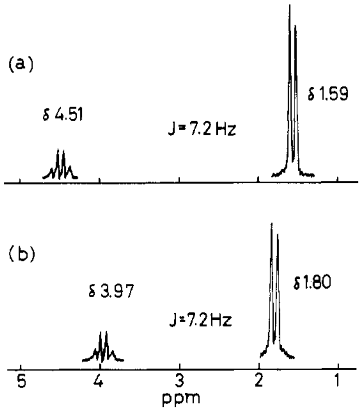
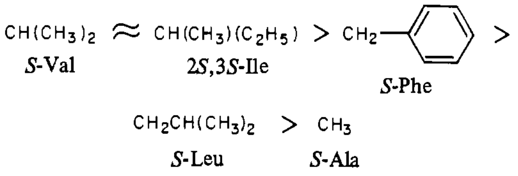


Figure 4. ^{1}H NMR spectra of the (a) Λ- and (b) Δ-$[Co(phen)_2(S\text{-}Ala)]^{2+}$ in D_2O solutions.

configuration about the cobalt(III) ion. The energy difference between the diastereoisomers due to the repulsive interactions can be correlated with the distances between α-proton of one of the phenanthroline ligand and the amino acid substituents. The distance in the Δ configuration can be seen to be smaller than that in the Λ configuration. This may be reflected in the relationship between the degree of the stereoselectivity and the size or the length of the substituent groups. The degree of the stereoselectivity was observed to vary with the substituent group on the amino acid in the order of



The stereoselectivity of the (*S*)-phenylalanine and the (*S*)-leucine complex was smaller than that of the (2*S*,3*S*)-isoleucine or the (*S*)-valine complex. This result may be due to the increase of distance corresponding to one methylene chain from the chelate ring of the phenyl group or the isopropyl group in the (*S*)-phenylalanine and the (*S*)-leucine complex. Thus, the large size and the short distance from the chelate ring of the substituent group can lead to the great stereoselectivity because of more increase of the repulsive interactions with α-proton of the phenanthroline in the Δ isomer than those in the Λ isomer. The ^{1}H NMR spectra of the Λ- and the Δ-$[Co(phen)_2(S\text{-}Ala)]^{2+}$ ions are shown in Figure 4. For both isomers, the peaks at 1.5–1.9 and 3.8–4.7 ppm were assigned to the methyl and methine protons of the chelated (*S*)-alaninate ion, respectively. The methyl group of the Λ isomer resonates at higher field (1.59 ppm) than that of the Δ isomer (1.80 ppm). This upfield shift strongly suggests that schielding of the methyl protons due to the ring current of the phen ligand is greater for the Λ isomer than for the Δ isomer. The methyl protons of the Λ isomer lie above the plane of the pyridine ring of a phen ligand and, consequently, resonate at high field. On the other hand, the methyl protons of the Δ isomer lie near the expansion of the pyridine plane (in a deshielding region) and, therefore, may cause some repulsive interactions with α-position hydrogen atom of a phen ligand. This result from ^{1}H NMR spectra supports the discussion in the stereoselectivity. The methine proton resonance of (*S*)-alanine in the complexes occurs at higher field for the Δ isomer (3.97 ppm) than for the Λ isomer (4.51 ppm). In the Δ isomer the methine proton is above the aromatic ring of another phen ligand in the complex, but it is far removed from this region in the Λ isomer. This shift is even greater than for the methyl protons, as has been observed by Yasui et al. for $[Co(S\text{-}Ala)_2(bpy)]^+$ complexes.[3] Further study of the bis(phenanthroline) complexes with the other amino acid is planned to elucidate how the nonbonded interactions between the neighboring phenanthroline ligand and a variety of the substituents of the amino acid affect the stereoselectivity.

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Registry No. **1**, 81132-17-4; **2**, 81132-19-6; **3**, 81097-85-0; **4**, 81176-55-8; **5**, 81176-57-0; **6**, 81097-87-2; **7**, 81097-89-4; **8**, 81132-21-0; **9**, 81097-91-8; **10**, 81132-23-2; **11**, 81097-93-0; **12**, 81132-25-4.

