

such as an empty d^2sp^3 or sf^3d^2 hybrid orbital,³ coupled with back-bonding from the filled metal 4f orbitals into the CO antibonding orbitals. The direct relationship between frequency and coordination can then be explained by the back-bonding. The back-bonding would be more effective with fewer ligands attached to the metal since there are fewer orbitals competing for the available electrons. The metal carbonyl with the lower coordination number would then have the greater back-bonding causing a lower stretching frequency.

In contrast to the variation of the frequencies with coordination, these quantities are almost independent of the nature of the metal for a given coordination. This point is evident from Figure 5. This result is rather surprising in view of the fact that the number of electrons potentially available for back-bonding varies across the lanthanide series. One might conclude either that the 4f electrons play no part in the π bonding of the ligands and the compounds are formed solely by σ donation of lone pairs on the CO or that the 4f electrons make a relatively constant contribution across the series. The former conclusion seems implausible as mentioned above. On the other hand, the contraction of the f orbitals with increasing atomic number across the lanthanide series, which forces these electrons to remain on the metal rather than being delocalized to the ligands, provides a mechanism for understanding the relatively constant net contribution of these electrons to the bonding. The increased number of available back-bonding electrons across the series is almost exactly offset by a decreased capability

of the electrons to participate in such bonding. There is evidence that this compensation effect occurs in other transition metal carbonyls. For example, Ta with five 5d electrons would be expected to form a weaker hexacarbonyl with CO than W, which has six 5d electrons. In fact, the CO stretching frequencies, shown in Figure 5, suggest that the opposite is the case. The stretching frequency of $Ta(CO)_6$ is 20 cm^{-1} lower than $W(CO)_6$, indicating that Ta forms the stronger bond.

If the assignment of the europium carbonyl data is correct, the higher frequency for $Eu(CO)_6$ indicates a lower capacity for back-bonding by the half-filled 4f electron shell.

In summary, all of the spectra of the carbonyl compounds of the lanthanides Pr, Gd, Ho, Nd, and Eu can be interpreted as arising from species of the type $M(CO)_x$, $x = 1-6$. The regularities and trends observed in the spectra can be correlated with the classical π -back-bonding model for metal carbonyls provided that consideration is given to the effect of the lanthanide contraction on the 4f electrons.

Registry No. Pr(CO)₆, 51540-22-8; Pr(CO)₅, 51540-23-9; Pr(CO)₄, 51567-35-2; Pr(CO)₃, 51540-24-0; Pr(CO)₂, 51540-25-1; Pr(CO), 51540-26-2; Nd(CO)₆, 51540-27-3; Nd(CO)₅, 42494-80-4; Nd(CO)₄, 51540-28-4; Nd(CO)₃, 42494-82-6; Nd(CO)₂, 51540-29-5; Nd(CO), 51540-30-8; Gd(CO)₆, 51540-31-9; Gd(CO)₅, 51540-32-0; Gd(CO)₄, 51540-33-1; Gd(CO)₃, 51540-34-2; Gd(CO)₂, 51540-35-3; Gd(CO), 51540-36-4; Ho(CO)₆, 51540-37-5; Ho(CO)₅, 51540-38-6; Ho(CO)₄, 51540-39-7; Ho(CO)₃, 51540-40-0; Ho(CO)₂, 51540-41-1; Ho(CO), 51540-42-2; Eu(CO)₆, 51540-43-3; Eu(CO)₅, 51540-44-4; Eu(CO)₄, 51540-45-5; Eu(CO)₃, 51540-46-6.

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Preparation, Phase Equilibria, Crystal Chemistry, and Some Properties of Lanthanide Hydroxide Nitrates

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The preparative reactions and phase equilibria of solid lanthanide hydroxide nitrates in aqueous media at 400° and 1200 atm have been investigated. Stable members of an anionic substitution series, $Ln_2(OH)_{6-x}(NO_3)_x$ ($Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb, Y$), which include the $x = 2$ ($Ln = La-Dy$ and Y), $x = 0.85 \pm 0.05$ ($Ln = La-Nd$), $x = 0.6 \pm 0.1$ ($Ln = Sm-Yb$), and $x = 0$ compositions, have been characterized. For the smaller ions, the hydrated phases $Ln(OH)_2NO_3 \cdot 2H_2O$ ($Ln = Yb$) and $Ln_2(OH)_5NO_3 \cdot 2H_2O$ ($Ln = Y, Yb$) are observed. X-Ray crystallographic and thermal decomposition data are reported for the polymorphic hydroxide nitrates. Decomposition intermediates include $Ln_2O_2(OH)NO_3$ ($Ln = La-Nd$), $LnONO_3$ ($Ln = La-Gd$), $Ln_3O_4NO_3$ ($Ln = La-Gd$), and $Ln_4O_5(NO_3)_2$ ($Ln = Dy-Yb$); $GdONO_3$ exists in the $PbFCl$ -type structure. The crystal chemistry of the anhydrous hydroxide nitrate phases is discussed and employed in interpreting their structural similarities, phase equilibria, and crystal growth habits.

Introduction

Hydrothermal conditions have been extensively employed in studies of geological systems and in crystal growth procedures,¹ but the investigation of chemical systems in aqueous media at high temperatures and pressures has been limited. A review of the literature shows that neither the preparative inorganic chemistry nor the phase equilibria of simple metal-anion systems have been extensively or systematically investigated. In this respect the lanthanide elements are typical. The hydrothermal phase equilibria of lanthanide oxides were first examined by Roy and coworkers,^{2,3} the preparation

and crystallographic data for the trihydroxides and oxide hydroxides have been reported by Christensen.^{4,5} More recent hydrothermal investigations have been extended to the lanthanide hydroxide anion phases. These anionic systems include fluoride,⁶ chloride,⁷ nitrate,⁸ and carbonate.⁸⁻¹⁰

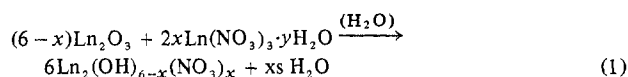
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The cursory study of the trivalent praseodymium hydroxide nitrates⁸ indicated the existence of a homologous series of anion substitution phases with the general formula $\text{Pr}_2(\text{OH})_{6-n}(\text{NO}_3)_n$. Two series members, $n = 1, 2$, were characterized and subsequently employed as reactants for the *in situ* generation of high-pressure oxygen in the growth of praseodymium dioxide single crystals.¹¹ These initial results suggested potential applications of these materials in crystal growth procedures and in elucidation of the crystal chemistry of ionic substitution in solids. In an effort to obtain comprehensive data on the reactions and properties of inorganic materials which are stable in aqueous media at high temperature and pressure, an investigation of the lanthanide hydroxide nitrate systems was initiated.

