Contribution from the Chemistry Division, Argonne National Laboratory,
Argonne, Illinois 60439

A New Series of Anhydrous Double Nitrate Salts of the Lanthanides. Structural and Spectral Characterization[1]

W. T. CARNALL,* S. SIEGEL, J. R. FERRARO, B. TANI, and E. GEBERT

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Anhydrous double nitrates of the lanthanides with potassium have been obtained in crystalline form. Crystallographic and spectroscopic studies are reported. $K_3Pr_2(NO_3)_9$ is cubic, with $a = 13.52$ (1) Å and space group O^6-$P4_332$. The experimental density is 2.53 (3) g cm^{-3} and the computed value is 2.57 (1) g cm^{-3} for four formula weights. The structure was solved with 529 independent reflections recorded with an automatic diffractometer utilizing the θ–2θ scan method. A least-squares refinement based on all reflections and with isotropic temperature factors for all atoms gave $R = 0.058$. Each Pr atom is surrounded by twelve oxygen atoms belonging to six nitrate groups which form a distorted icosahedron. The nitrates form two nonequivalent sets, each with its distinct bonding characteristics to the Pr and K atoms. Infrared and Raman studies confirm a strong interaction between the oxygen atoms and the lanthanide ion and indicate typical bidentate bonding. The optical spectrum of $K_3Nd_2(NO_3)_9$ was investigated at ambient and at high pressure. The enhancement of hypersensitive transitions was noted and discussed in comparison to other crystals in which the Nd^{3+} exists in low site symmetries.

Introduction

General Information. While anhydrous lanthanide nitrates are known,[2] double nitrate salts prepared under anhydrous conditions are much less common. In the course of investigations of the chemistry and spectra of lanthanide nitrates in anhydrous molten $LiNO_3$-KNO_3 eutectic we were able to grow crystals in the melt at 170-180°. Analysis revealed a general formula $K_3Ln_2(NO_3)_9$ for the lighter lanthanides and suggested a shift to other structures for the heavy end of the series. While large (>5 mm^3) single crystals of good optical quality could be grown for the Pr and Nd salts, only masses of numerous smaller crystals were obtained for heavier lanthanides. We report here the results of crystallographic as well as spectroscopic investigations of the bonding exhibited in the samples isolated.

Preparative Techniques. Crystals were grown in molten $LiNO_3$-KNO_3 eutectic (65 mol % K) in the temperature range 170-190°, containing up to 2 *M* Ln^{3+}. The clear molten salt solutions were purged with dry N_2 at ∿220° and then lowered to the crystal growing temperature and maintained for several weeks. Evidence for the rapid expulsion of H_2O from the system during the pretreatment was obtained by following the decrease to a stable minimum of the strong OH-overtone absorption band near 1.9 μ.

While analyses were performed on samples of each of the lanthanides studied, the results for Pr and Nd were considered to be most accurate because small sections of clear crystalline material could be broken out of larger pieces. Thus, possible occlusion of salt from the solvent matrix could be minimized. Typical results showed the composition by weight to be as follows.

	$K_3Pr_2(NO_3)_9$		$K_3Nd_2(NO_3)_9$	
	Exptl	Calcd	Exptl	Calcd
% K	13.3, 12.07	12.3	11.9	12.2
% Pr	30.7, 29.0	29.4		
% Nd			29.4	29.9
% Li	<0.04		<0.04	

The analysis of the Er salt suffered from possible occlusion of excess melt. The average of three determinations gave ∿16% K, 23.9% Er, and 60% NO_3, but recent structural analysis gives the formula $K_2Er(NO_3)_5$. Density measurements in a micropycnometer using toluene yielded 2.53 g cm^{-3} for $K_3Pr_2(NO_3)_9$ and 2.53 g cm^{-3} for $K_3Nd_2(NO_3)_9$. and 2.53 g cm^{-3} for $K_3Nd_2(NO_3)_9$.

Structural and Spectroscopic Methods. A complete structural analysis of $K_3Pr_2(NO_3)_9$ was carried out using single-crystal methods. The compound is cubic and the Nd and Sm salts are believed to be isostructural, insofar as this can be judged from X-ray powder diffraction data. The Er salt has been found to be monoclinic and is currently being investigated. Preliminary results indicate that the Tm salt exhibits a cell different from that of the Er compound, but the powder diffraction patterns obtained to date have been of poor quality. Cell dimensions for these compounds are as follows.

