollen, *J. Geophys. Res.*, **73**, 6598 (1968).

CONTRIBUTION FROM THE TRANSURANIUM RESEARCH LABORATORY,
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Preparation and Properties of Triindenylthorium Chloride and Triindenyluranium Chloride[1]

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The syntheses of $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ are reported. Evidence is given for the existence of $Th(C_9H_7)_4$, $U(C_9H_7)_4$, $Th(C_9H_7)_2Cl_2$, and $U(C_9H_7)_2Cl_2$. Some properties of the triindenylactinide halide complexes are described. Mass spectra, nmr spectra, infrared spectra, and electronic spectra are given and discussed together with X-ray powder diagrams and results from X-ray single-crystal data obtained with the precession method. $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ are isomorphous. Evidence is given for the presence of metal to indenyl ligand bonds with the C_5-ring parts of the ligands centrally bonded to the metals. The indenyl to uranium bonds seem to be more covalent in character than the indenyl to thorium bond.

Cyclopentadienyl complexes of many lanthanides and actinides are known[5] and have been studied extensively, yet the nature of the ring-to-metal bond is not sufficiently understood. Recently Streitwieser, *et al.*, prepared the first cyclooctatetraenyl compounds of the actinides[6–8] and were able to postulate metal-to-ligand bonds with the participation of f electrons. Their view is supported by the structure of the dicyclooctatetraenylactinides. Determinations of the crystal struc-

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