Experimental Section

The hydrothermal equilibria of the lanthanide-hydroxide-nitrate systems were investigated along isobaric sections of the phase diagrams. Hydroxide to nitrate ratios were varied by combining the calcined sesquioxides (99.9% or higher purity, American Potash and Chemical Corp.) and the corresponding hydrated nitrates according to the equation



For these studies, in which $\text{Ln} = \text{La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb, and Y}$, compositions were generally confined to the limits $0.5 \leq x \leq 2.5$; however, for La, Gd, and Yb, x was varied in increments of 0.25 between $x = 0$ and $x = 4$. Although $\text{PrO}_{1.833}$ was substituted for the sesquioxide in eq 1, the slow reaction of the intermediate terbium oxides with water necessitated their reduction to Tb_2O_3 under hydrogen at 900° before reaction with the nitrate. The hydrated nitrates were prepared by digesting excess oxide in nitric acid, condensing the filtrate, and drying in air at 100° . Samples (0.1–1.0 g) of the selected stoichiometry and water were sealed by welding in gold capsules (4.5-mm i.d. and 20–40 mm in length) and allowed to react for 3–5 days in cold-seal pressure vessels by procedures similar to those described previously.⁸ Although reaction temperatures were confined to the $400 \pm 50^\circ$ range and total applied water pressures were maintained at 1200 ± 30 atm during normal preparative procedures, investigations of the La, Yb, and Nd equilibria were conducted up to $800, 700,$ and 500° , respectively.

The approximate stoichiometries established by eq 1 permitted the identification of equilibrium phases along sections of variable hydroxide to nitrate ratio. Quenched equilibrium phases were removed from the reaction capsule, washed with acetone and/or water, and subjected to crystallographic analysis with a 114.6-mm diameter Haegg-type Guinier camera using $\text{Cu K}\alpha_1$ radiation and silicon ($a_0 = 5.43062 \text{ \AA}$) as an internal standard. Single-crystal diffraction data were obtained with an equiinclination Weissenberg camera using $\text{Cu K}\alpha$ radiation.

Compositions of the equilibrium phases were determined by chemical analyses of crystallographically pure products. Metal contents were determined by ignition to the sesquioxide, and nitrate analyses were obtained by a Kjeldahl method which involved dissolution of the sample in HCl and subsequent reduction in basic solution with Devarda's alloy.¹² Since nitrate could not be reduced in the presence of the lanthanides, the metal ions were first precipitated with $\text{Na}_2\text{C}_2\text{O}_4$ and removed by filtration. The procedure was scaled for analysis of samples containing 0.2–0.5 mmol of nitrogen. Hydroxide contents were determined for compounds in which hydroxide pyrolyzed at a temperature that was lower than and distinctly separated from that of the nitrate ion. Samples were heated at selected temperatures under dry nitrogen, and the product water was determined gravimetrically by collection on anhydrous magnesium perchlorate.

Thermal decomposition reactions of the hydroxide nitrate phases were investigated with a Perkin-Elmer TGS-1 thermobalance. Samples (3–15 mg) were pyrolyzed in Pt boats under dry nitrogen at temperatures up to 775° ; heating rates were linear at 2.5° or $4^\circ/\text{min}$.

Results and Discussion

Phase Equilibria. Reaction of the lanthanide sesquioxides with the corresponding nitrates according to eq 1 proceeded rapidly with hydration of the oxide and formation of metal hydroxide nitrates. The products exhibited the characteristic colors of the trivalent lanthanides and usually contained both single crystals and polycrystalline material. At fixed hydroxide to nitrate ratios the ternary lanthanide-hydroxide-nitrate systems of the lighter elements (La–Dy) behaved in a pseudobinary manner. X-Ray diffraction analysis of the products for the lighter elements (La–Nd) indicated the coexistence of two condensed phases in the nominal composition ranges $0 < x < 1$ and $1 < x < 2$. For Sm through Dy, similar two-phase regions were observed at $0 < x < 0.5$ and $1 < x < 2$. In the heavy lanthanide and yttrium systems, water behaved as an active component, and hydrated hydroxide nitrate phases were observed. These equilibria involved the coexistence of three condensed phases in the regions $0 < x < 0.75$ and $1 < x < 2$. For all compositions with $x > 2$ only one solid phase, that which was observed at $x = 2$, coexisted with an aqueous lanthanide nitrate solution. These results suggest that stable solid phases exist for all the lanthanides at the nominal compositions $\text{Ln}(\text{OH})_2\text{NO}_3$, $\text{Ln}_2(\text{OH})_5\text{NO}_3$, and $\text{Ln}(\text{OH})_3$; however, precise definition of phase compositions from these equilibration studies is precluded by such factors as variability of y in eq 1, high solubility of nitrate in the aqueous phase, and the possibility of capsule leakage during the reaction cycle. Since variations are observed in the equilibrium compositions, crystallographic properties, and pyrolysis reactions across the lanthanide series, these properties are discussed for each nominal composition in the following sections.