$K_3Pr_2(NO_3)_9$	13.52 (1) Å	Cubic
$K_3Nd_2(NO_3)_9$	13.50 (2) Å	Cubic
$K_3Sm_2(NO_3)_9$	13.43 (2) Å	Cubic
$K_2Er(NO_3)_5$	$a = 7.93$ (1) Å $b = 11.92$ (1) Å $c = 14.26$ (4) Å $\beta = 102.81$ (6)°	Monoclinic

Absorption spectra in the visible and near-infrared regions were measured in a Cary Model 14R spectrophotometer at room temperature. Large single-crystal samples had previously been placed in thin-walled quartz tubes in a dry atmosphere and sealed.

The infrared spectra were obtained using an opposed diamond-anvil high-pressure cell and a Beckman IR-12 spectrophotometer, interfaced with a 6X beam condenser. The solid was loaded in a drybox containing a dry nitrogen atmosphere. Details of the technique have been previously published.[3]

The Raman spectra were obtained on the solids with a Spex 1400 Raman spectrophotometer using a Coherent Co. krypton laser source (6471-Å line) equipped with a cooled ITT FW 130-S-20 detector having a slit-shaped sensitive area. The slit width used was 4 cm^{-1}.

Pressure studies were also carried out in the visible region using the above-mentioned opposed diamond-anvil cell. The material was pressure cycled several times. The pressure was alternately increased and decreased to distribute the material evenly between the anvils. During this pressure cycling, the sample was observed under a microscope.

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] A. Walker and J. R. Ferraro, *J. Chem. Phys.*, **43**, 2689 (1965).

[3] J. R. Ferraro, S. S. Mitra, and C. Postmus, *Inorg. Nucl. Chem. Lett.*, 2, 269 (1966); L. J. Basile, C. Postmus, and J. R. Ferraro, *Spectrosc. Lett.*, 1, 189 (1968).

Crystallographic Investigation

The symmetry of $K_3Pr_2(NO_3)_9$ (mol wt 957.1) as shown by Weissenberg patterns is cubic, with $a = 13.52$ (1) Å. All reflections are observed except $h00$, $h \neq 4n$. The space group is therefore O^6-$P4_332$ or O^7-$P4_132$. Space group O^6 was chosen for the study. The observed density is 2.53 g cm^{-3}, leading to a computed value of 2.57 (1) g cm^{-3} for four formula weights in the unit cell.

Data were collected with a GE XRD-490 computer-controlled diffractometer by the θ–2θ scan method utilizing Zr-filtered Mo $K\bar{\alpha}$ radiation (λ 0.71069 Å). Reflections hkl and $\overline{hkl}$ $(l > k > h)$, totaling 1098 in number and corresponding to 529 symmetry-non-equivalent reflections, were recorded for scattering angles up to 2θ = 52°.

Approximately 63 reflections of zero or weak intensity were reevaluated by recording the diffraction maxima on a strip chart, using a 2θ scanning rate of 2°/min. The line width and background of a reflection were carefully assessed and the intensity was evaluated with a planimeter. Reflections too weak to determine in this manner were given intensity values corresponding to a lower limit of observation. All intensities were then normalized relative to the primary set of data.

The linear absorption coefficient based on Mo Kα radiation was only 47.9 cm^{-1}. Nevertheless, a small sphere was ground to give $\mu r = 1.2$, and a spherical absorption correction was accordingly used. Lorentz and polarization corrections were applied in the usual manner.

The eight Pr atoms can be located in one set of eightfold positions with one coordinate to be evaluated or in two sets of fourfold positions with no unknown parameters. Trial intensity considerations ruled out the fourfold positions. The positions of the Pr atoms were determined from a three-dimensional Patterson function plot. This analysis was obtained from a modified version of the Sly and Shoemaker Fourier program[4] and led to a coordinate value of $x \approx 0.3$. The K atoms were deduced from a two-dimensional Fourier synthesis which shows a center of symmetry in projection. This analysis was based on signs of the structural factors determined from the Pr positions. The contribution of the K atoms was then added to that of the Pr and subsequent Fourier syntheses led to the identification of the remainder of the atoms.