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Circular Dichroism of Eu^{3+} and Nd^{3+} in a $K_3Nd_2(NO_3)_9$ Single Crystal

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The chirooptical technique, as applied to the naturally optically active transition-metal complexes, has proved to be of great value in stereochemical and electronic structural studies.[1,2] Of late the method has been extended to lanthanides and actinides. While most of the studies on lanthanide optical activity refer to complexes in solution media (where coordination numbers and metal ligand stoichiometries are ill-defined and where the source of optical activity is the asymmetric ligand), a few studies have been made with well-defined single crystals[3,4] where the optical activity originates from the asymmetric environment of the Ln^{3+} ion. Encouraged by the success of the spectra–environment correlation[5-7] in case of the Ln–DG single crystal we have searched for new systems and extended our studies to an interesting cubic crystal system of anhydrous Ln^{3+} double nitrates (Ln, = Pr, Nd, Sm).

This paper reports the low-resolution CD and absorption spectra of doped Nd^{3+} crystals primarily with a view to verify the expectations of Richardson[8] regarding low-resolution lanthanide optical activity. In order to compare the CD of the Nd^{3+} transition, which are commonly considered as electric-dipole allowed, with that of primarily magnetic-dipole-allowed Eu^{3+} transitions having an identical environment, we have grown and studied a single crystal of $K_3Nd_2(NO_3)_9$ with Eu^{3+} as dopant.

The anhydrous double nitrate has the general formula $K_3Ln_2(NO_3)_9$ where Ln is Pr, Nd, or Sm. The crystal system is cubic and has the unusual space group $P4_332$. The unit cell consists of four formula units; eight equivalent RE (rare earth) ions are situated at the eight corners of the cubic unit cell, each being 12-coordinated, the 12 oxygen atoms coming from six

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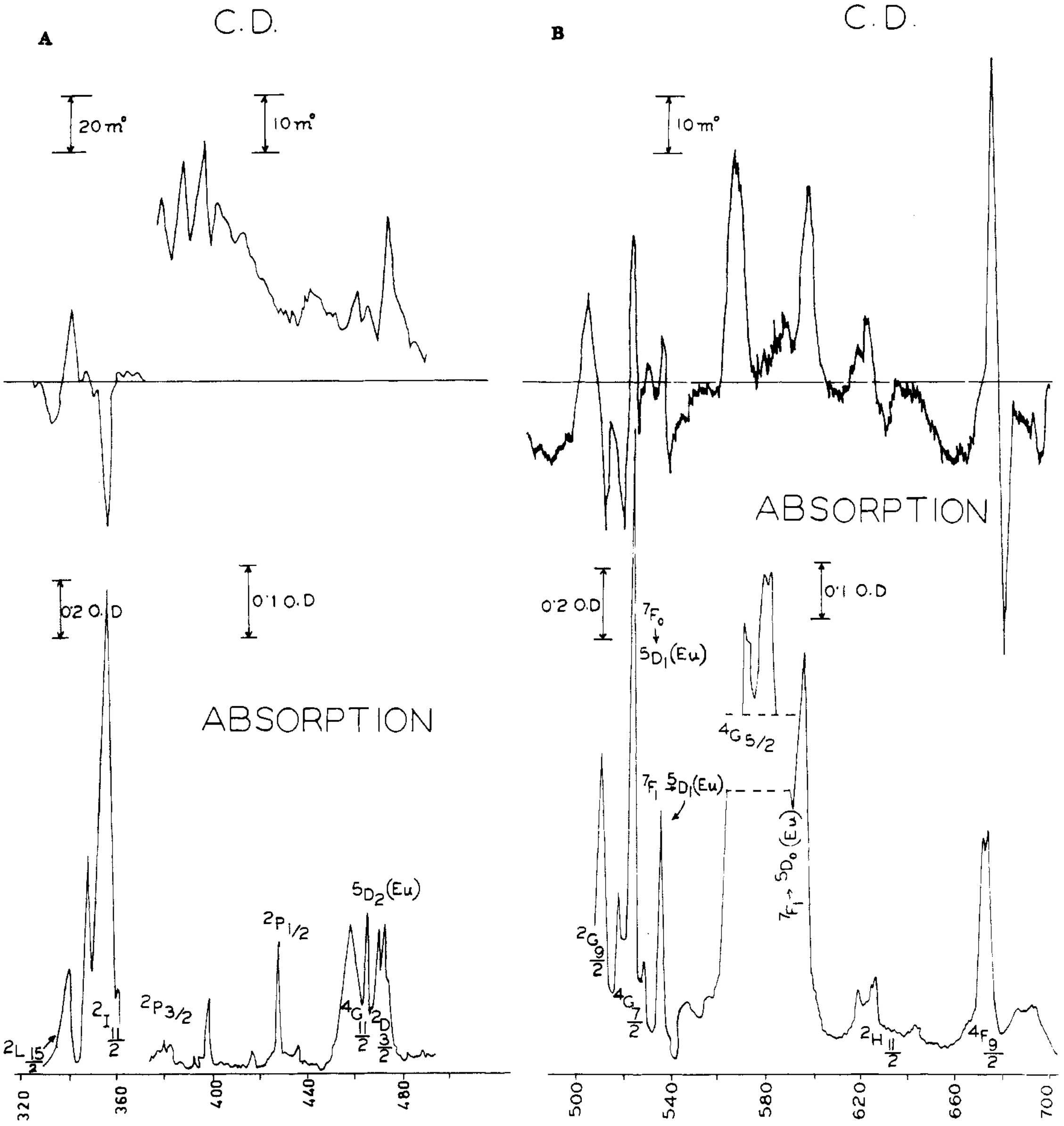