$\text{Ln}(\text{OH})_2\text{NO}_3$ Phases ($x = 2$). X-Ray diffraction studies show the presence of both polymorphism and variations in phase equilibria across the lanthanide series. Crystallographic data for various dihydroxide mononitrate phases are presented in Tables I and II. At or below 400° and $x > 2$, all elements from La to Dy plus Y form a monoclinic dihydroxide mononitrate. Single-crystal data for $\text{La}(\text{OH})_2\text{NO}_3$ in Table I and identical results for $\text{Dy}(\text{OH})_2\text{NO}_3$ suggest that these phases are isostructural with monoclinic $\text{Ln}(\text{OH})_2\text{Cl}$,^{7,13,14} the hydroxide nitrates and hydroxide chlorides have similar lattice parameters and identical systematic extinctions, but an uncertainty exists concerning centricity of the space group.⁷ Refined lattice parameters for the $\text{Ln}(\text{OH})_2\text{NO}_3$ phases are presented in Table II. Variations of these parameters with the radii of the Ln^{3+} ions are evident. For La through Nd, the anticipated regular decrease is observed for all parameters, but for Sm through Y the c parameter remains constant within experimental uncertainty. Examination of the monoclinic parameters for the $\text{La}(\text{OH})_2\text{Cl}$ phases⁷ shows that c decreases in a regular way from La to Y. This difference between the nitrate and chloride systems may be explained by consideration of the monoclinic structure¹⁴ which consists of alternating hydrogen-bonded $\text{Ln}(\text{OH})_2^+$ and Cl^- layers approximately perpendicular to $[001]$. It is reasonable that the larger size of the nitrate ion and possibly a more limited hydrogen-bonding ability arising from its nonspherical electron distribution prevent contraction of the lattice along the c axis and give rise to less favorable interaction of the nitrate layer with the constantly

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Table I. Crystallographic Data for Representative Lanthanide Hydroxide Nitrate Phases

Compd	Crystal morphology	Symmetry Molecules/cell X-Ray density	Reflection conditions	Possible space groups
La(OH) ₂ NO ₃	Long rectangular platelets (long axis collinear with <i>a</i>)	Orthorhombic 4 4.062	<i>hkl</i> , <i>h</i> + <i>k</i> = 2 <i>n</i> <i>h0l</i> , <i>l</i> = 2 <i>n</i>	<i>Cmc</i> 2 ₁ <i>Cmcm</i> <i>Ama</i> 2
La(OH) ₂ NO ₃	Irregular platelets (thin dimension ⊥ to <i>a-b</i> plane)	Monoclinic 2 3.966	<i>0k0</i> , <i>k</i> = 2 <i>n</i>	<i>P</i> 2 ₁ <i>P</i> 2 ₁ / <i>m</i>
Yb(OH) ₂ NO ₃ ·2H ₂ O	Prismatic polyhedra	Triclinic 8 4.685	None	<i>P</i> 1 <i>P</i> 1̄
La ₂ (OH) _{5.1} (NO ₃) _{0.9}	Fine needles (needle axis collinear with <i>c</i>)	Hexagonal 10 4.919	<i>00l</i> , <i>l</i> = 2 <i>n</i>	<i>P</i> 6 ₃ <i>P</i> 6 ₃ / <i>m</i> <i>a</i>
Sm ₂ (OH) _{5.4} (NO ₃) _{0.6}	Needles (needle axis collinear with <i>b</i>)	Orthorhombic 10 5.028	<i>0kl</i> , <i>k</i> + <i>l</i> = 2 <i>n</i> <i>hk0</i> , <i>h</i> = 2	<i>Pnma</i>
Tb ₂ (OH) _{5.4} (NO ₃) _{0.6}	Needles (needle axis collinear with <i>b</i>)	Orthorhombic 10 5.322	<i>hkl</i> , <i>h</i> + <i>k</i> = 2 <i>n</i> <i>00l</i> , <i>l</i> = 2 <i>n</i>	<i>C</i> 222 ₁
Yb ₂ (OH) ₅ NO ₃ ·2H ₂ O	Thin platelets (thin dimension ⊥ to <i>a-b</i> plane)	Orthorhombic 1 4.607	<i>hk0</i> , <i>k</i> + <i>l</i> = 2 <i>n</i>	<i>Pnm</i> 2 ₁ <i>Pmmn</i>

^a Space group *P*6₃22 was excluded on the basis of Laue symmetry.

Table II. Lattice Parameters for Ln(OH)₂NO₃ phases^{a,b}

Ln	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>β</i> , deg
La ^c	4.076 (2)	13.070 (8)	7.208 (4)	
La	6.488 (4)	3.962 (3)	7.770 (5)	99.96 (4)
Pr	6.449 (5)	3.881 (5)	7.747 (8)	98.73 (6)
Nd	6.432 (4)	3.839 (4)	7.739 (8)	98.25 (6)
Sm	6.378 (3)	3.781 (2)	7.734 (4)	97.60 (3)
Eu	6.369 (2)	3.753 (2)	7.730 (4)	97.26 (2)
Gd	6.346 (6)	3.728 (4)	7.737 (8)	96.84 (6)
Tb	6.324 (5)	3.701 (3)	7.734 (6)	96.67 (4)
Dy	6.301 (3)	3.669 (2)	7.736 (5)	96.47 (5)
Y	6.265 (5)	3.646 (5)	7.727 (9)	96.25 (8)
Y _{0.7} Yb _{0.3}	6.252 (6)	3.624 (6)	7.732 (9)	96.19 (9)

^a Powder X-ray data will be submitted for publication in the Powder Diffraction File. ^b Uncertainties in last digit given in parentheses. ^c Orthorhombic form.

shrinking Ln(OH)₂⁺ layer lying in the *a-b* plane.

If structural stress exists, ultimate instability of the monoclinic phase is anticipated. For Yb the only product obtained at *x* ≥ 2 is a highly soluble triclinic dihydrate, Yb(OH)₂·NO₃·2H₂O, with *a* = 10.29 (2) Å, *b* = 9.81 (2) Å, *c* = 10.01 (4) Å, α = 84.0 (2)°, β = 112.9 (3)°, and γ = 111.6 (2)°. All attempts to prepare the anhydrous compound under hydrothermal conditions were unsuccessful; however, as the data in Table II indicate, a monoclinic mixed yttrium-ytterbium phase, (Y_{0.7}Yb_{0.3})(OH)₂NO₃, has been prepared. Although the limit to which Yb can be substituted into Y₁₋₂Yb₂(OH)₂NO₃ has not been determined, these results suggest that the monoclinic phase is stable for Er and possibly Tm. The anhydrous ytterbium compound is obtained only by heating the dihydrate in air at 200°. This product has a complex diffraction pattern¹⁵ which is different from that of any of the other Ln(OH)₂NO₃ phases.