Scattering curves for all atoms were taken from tabulated values given in ref 5a and anomalous dispersion corrections reported by Cromer[5b] were applied to the Pr scattering.

Final coordinates were obtained from a least-squares analysis derived from the Busing, Martin, and Levy ORFLS least-squares program.[6] All reflections were given unit weight. The final refinement gave a value for R $(\Sigma\| F_o| - |F_c\| / \Sigma|F_o|)$ of 0.058 for all reflections, based on isotropic temperature factors for all atoms, with a standard deviation for an observation of unit weight of 5.8. Coordinates and thermal parameters are shown in Table I. Observed and computed structure factors are presented in Table II.[7]

Table I. Position and Thermal Parameters[a]

Atom	x	y	z	B, Å^2
Pr	0.29952 (2)			0.86 (1)
K	0.3116 (1)			2.33 (4)
O(1)	0.4039 (3)	0.7426 (3)	0.0920 (3)	1.53 (7)
O(2)	0.5539 (3)			1.31 (9)
O(3)	0.3108 (3)	0.1400 (3)	0.1959 (3)	1.70 (7)
O(4)	0.4272 (4)	0.1071 (4)	0.0900 (4)	2.70 (10)
O(5)	0.4255 (3)	0.2466 (4)	0.1664 (3)	1.91 (8)
N(1)	0.4852 (4)			1.37 (12)
N(2)	0.3876 (4)	0.1645 (4)	0.1478 (4)	1.70 (9)

[a] Standard deviations are given in parentheses and refer to the last decimal positions. Pr in 8-fold positions; K, O(2), and N(1) in 12-fold positions; O(1), O(3), O(4), O(5), and N(2) in 24-fold positions.

Table III. Bond Distances and Angles in $K_3Pr_2(NO_3)_9$ [a]

"A" configuration		"B" configuration	
O–O, Å		O–O, Å	
O(2)–O(1)	2.170 (7)	O(3)–O(4)	2.173 (7)
O(1)–O(1)	2.171 (9)	O(3)–O(5)	2.155 (7)
O(1)–O(2)	2.170 (7)	O(4)–O(5)	2.150 (7)
N–O, Å		N–O, Å	
N(1)–O(2)	1.314 (9)	N(2)–O(3)	1.270 (7)
N(1)–O(1)	1.224 (6)	N(2)–O(4)	1.223 (7)
N(1)–O(1)	1.224 (6)	N(2)–O(5)	1.248 (7)
O–N–O, Deg		O–N–O, Deg	
O(2)–N(1)–O(1)	117.5 (4)	O(3)–N(2)–O(4)	121.3 (5)
O(1)–N(1)–O(1)	125.0 (7)	O(4)–N(2)–O(5)	120.9 (6)
O(1)–N(1)–O(2)	117.5 (4)	O(5)–N(2)–O(3)	117.7 (5)
Pr–O, Å		Pr–O, Å	
Pr–(3)O(2)	2.631 (3)	Pr–(3)O(3)	2.577 (5)
Pr–(3)O(1)	2.745 (6)	Pr–(3)O(5)	2.580 (5)
K–O, Å		K–O, Å	
K–(2)O(1)	2.961 (6)	K–(2)O(4)	2.916 (6)
		K–(2)O(5)	3.146 (6)
		K–(2)O(4)	2.806 (6)
		K–(2)O(3)	2.889 (6)

[a] Standard deviations are given in parentheses and refer to the last decimal positions.

Discussion of the Structure

Bond distances and angles were computed with the Busing, Martin, and Levy ORFFE program[8] and are shown in Table III.

A Pr atom on a threefold axis is surrounded by twelve oxygen atoms. These oxygen atoms, belonging to six nitrate groups, are located at the corners of a somewhat distorted icosahedron. The deviation of the configuration from a regular icosohedron does not portray clearly the asymmetry in the distribution of oxygen atoms about a Pr atom. Such asymmetry is best described in terms of the types of oxygen atom forming the nitrate ions and the nature of the bonding.