Under hydrothermal conditions above 400°, La(OH)₂NO₃ exists in a side-centered orthorhombic modification. Crystallographic data for this polymorph also appear in Tables I and II. The powder X-ray diffraction pattern of this phase agrees with that reported by Daire and Lehuède¹⁶ for La-

(OH)₂NO₃ which was obtained by thermal decomposition of the trinitrate under water vapor. The orthorhombic cell proposed by these investigators has a volume which is approximately 1.7 times that of the cell assigned from Weissenberg data; the relationship between the two is not known. Preliminary results of a single-crystal X-ray structure determination for orthorhombic La(OH)₂NO₃¹⁷ indicate a layered structure which is very similar to that of orthorhombic Y(OH)₂Cl described by Klevtsova and Klevtsov.¹⁸ Although the lanthanum and yttrium lattices are centered and primitive, respectively, the lattice parameters of Y(OH)₂Cl, *a* = 6.244 Å, *b* = 12.645 Å, and *c* = 3.605 Å,⁷ correspond closely with those of La(OH)₂NO₃. Both orthorhombic structures are similar to the monoclinic form and may be represented by alternating layers of Ln(OH)₂⁺ and X⁻ perpendicular to the *b* axis. The dissimilar lattice centerings arise from small differences in the metal and hydroxide positions in the Ln(OH)₂⁺ layers and in the relative positions of alternate layers; however, complete determination of the nitrate structure has been hindered by an inability to refine completely the nitrate positions within the anion layers. Although this difficulty may arise from disordered orientations of the nitrates or from partial replacement of nitrate by hydroxide, possible complications from long-range order are suggested by the presence of an extremely weak superlattice in which *a* = 2*a*_{subcell}, *b* = *b*_{subcell}, and *c* = 3*c*_{subcell}. Attempts to prepare other orthorhombic dihydroxide mononitrates at high temperature have been unsuccessful; at 500° a Nd sample at the *x* = 2 composition gave only the monoclinic product. Studies at significantly higher temperatures are precluded by thermal instability of the nitrate ion.^{8,11} Chemical and thermogravimetric analyses of the *x* ≥ 2 products are consistent with the Ln(OH)₂NO₃ composition. Results for representative phases appear in Table III and Figure 1.

The thermal decomposition reactions have been deduced from the tga data. Different decomposition paths are observed for La through Gd (eq 2) and Dy through Yb (eq 3).

(15) Powder X-ray data will be submitted for publication in the Powder Diffraction File.

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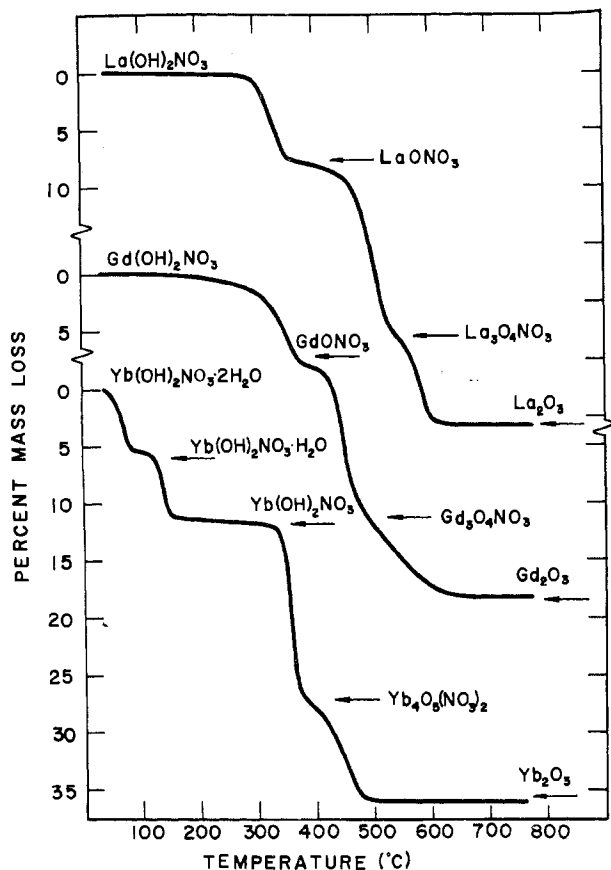
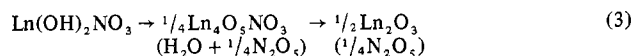
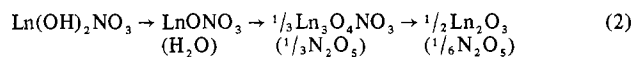
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Table III. Analytical Data for Selected Lanthanide Dihydroxide Mononitrate Phases

Compd	% Ln		% OH		% NO ₃	
	Calcd	Found	Calcd	Found	Calcd	Found
La(OH) ₂ NO ₃ ^a	59.13	59.17 (8)	14.47	14.5 (9)		
La(OH) ₂ NO ₃ ^b	59.13	59.02 (9)			26.39	24.3
Yb(OH) ₂ NO ₃ ·2H ₂ O	56.72	56.41 (7)				

^a Orthorhombic form. ^b Monoclinic form.

**Figure 1.** Thermal decomposition data for selected lanthanide dihydroxide mononitrates.

In these equations successive solid phases are indicated with the composition of the gaseous products below in parentheses. In Figure 1, the theoretical mass loss percentage for each solid intermediate is indicated by a horizontal arrow. Although water was found to be a product of these reactions, observation of the characteristic brown color of NO₂ during pyrolysis and the known instability of N₂O₅ suggest that the pentoxide is not actually a product. Since similarities between the lanthanide oxide nitrates and oxide bromides might be expected from size and charge considerations, the formation of LnONO₃ and Ln₃O₄NO₃ as decomposition intermediates is not surprising; the analogous bromide compositions are well characterized.¹⁹ The only exception to eq 2 was the Pr(OH)₂NO₃ system which formed only the Pr(OH)₂NO₃ intermediate and PrO_{1.833} as the terminal oxide. Its decomposition under nitrogen is markedly dif-

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Table IV. Controlled Pyrolysis and Water Collection Data for Lanthanide Hydroxide Nitrates

Compd	Dec pt, °C	Residue compn	% H ₂ O loss	
			Calcd	Found
La(OH) ₂ NO ₃ ^a	325	LaONO ₃	7.66	7.7 (5)
Gd(OH) ₂ NO ₃	325	GdONO ₃	7.11	7.2 (2)
La ₂ (OH) _{5.1} (NO ₃) _{0.9}	340	La ₂ O ₂ (OH) _{1.1} (NO ₃) _{0.9}	8.56	8.7 (5)
Gd ₂ (OH) _{5.5} (NO ₃) _{0.5}	400	0.5Gd ₂ (OH) ₅ NO ₃ + 0.5Gd ₂ O ₃	6.15	6.9 (6)

^a Orthorhombic form.

ferent from the one-step process observed under vacuum.⁸ The initial step of eq 2 has been verified by constant-temperature pyrolysis and H₂O collection experiments; results for La(OH)₂NO₃ and Gd(OH)₂NO₃ are presented in Table IV. Powder X-ray diffraction data for the monoxide mononitrate products of La and Gd¹⁵ are different from each other and those of the cubic LaONO₃ obtained by pyrolysis of the trinitrate.¹⁶ The GdONO₃ data have been indexed on a tetragonal unit cell, *a* = 3.945 (5) Å and *c* = 9.57 (1) Å. These parameters and the relative reflection intensities indicate that gadolinium monoxide mononitrate has a layered PbFCl-type structure like the lanthanide monoxide monochlorides and monobromides.¹⁹ Verification of eq 3 for the heavier lanthanides has not been possible by either water collection or X-ray diffraction because of the shortness of the intermediate plateaus; however, the formation of Ln₄O₅(NO₃)₂ is consistent with the production of Yb₄O₅CO₃ during the thermal decomposition reactions of ytterbium carbonate²⁰ and formate.²¹

Ln₂(OH)₅NO₃ Phases (0.5 < *x* < 1). At the nominal Ln₂(OH)₅NO₃ composition, the hydroxide nitrate systems are complex. The initial-phase studies indicate a rather large uncertainty, 0.5 < *x* < 1, in the compositions of the Ln₂(OH)_{6-*x*}(NO₃)_{*x*} products, and X-ray data show polymorphism and variations in phase equilibria across the lanthanide series. The lighter metals (La-Nd) form hexagonal phases near the *x* = 1 composition. At somewhat lower values of *x*, the products of Sm through Yb are orthorhombic; however, two different orthorhombic modifications are observed. The Sm product has a unique X-ray pattern and exists in a primitive space group instead of the side-centered lattice exhibited by the heavier elements. In the Y and Yb systems, the involvement of water as an active component is also observed; at the *x* = 1 composition, minor quantities of a second orthorhombic product, Ln₂(OH)₅NO₃·2H₂O, coexist with the anhydrous hydroxide nitrate. Lattice parameters for the Y and Yb dihydrates are *a* = 6.040 (4) Å, *b* = 3.800 (1) Å, *c* = 8.533 (3) Å and *a* = 5.964 (2) Å, *b* = 3.750 (1) Å, *c* = 8.526 (3) Å, respectively. Crystallographic data for the anhydrous Ln₂(OH)_{6-*x*}(NO₃)_{*x*} phases appear in Tables I and V.

Compositions of these hydroxide nitrates have also been determined from chemical and tg analyses. Results of these measurements appear in Table VI and Figure 2. These data indicate that all the phases have *x* < 1. The hexagonal compounds, with *x* = 0.85 ± 0.05, most closely approach the pentahydroxide mononitrate composition. These results account for the apparently high metal contents reported previously for the praseodymium phase;⁸ the observed percentage is in good agreement with the Pr₂(OH)_{5.15}(NO₃)_{0.85} composition. The orthorhombic products have significantly

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(21) R. P. Turcotte, J. M. Haschke, M. S. Jenkins, and L. Eyring, *J. Solid State Chem.*, **2**, 593 (1970).

Table V. Lattice Parameters for $\text{Ln}_2(\text{OH})_{6-x}(\text{NO}_3)_x$ Phases^a

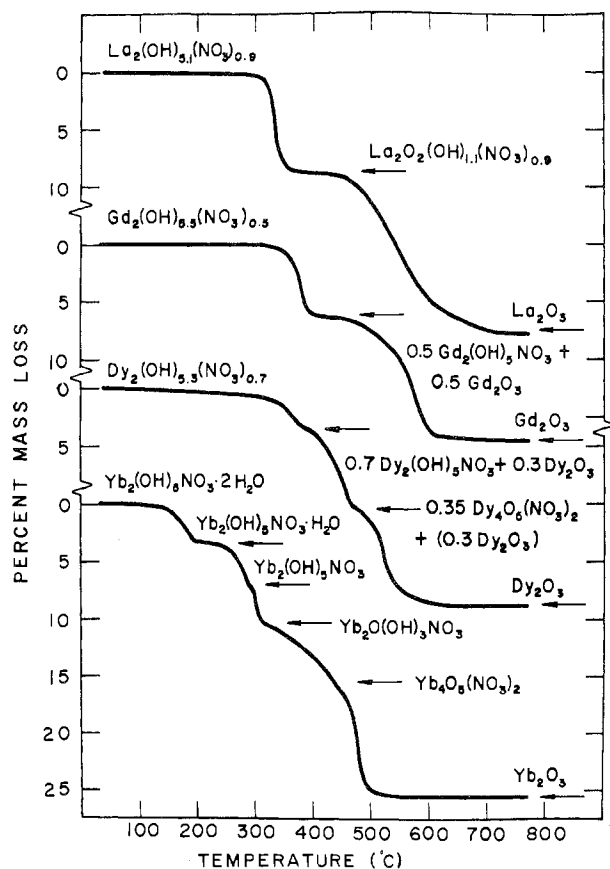
Ln	a, Å	b, Å	c, Å
La	18.601 (9)		3.888 (2)
Pr	18.408 (8)		3.802 (1)
Nd	18.370 (3)		3.803 (6)
Sm ^b	17.19 (2)	3.693 (3)	18.10 (2)
Eu	18.729 (8)	3.733 (1)	16.647 (4)
Gd	18.631 (7)	3.707 (1)	16.618 (5)
Tb	18.600 (9)	3.672 (4)	16.530 (8)
Dy	18.497 (7)	3.653 (2)	16.484 (7)
Y	18.403 (8)	3.624 (3)	16.424 (9)
Yb	18.223 (9)	3.561 (2)	16.261 (8)

^a See ref 15. For hexagonal forms (La–Nd), $x = 0.85 \pm 0.05$; for orthorhombic forms (Sm–Yb), $x = 0.6 \pm 0.1$. ^b Sm forms a unique orthorhombic lattice.