The nitrate configurations fall into two groups, A and B, which are shown in projection in Figures 1a and 1b. In type A, Figure 1a, every oxygen atom is bonded to a Pr atom but O(2) shares with two Pr atoms while each O(1) oxygen shares between a Pr and a K atom. The entire configuration is distributed on a twofold axis. On the other hand, in type B nitrate ions, Figure 1b, only two oxygen atoms O(3) and O(5) share with a Pr atom while the third, O(4), shares exclusively with K atoms. In addition, O(3) and O(5) share with K and Pr atoms. Thus, although the environment of a Pr atom appears the same relative to the number of oxygen atoms of each group of nitrate ions (*i.e.*, a Pr atom always is bonded to two oxygen atoms of any nitrate ion), the overall environment of oxygens in group A is distinct from that in group B. The coordination of oxygen atoms to a K atom is also substantially different for the two cases. For type A, a K atom is coordinated to two equivalent oxygen atoms O(1) while in type B, a K is coordinated to eight oxygen atoms, O(3), O(4), and O(5). As noted in Table III, the Pr–O distances in the type A configuration are slightly longer than those in type B.

The weighted average Pr–(12)O distance of 2.63 Å may be compared with a value of Ce–(12)O = 2.64 Å found in $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$ by Zalkin, Forrester, and

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(4) W. G. Sly and D. P. Shoemaker, Technical Report, Office of Ordinance Research, Contract DA-19-020-ORD-4696, Massachusetts Institute of Technology, Cambridge, Mass., 1960.

(5) (a) "International Tables for X-Ray Crystallography," Vol. III, Birmingham, England, Kynoch Press, 1962; (b) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(6) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS: A Fortran Crystallographic Least Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(7) Table II will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-560.

(8) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE: A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

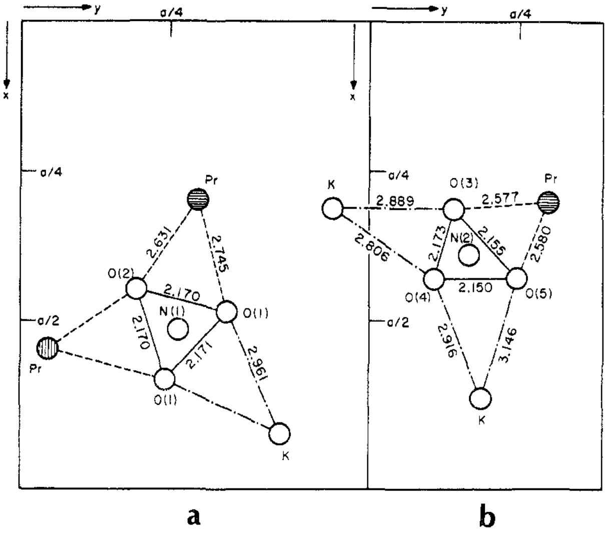

Figure 1. Projections of "A"-type (a) and "B"-type (b) configurations, on the *xy* plane of $K_3Pr_2(NO_3)_9$.

Templeton.[9] Here, also, the Ce is coordinated to twelve oxygen atoms, derived from six nitrate ions, with the oxygen atoms located at the corners of an irregular icosahedron. A value Pr-O = 2.65 Å is deduced from the Zachariasen radii corrected for the twelvefold coordination. The potassium-oxygen distances vary from 2.81 to 3.15 Å. However, the weighted average value is 2.94 Å, and this may also be compared with the Zachariasen radii, leading to K-O = 2.93 Å when corrected for the tenfold coordination. Nearest neighbor oxygen contacts do not vary substantially. They are O(1)-O(1) = 2.841 (8) Å, O(1)-O(2) = 2.871 (5) Å, O(3)-O(3) = 2.884 (7) Å, O(3)-O(5) = 2.970 (6) and 3.242 (8) Å, and O(4)-O(5) = 3.506 (8) Å.

The structure of $Pr(NO_3)_3 \cdot 6H_2O$ has been reported by Rumanova, Volodina, and Belov.[10] A high and asymmetric coordination is apparent here. The coordination about the Pr atom consists of $Pr(NO_3)_3 \cdot 4H_2O$ polyhedra with each Pr sharing two oxygen atoms of each nitrate group. Four water oxygens then lead to a tenfold coordination of oxygen atoms about a Pr. The remaining two water oxygens do not complete the twelvefold coordination but, instead, are involved in the sharing of the polyhedra.