Table VI. Analytical Data for $\text{Ln}_2(\text{OH})_{6-x}(\text{NO}_3)_x$ Phases

Ln	% Ln		% NO ₃		x in $\text{Ln}_2(\text{OH})_{6-x}(\text{NO}_3)_x$
	Calcd ^a	Found	Calcd ^a	Found	
La	66.38	65.8 (5)	12.74	12.7 (2)	0.86 (3)
Sm	70.34	69.9	7.98	7.0	0.55
Eu	70.20	70.9	8.59	9.3	0.60
Gd	71.49	71.8 (5)	7.33	7.4 (4)	0.52 (3)
Dy	70.74	70.6	9.72	9.7	0.72
Yb	72.77	72.6 (3)	7.82	7.9 (9)	0.61 (5)

^a Calculated values based on x listed in the last column.

**Figure 2.** Thermal decomposition data for selected $\text{Ln}_2(\text{OH})_{6-x}(\text{NO}_3)_x$ Phases.

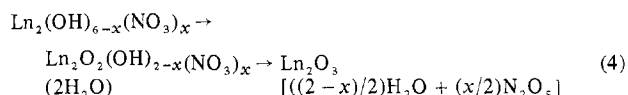
lower nitrate contents with $x = 0.6 \pm 0.1$. Although the hexagonal and orthorhombic phases are conveniently described as pentahydroxide mononitrates in this report, neither the ideal $\text{Ln}_2(\text{OH})_5\text{NO}_3$ ($x = 1$) nor the $\text{Ln}_4(\text{OH})_{11}\text{NO}_3$ ($x = 0.5$) stoichiometries are observed. The sizable and seemingly random variations of x across the lanthanide series suggest that these hydroxide nitrates are more accurately classified

as simple anion substitution phases than as integral homologous series systems.

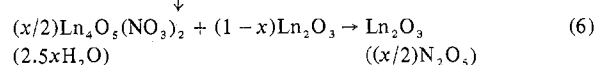
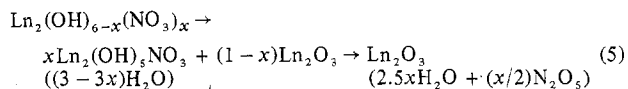
The variations in stoichiometry observed across the series suggest that regions of variable composition might be observed within each lanthanide system; however, indications of gross stoichiometric variations are not evident. Within the experimental uncertainties listed in Table V, the lattice parameters are identical in the two phase regions bracketing the $\text{La}_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86}$ and $\text{Yb}_2(\text{OH})_{5.39}(\text{NO}_3)_{0.61}$ compositions. Although the parameters are apparently independent of reaction temperature, the effects of water fugacity and the effectiveness of sample quenching are not known. Since fluctuations in x for these $\text{Ln}_2(\text{OH})_{6-x}(\text{NO}_3)_x$ phases neither arise because of broad single-phase regions nor correlate with electronic configurations, ionic radii, or basicities of the lanthanides, the observed composition variations cannot be explained.

Characterization of the orthorhombic $\text{Ln}_2(\text{OH})_5\text{NO}_3 \cdot 2\text{H}_2\text{O}$ phases has been complicated by difficulties in obtaining sufficient quantities of pure sample for complete chemical analysis. Only metal contents have been determined. *Anal.* Calcd for $\text{Yb}_2(\text{OH})_5\text{NO}_3 \cdot 2\text{H}_2\text{O}$: Yb, 65.41. Found: Yb, 65.3 (9). These data are not conclusive because the metal content of $\text{Yb}(\text{OH})_2\text{NO}_3$ is 64.32%. The coexistence of either of these phases with $\text{Yb}(\text{OH})_2\text{NO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Yb}_2(\text{OH})_{5.4}(\text{NO}_3)_{0.6}$ is allowed by the phase rule. The tg data, which are given for the ytterbium compound in Figure 2, are readily assigned to rational decay products of the dihydrate. The initial loss of 1 mol of H_2O at a comparatively low temperature (150°) and the subsequent steps involving loss of a second mole of H_2O , a third mole of H_2O , 1.5 mol of H_2O , and ultimately 0.5 mol of N_2O_5 agree well with the data. Assignment of the mass loss steps to products of $\text{Yb}(\text{OH})_2\text{NO}_3$ requires the existence of several rather irrational intermediates. Preliminary results of a single-crystal X-ray structure determination²² also support the dihydrate composition.

Three different thermal decomposition processes are observed for the anhydrous pentahydroxide mononitrates. The general reactions for La through Nd (eq 4), Eu and Gd



(eq 5), and Dy through Yb (eq 6) are given. Representative



tg curves for each reaction type appear in Figure 2. The results of water collection experiments in Table IV substantiate the assignment of decomposition intermediates in eq 4 and 5. Powder X-ray diffraction data¹⁵ which were collected for the La and Gd intermediates produced at 340 and 400°, respectively, are consistent with the proposed processes. The data for $\text{La}_2\text{O}_2(\text{OH})_{1.1}(\text{NO}_3)_{0.9}$ have been indexed on the basis of a tetragonal cell with $a = 9.71$ (7) Å and $c = 6.30$ (5) Å; a layered orthogonal structure is to be expected for systems containing Ln_2O_2^+ ions.²³ The product from Gd_2

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(23) P. Caro, *J. Less-Common Metals*, 16, 367 (1968).

$(\text{OH})_{5.5}(\text{NO}_3)_{0.5}$ showed only a diffuse diffraction pattern for C-type Gd_2O_3 , a result which strongly supports the intermediate disproportionation and oxide formation processes proposed in eq 5 and 6. For the Sm phase, the decomposition steps are poorly resolved and suggest that pyrolysis occurs simultaneously according to eq 4 and 5.