Spectroscopic Studies

Vibrational Spectra. The infrared and Raman data for the Pr and Nd salts of the type $K_3Ln_2(NO_3)_9$ are given in Table IV. The results are consistent with an environment involving coordinated nitrates around the lanthanide metal. The spectra of the salts are typical for nitrato-type complexes. The ionic vibration $\nu_3(e')$ for an ionic D_{3h} symmetry at ∿1390 cm^{-1} does not appear. The mode $\nu_1(a_1)$ at ∿1040 cm^{-1}, normally unallowed in the infrared spectrum for ionic nitrates, becomes allowed. The degenerate vibrations (ν_3 and ν_4) have split, indicative of coordination occurring to the nitrate.[11] The separation of the nitrate stretching fundamentals at ∿1400 and ∿1300 cm^{-1} ($\Delta\nu$) has been used as a criterion to distinguish between the degree of covalency of the nitrate coordination.[12] $\Delta\nu$ increases as the coordination of the nitrate group increases for monodentate to bidentate and/or bridging. The magnitude is used to establish the type of nitrate coordination. For the Pr salt $\Delta\nu_{ir} = \nu_1 - \nu_4 = 154\ cm^{-1}$ and $\Delta\nu_{Raman} = 171\ cm^{-1}$. For the Nd salt $\Delta\nu_{ir} = \nu_1 - \nu_4 = 147\ cm^{-1}$ and $\Delta\nu_{Raman} = 167\ cm^{-1}$. The size of this splitting is indicative of a strong interaction of the oxygens of the nitrate with the rare earth ion and typical of bidentate bonding. Corollary evidence comes from the splitting of the combination bands of the NO_2 bending and the symmetrical NO_2 stretching vibrations in the 1680-1800 cm^{-1} region.[13,14] $\Delta\nu'$ is defined as equal to $(\nu_2 + \nu_3) - (\nu_2 + \nu_5)$. For Pr $\Delta\nu' = 38\ cm^{-1}$ and for Nd $\Delta\nu' = 26\ cm^{-1}$, and this amount of splitting is typical of bidentate nitrate coordination.

Table IV. Infrared and Raman Frequencies and Assignments for $K_3Pr_2(NO_3)_9$ and $K_3Nd_2(NO_3)_9$ (cm^{-1})

	Ir		Raman	
Assignments[a]	ν	$(\nu_1 - \nu_4)$	$\Delta\nu$	$(\nu_1 - \nu_4)$
	$K_3Pr_2(NO_3)_9$			
$\nu_2 + \nu_3$	1788 m			
	1768 sh			
$\nu_2 + \nu_5$	1762 m			
			1504 vvs	
ν_1 (a_1)	1465 vs		1461 vs	
			1406 vw	
	1358 vs	154	1366 m	171
	1330 vs		1341 m	
			1333 sh	
ν_4 (b_1)	1311 s			
ν_2 (a_1)	1047 vs		1048 vs	
	1041 vs		1042 s	
ν_6 (b_2)	818 vs			
	810 sh			
ν_3 (a_1)	750 vw		753 m	
			745 s	
ν_5 (b_1)	730 m		727 m	
			719 m	
	$K_3Nd_2(NO_3)_9$			
	1804 sh			
$\nu_2 + \nu_3$	1790 m			
	1788 sh			
$\nu_2 + \nu_5$	1762 m			
			1502 w	
ν_1 (a_1)	1480 vs		1453 w	
		147	1405 w	167
	1358 sh			
ν_4 (b_1)	1333 s		1335 s	
ν_2 (a_1)	1048 sh		1040 vs	
	1043 vs			
ν_6 (b_2)	815 vs			
	810 sh			
ν_3 (a_1)	750 vs		754 vs	
			746 vs	
ν_5 (b_1)	729 w		727 m	
			720 m	

[a] Assignments are made according to nomenclature established by Addison, *et al.*,[15,16] for bidentate nitrate.

Since the nondegenerate modes (a_1 and a_2'' at 820 cm^{-1}) also show splitting, more bands than one would expect for a lowering to C_{2v} symmetry are actually obtained.[15,16] Since the number of molecules per primitive unit cell is 4, some of this additional splitting may be caused by factor-group

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(9) A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Chem. Phys.*, 39, 2881 (1963).

(10) I. M. Rumanova, G. F. Volodina, and N. V. Belov, *Sov. Phys.—Crystallogr.*, 9, 545 (1965).

(11) J. R. Ferraro, "Low Frequency Vibrations of Inorganic and Coordination Compounds," Plenum Press, New York, N. Y., 1971, pp 76-82, and references therein.

(12) J. R. Ferraro, *J. Inorg. Nucl. Chem.*, 10, 319 (1959).

(13) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 4, 804 (1965).

(14) J. R. Ferraro, C. Cristallini, and I. Fox, *J. Inorg. Nucl. Chem.*, 29, 139 (1967).

(15) C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.*, 613 (1960); B. M. Gatehouse, S. E. Livingston, and R. S. Nyholm, *ibid.*, 4222 (1957).

(16) C. C. Addison, D. W. Amos, and D. Sutton, *J. Chem. Soc. A*, 808 (1967).

splitting. The data may also be interpreted in terms of several different environments for the coordinated nitrate groups, and thus the vibrational data are consistent with the X-ray data.

Pressure Studies. Both salts were subjected to high external pressures. The Pr and Nd salts show phase transitions at 12 and 20 kbars, respectively, as observed by means of a microscope. The phase transitions are immediately reversible upon release of pressure.

Table V lists the pressure effects made on the "f" electron transitions in the visible region of the hypersensitive transitions (∿0.58 μ or ∿17,240 cm^{-1}) for $K_3Nd_2(NO_3)_9$. The Nd salt gave four absorption bands between 16,779 and 17,513 cm^{-1}. The 17,182-cm^{-1} absorption is the most intense at ambient pressure. With increasing pressure, the absorption at 17,271 cm^{-1} becomes the most intense, and the 17,182-cm^{-1} absorption decreases in intensity. At 24 kbars the 17,182-cm^{-1} band becomes only a shoulder on the main peak. At 60 kbars the main peak is at 17,241 cm^{-1} and has become broader but is still intense. The high-frequency band is still observable but has now shifted to 17,544 cm^{-1}. The pressure effects for "f" electrons are different from those found for the "d" electrons in transition metal compounds.[17] The shifts in the Nd salts are very small,[18] whereas for "d" electrons in five-coordinate systems, significant blue shifts are observed.[17] As has been cited,[17,19] the blue shifts of "d–d" transitions with increasing pressure implies an increasing ligand-field interaction with the central metal ion. This difference with pressure may be a reflection of the lower ligand-field effect occurring for rare earth compounds involving shielded 4f electrons.[20]

The observed pressure effects on the "f" electronic transitions for the Nd salt were found to be nonreversible. After several hours the original spectra at ambient pressure did not ensue. No explanation of this nonreversibility is presently available.

Absorption Spectra. Since the crystallographic and infrared studies show that the lanthanide ion in $K_3Pr_2(NO_3)_9$-type structures is subject to a highly asymmetric field and strong covalent bonding, it was of interest to examine the effects of this type of environment on the inter f-electron transitions. The results for $K_3Nd_2(NO_3)_9$ reveal an interesting new example of a structure in which hypersensitive transitions are induced.