$\text{Ln}(\text{OH})_3$ and $\text{LnO}(\text{OH})$ Phases ($x = 0$). For $0 < x < 0.5$, the solid phases which coexist with the pentahydroxide mononitrates vary across the series. The hexagonal trihydroxides and monoclinic oxide hydroxides are observed for La through Gd and Dy through Yb, respectively; the close agreement of their lattice parameters with those reported previously²⁴ suggests that the miscibility of nitrate in these phases is negligible. In the presence of the pentahydroxide mononitrates, the rapid growth of $\text{Ln}(\text{OH})_3$ and $\text{LnO}(\text{OH})$ single crystals (maximum dimensions >1 mm) is observed.

High-Temperature Equilibria. At high temperatures, the hydroxide nitrates are unstable. In the La system at 800° , the only solid product is $\text{La}(\text{OH})_3$. Above 550° the Yb phases are unstable, but the equilibrium products, which may include such compositions as oxide hydroxide nitrates similar to $\text{Yb}_3\text{O}(\text{OH})_5\text{Cl}_2$,⁷ have not been characterized. The evolution of gaseous products indicates that nitrate ion has decomposed with the formation of nitrogen and oxygen⁸ and suggests that the trivalent oxides of the heavier lanthanides might be stabilized by *in situ* oxygen generation procedures.¹¹

Conclusions

Similarities between the hydroxide nitrate systems in hydrothermal media and in basic lanthanide nitrate solutions²⁵ are evident. Precipitation experiments involving potentiometric and conductometric measurements have indicated the compositions $\text{LaOH}(\text{NO}_3)_2$, $\text{La}(\text{OH})_2\text{NO}_3$, $\text{La}_2(\text{OH})_5\text{NO}_3$, $\text{La}_5(\text{OH})_{13}(\text{NO}_3)_2$ ($\text{La}_2(\text{OH})_{5.2}(\text{NO}_3)_{0.8}$), and $\text{La}_5(\text{OH})_{14}\text{NO}_3$ ($\text{La}_2(\text{OH})_{5.6}(\text{NO}_3)_{0.4}$), which are similar to those reported in this work. The inability to reduce nitrate in basic solutions of the lanthanides results because of its precipitation as an amorphous hydroxide nitrate.

The emerging structural features of the lanthanide hydroxide chlorides^{13,14,18} and hydroxide nitrates^{17,22} are important in understanding and interpreting the crystallographic properties, crystal growth habits, and phase equilibria of the hydroxide nitrate systems. Examination of the diffraction data for the anhydrous phases in Tables II and V shows: (a) all lattices have one short axis which decreases regularly with Ln^{3+} radius from approximately 4.0 Å at La to approximately 3.5 Å at Yb; (b) this short axis is always of twofold or higher symmetry, *i.e.*, an orthorhombic axis, the *b* axis in monoclinic systems, or *c* axis in hexagonal systems; (c) one of the axes perpendicular to the short lattice dimension is always 6–7 Å in length or some integral multiple of that distance. The key structural feature common to all these phases appears to be the layering of alternate sheets of hydroxide-coordinated lanthanide ions, $\text{Ln}(\text{OH})_2^+$, and anion, X^- , in the sequence $\text{Ln}(\text{OH})_2^+ \text{X}^- \text{Ln}(\text{OH})_2^+ \dots$. One lattice vector, the short crystallographic dimension, appears always to lie within the plane of the layers. The other lattice vectors are orthogonal to the first; one always lies perpendicular to the alternating layers in orthorhombic systems and nearly perpendicular in monoclinic and hexagonal systems, while the orientation of the third vector is of course determined by the total structural symmetry. Ob-

servations (a) and (b) are consequences of the coincidence of the short vector with the layering plane. A minimum twofold symmetry arises because of the inherent twofold nature of the layers. The short lattice dimension corresponds to the unit translation distance of a lanthanide hydroxide coordination polyhedron in a $\text{Ln}(\text{OH})_2^+$ layer. This interpretation also accounts for the regular variations of the short parameter with Ln^{3+} radius. Observation (c) arises because the approximate separation of successive $\text{Ln}(\text{OH})_2^+$ layers is 6–7 Å; the observed lattice parameter is of course increased by nonorthogonality of the lattice vector with the layering planes and by increased ionic radii. Multiple parameters naturally arise when successive cation or anion layers are dissimilar.

The layer structure also accounts for the crystal growth habits given in Table I. In all cases, the most rapid growth direction is coincident with the short lattice parameters, while the least rapid growth occurs in the direction perpendicular to the layers. Extension of existing layers containing the short axis is understandably more facile than the addition of new layers which appear to be rather weakly associated by hydrogen bonding.¹⁴

The essential features of the hydroxide nitrate phase equilibria may also be explained by the stability of the layered $\text{Ln}_2(\text{OH})_{6-x}(\text{NO}_3)_x$ structures. Although $\text{LaOH}(\text{NO}_3)_2$, for which $x = 4$, has been precipitated from aqueous solution,²⁴ a maximum value of $x = 2$ is found in hydrothermal media. In a layered structure, the $x = 2$ composition, $\text{Ln}(\text{OH})_2\text{NO}_3$, is achieved by simple alteration of $\text{Ln}(\text{OH})_2^+$ and NO_3^- layers. Any value of $x < 2$ may easily be obtained by statistical or random replacement of nitrate by hydroxide. A continuous solid solution could theoretically exist from $\text{Ln}(\text{OH})_2\text{NO}_3$ to $\text{Ln}(\text{OH})_3$; however, only one narrow intermediate composition is observed in the lanthanide systems. The reason for the random composition variations in the intermediate phases is not understood, but the apparent instability or high solubility of phases with $x > 2$ is readily explained. With the charge-balance restrictions of the system, the only mechanism for increasing x in the $\text{Ln}(\text{OH})_2\text{NO}_3$ structures is nitrate replacement of hydroxide in the $\text{Ln}(\text{OH})_2^+$ layers, a process which obviously disrupts the metal coordination sphere and presumably destroys the stability of the $\text{Ln}(\text{OH})_2^+$ sheets. Under hydrothermal conditions, a high solubility is expected for any nitrate-containing phase which does not have the layered structure or similar rigid network. A test of these proposals could be made by examination of the phase equilibria in other $\text{Ln}-\text{OH}-\text{X}$ systems in which X is large compared to hydroxide, *e.g.*, $\text{X}^- = \text{Cl}^-, \text{Br}^-$.