It has been known for many years that one or two absorption bands in the optical spectra of most of the lanthanide ions are particularly sensitive to certain environments. These bands in general obey the selection rule $\Delta J = 2$ and may be enhanced in intensity by a factor of 3-4 compared to the same bands in a convenient reference medium such as aqueous solution.[21] In Pr^{3+}, the hypersensitive band lies in the near-infrared region where H_2O absorbs strongly. However in Nd^{3+}, the corresponding sensitive band is centered near 0.58 μ, and the absorption is characterized as due to transitions from the $^4I_{9/2}$ ground state to components of $^4G_{5/2}$ and $^2G_{7/2}$. Quantitative measurements[21] have shown that the intensities of most of the bands of Nd^{3+}(aq) at 25° are quite comparable to the corresponding bands for Nd^{3+} in molten $LiNO_3$-KNO_3 eutectic at ∿170°. However, the group at 0.58 μ is a factor of 3 more intense in the melt than in aqueous solution. This same hypersensitivity is revealed in the spectrum of a thin crystal of $K_3Nd_2(NO_3)_9$, shown in Figure 2. It is tempting to suggest that the short-range environment of the Nd^{3+} in the melt may not have changed appreciably during the process of crystallization since the spectra in the melt and in the crystal are distinctly similar. There is strong evidence that coordination of polyvalent cations in nitrate melts does occur. In some cases low-frequency bands that may be assigned to metal–oxygen stretching frequencies have been observed.[22] It should be noted that the pressure studies discussed earlier in this paper only resulted in shifting components of the hypersensitive band. There was no evidence of an overall loss of hypersensitivity in the crystal under pressure.

Judd[23] has related hypersensitivity in the lanthanides to the point symmetry of the lanthanide ion. In the few cases where crystal structure and spectra have been correlated, the hypersensitive transitions have been associated with a low site symmetry. In $K_3Pr_2(NO_3)_9$-type double nitrates the coordination of the Pr to twelve oxygen atoms from six nitrate ions is comparable to the environment of the lanthanide ion in $Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$-type compounds.[9] The gross features of the crystal field spectra in the Ce-Mg double nitrates have been analyzed assuming that the site symmetry of the lanthanide ion is approximately icosohedral, but more detailed analyses have required the assumption of C_{3v} or T_h symmetry with a distortion to C_3.[24] Judd has noted[23] that

Table V. Pressure Effects on "f" Electron Transitions in $K_3Nd_2(NO_3)_9$

ν, cm^{-1}		ν, cm^{-1}	
Ambient pressure	60 kbars	Ambient pressure	60 kbars
16,779 vw	Disappears	17,271 vs	17,241 s, br
17,182 vs	Disappears	17,513 m	17,544 w

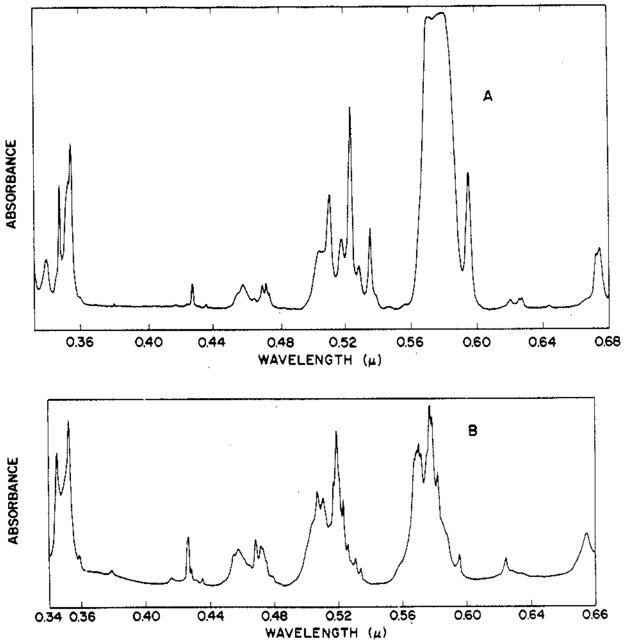

Figure 2. The absorption spectra of thin single-crystal samples of (A) $K_3Nd_2(NO_3)_9$ and (B) Nd^{3+}:LaF_3.

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[17] J. R. Ferraro, D. W. Meek, E. C. Siwiec, and A. Quattrochi, *J. Amer. Chem. Soc.*, 93, 3862 (1971).

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[21] W. T. Carnall, P. R. Fields, and B. G. Wybourne, *J. Chem. Phys.*, 42, 3797 (1965).

[22] R. E. Hester and K. Krishnan, *J. Chem. Phys.*, 47, 1747 (1967).

[23] B. R. Judd, *J. Chem. Phys.*, 44, 83 (1966).

[24] S. D. Devine, *J. Chem. Phys.*, 47, 1844 (1967).

hypersensitive transitions have been observed near 0.58 μ in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$.

The asymmetric site symmetry of the lanthanide ion in $Pr(NO_3)_3 \cdot 6H_2O$-type structures where there is a coordination to 10-oxygen atoms[10] may also be correlated with the existence of hypersensitive transitions. Observations by Selwood,[25] which we have confirmed, show clear hypersensitivity of the 0.58-μ band in $Nd(NO_3)_3 \cdot 6H_2O$. Infrared studies confirm the strongly covalent character of the nitrate groups in this class of compounds.[26]

Finally, it is instructive to compare the spectra of the Nd^{3+} ion in the previously discussed nitrate salts with that of Nd^{3+}: LaF_3, Figure 2. In this case, the site symmetry is again low, C_2,[27] but the spectrum is "normal;" *i.e.*, the intensity of the 0.58-μ band is similar to that observed for $Nd^{3+}(aq)$.[21,28,29] Since C_2 symmetry is included in the group which Judd identified with hypersensitive transitions, we may conclude, as Bukietynska and Choppin[30] have suggested, that symmetry may be a necessary but not a sufficient condition to the existence of hypersensitive transitions. In the case of $K_3Nd_2(NO_3)_9$ and the other crystalline salts discussed here, the correlation between strong covalent bonding of the lanthanide ion and the existence of intensity enhancement was indicated.

Registry No. $K_3Pr_2(NO_3)_9$, 37209-71-5; $K_3Nd_2(NO_3)_9$, 37209-70-4; $K_3Sm_2(NO_3)_9$, 37209-72-6; $K_2Er(NO_3)_5$, 37248-54-7.

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Contribution from Ames Laboratory–USAEC and the Department of Chemistry, Iowa State University, Ames, Iowa 50010

Kinetics of the Reduction of Cobalt(III) and Chromium(III) Complexes by Ytterbium(II) Ions[1a]

RICHARD J. CHRISTENSEN,[1b] JAMES H. ESPENSON,*[1c] and ANDREW B. BUTCHER

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Generation of solutions of Yb^{2+} in dilute perchloric acid was accomplished electrochemically. The Yb^{2+} solutions thus produced underwent solvent reduction over 10–30 min in the absence of oxygen but were sufficiently stable to permit kinetic studies on the reduction of some Co(III) and Cr(III) complexes. Measurements were made for $Co(NH_3)_6{}^{3+}$, $Co(en)_3{}^{3+}$, and $Co(NH_3)_5H_2O^{3+}$, as well as for halide and pseudohalide complexes of the series $Cr(NH_3)_5X^{2+}$ and $Cr(H_2O)_5X^{2+}$. The effects of $[H^+]$ and $[Cl^-]$ were examined for some reactions, as was the effect of temperature. The results are interpreted in terms of inner-sphere and outer-sphere mechanisms for different reactions.

Introduction

The reduction of metal complexes by one-electron reducing agents has occupied an important position in the field of inorganic reaction mechanisms ever since the original studies of Taube and coworkers[2] demonstrating the inner-sphere (IS) mechanism for certain Cr^{2+} reactions. Since that time, the IS mechanism has been found to be a rather general one for appropriately constituted 1-equiv reducing agents.[3,4] For many reducing agents, however, the mechanism for electron transfer cannot be inferred as directly as in Cr^{2+} reductions, for which the transfer and capture of the bridging group X as the Cr(III) complex can be established. In some other cases, especially V^{2+} [5] and Fe^{2+},[6] X transfer could also be demonstrated unequivocally. Even for these cases, the proof for an IS mechanism in certain reactions by no means establishes this as a general mechanism. Thus for many of the reactions of V^{2+} [3,7] and Fe^{2+} [7a,8] and for virtually all of the related redox reactions of Cu^+,[9] U^{3+},[10] and Eu^{2+},[7a,11] what conclusions can be drawn about the most elementary aspect of the mechanism—whether or not the structure of the transition state involves a bridging group—can be approached only by a very indirect means.

It thus seemed of some interest to attempt studies which would extend the number of reducing agents, because such

(1) (a) Based in part on the M.S. thesis of R. J. C., Iowa State University, Nov 1969. (b) NDEA predoctoral trainee. (c) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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