An interest in these materials is more than academic. As Carter and Levinson have noted for the isostructural hydroxide chlorides,⁷ the layered hydroxide nitrates may show ferromagnetic and ferroelectric properties as well as magnetic clustering. Evidence for a more tangible spin-off lies in the multifold enhancement of lanthanide crystal growth rates in nitrate systems. Although the mineralizer effects of hydroxide ion in lanthanide systems has been studied,²⁶ complex ion formation by other anionic species has apparently not been investigated. In hydrothermal media the solubilities of lanthanide ions in the fluid phase are presumably increased by formation of $\text{Ln}(\text{NO}_3)_n^{(n-3)-}$ species. The present investigation should provide a base for further in-

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vestigation of the chemistry and properties of hydrothermal materials.

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Registry No. La(OH)₂NO₃, 12507-74-3; Pr(OH)₂NO₃, 36306-07-7; Nd(OH)₂NO₃, 51364-99-9; Sm(OH)₂NO₃, 51365-00-5; Eu(OH)₂-

NO₃, 51365-01-6; Gd(OH)₂NO₃, 51365-02-7; Tb(OH)₂NO₃, 51365-03-8; Dy(OH)₂NO₃, 51381-69-2; Y(OH)₂NO₃, 51365-04-9; Yb(OH)₂NO₃, 51365-05-0; Yb(OH)₂NO₃·2H₂O, 51365-06-1; La(OH)₃, 14507-19-8; Pr(OH)₃, 16469-16-2; Nd(OH)₃, 16469-17-3; Sm(OH)₃, 20403-06-9; Eu(OH)₃, 16469-19-5; Gd(OH)₃, 16469-18-4; Tb(OH)₃, 12054-65-8; Dy(OH)₃, 1308-85-6; Y(OH)₃, 16469-22-0; Yb(OH)₃, 16469-20-8; La(NO₃)₃, 10099-59-9; Pr(NO₃)₃, 10361-80-5; Nd(NO₃)₃, 10045-95-1; Sm(NO₃)₃, 10361-83-8; Eu(NO₃)₃, 10138-01-9; Gd(NO₃)₃, 10168-81-7; Tb(NO₃)₃, 10043-27-3; Dy(NO₃)₃, 10143-38-1; Y(NO₃)₃, 10361-93-0; Yb(NO₃)₃, 13768-67-7; Y₂(OH)₂NO₃·2H₂O, 51391-32-3; Yb₂(OH)₂NO₃·2H₂O, 51391-33-4; GdONO₃, 14835-96-2; La₂O₂(OH)NO₃, 51391-31-2.

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Sulfite-, Acetate-, and Nitrate-Catalyzed Substitution Reactions of Chromium(III)^{1a}

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Oxygen-bonded sulfite, nitrate, and acetate labilizations of ligands coordinated to chromium(III) in aqueous solution have been investigated. Kinetic and stoichiometric measurements have been made for sulfite labilizations of acetato- and azidoaquo chromium(III) species, acetate labilization of acetatopentaaquo chromium(III), and nitrate labilizations of acetato- and fluoroaquo chromium(III) species. The rate law terms for the catalyses are of the general form $k[\text{oxy anion}][\text{Cr complex}][\text{H}^+]$. The results are interpreted in terms of cis effects arising from seven-coordinated intermediates or transition states formed by chelation of the labilizing oxy anion; the positive hydrogen ion dependence is attributed to protonation of the basic leaving group.

Introduction

Oxy anions have recently been shown to catalyze metal ion substitution reactions.²⁻¹⁰ It appears that the labilizing oxy anion is usually coordinated to the metal in cobalt(III) complexes, where S-bonded^{2-4,11} sulfite exerts primarily a trans effect,^{2,3} and in chromium(III) complexes, where O-bonded nitrite,⁵ nitrate,⁶ and carboxylates^{7,8} exert primarily cis effects and O-bonded sulfite⁹ exerts both cis and trans effects. Most of the chromium(III) studies that have been described previously⁵⁻⁹ have involved leaving groups not likely to be protonated in the transition state (chloride, bromide, thiocyanate, water, ammonia), although one study¹⁰ indicated that sulfite may be protonated in the bisulfite-catalyzed aquation of sulfitepentaquoiron(III) and that azide may be protonated in the bisulfite-catalyzed aquation of azidopentaaquo chromium(III).

The purpose of the work described in this paper was to learn whether the basicity of the leaving group in chromium(III) aquation reactions generally affects the form of the

empirical rate law for oxy anion catalysis and to obtain evidence regarding any associated changes in mechanism.

Experimental Section

Reagents. Acetatopentaaquo chromium(III) solutions were obtained by chromium(II) reduction of acetatopentaaquacobalt(III), as described by Deutsch and Taube.¹² Solutions of acetatopentaaquacobalt(III) were prepared in a sequence beginning with carbonatopentaaquacobalt(III) nitrate, made by the method of Lamb and Mysels;¹³ solutions of the carbonato complex were treated with perchloric acid and the water ligands in the resulting aquopentaaquacobalt(III) ions were replaced with acetate in the procedure reported by Sebera and Taube.¹⁴ The chromium(II) solutions were obtained by zinc reduction of hexaaquo chromium(III) perchlorate¹⁵ which was the product of hydrogen peroxide reduction of potassium dichromate.¹⁶

Each of three separate attempts to prepare acetatopentaaquo chromium(III) by equilibration of hexaaquo chromium(III) and acetate led to a species (or a mixture) elutable with 1.0 M electrolyte from Dowex 50W-X8 cation-exchange resin. The spectrum of the elutable species has maxima at 418 and 509 nm, with absorption coefficients of 16.7 and 28.1 (g-ion of Cr)⁻¹ cm⁻¹, respectively. A more complete characterization of this species was not attempted; it may be a chelated acetato complex but it is more probably the polynuclear species mentioned earlier.¹²

Azido- and fluoropentaaquo chromium(III) perchlorate solutions were prepared by the equilibration methods described in separate papers by Swaddle and King.^{17,18} Chloropentaaquo chromium(III) perchlorate solutions were prepared by partial aquation of commercial CrCl₃·6H₂O followed by ion-exchange separation using the procedure of Gates and King.¹⁹ Solutions of cyanopentaaquo chromium(III) perchlorate were made by partial aquation of potassium hexacyano-

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