Figure 1. Room-temperature absorption and circular dichroism spectra of (A) Nd^{3+} and (B) Eu^{3+} in a $K_3Nd_2(NO_3)_9$ single crystal (thickness of the crystals: (i) for absorption, 2 mm; (ii) for CD, 1 mm). Note: Absorption between 560 and 590 nm is very high and hence a high offset (1.8) setting is used to bring it inside the chart paper.

nitrate groups to form a distorted icosahedron, somewhat, but not quite, similar to the hydrated double nitrate studied by Hellwege and Hellwege.[9]

The crystals were grown following the method of Carnall et al.[10] from an eutectic melt of KNO_3, $LiNO_3$, $Nd(NO_3)_3$, and $Eu(NO_3)_3$ and kept at 180 °C for several weeks. The hygroscopic crystals are brought out of the flux, cut to sizes, polished, and kept in a desiccator. The absorption spectra and CD spectra were recorded at room temperature on a Cary 17D and Jasco J 500, respectively. Since the crystal system is cubic and hence optically isotropic, the rotational behaviors of the axial vector (i.e., magnetic dipole moment) and polar vector (i.e., electric dipole moment) are the same, and their scalar product, i.e., the CD, does not depend on the direction of light propagation through the crystal, unlike the axial Ln–DG crystal studied previously in this laboratory.[3]

Figure 1 shows the absorption and CD spectra of Nd^{3+} and Eu^{3+} transitions under comparable resolution at room temperature. In general, absorption spectrum on a Cary 17D is better resolved. For a few cases such as $^4I_{9/2} \rightarrow {}^4F_{9/2}$ in Nd^{3+}, where adjacent components have opposite CD, the resolution is better in CD compared to absorption spectroscopy.

Discussion

On the basis of several simplifying assumptions, Richardson has recently discussed a set of rough selection rules for low-resolution lanthanide optical activity.[8] If the rotational strength of a term-to-term transition is taken as proportional to PM and the corresponding dipole strength as P^2, then it is expected that the relative values of $R_K/D_K^{1/2}$ should roughly reflect the relative magnetic dipole allowedness of the transitions. Table I gives the $R_K/D_K^{1/2}$ along with the magnetic dipole moment for Nd^{3+} and Eu^{3+} transitions calculated from free ion wavefunctions. It is to be noted that the $R_K/D_K^{1/2}$ values here are found to be 1 order of magnitude less than those found in the corresponding RE–DG crystals.[11] If crystal-field-induced J mixing is not considered, $R_K/D_K^{1/2}$ for $\Delta J = 0, \pm 1$ transitions are expected to be high compared to

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Table I. Calculated Magnetic Dipole Moments (MDM) and $R_K/D_K^{1/2}$ Values for Different Transitions in the Nd^{3+} and Eu^{3+} Double Nitrate Single Crystals

band positions, nm	state ($^{2S+1}L_J$)	10^{21} × MDM_{calcd},[a] esu cm	10^{23} × $R_K/D_K^{1/2}$, esu cm
	Nd Transitions		
674[b]	$^4I_{9/2} \rightarrow {}^4F_{9/2}$	3.43	1.66
623[b]	$^4L_{9/2} \rightarrow {}^2H_{11/2}$	−0.58	0.94
574[c]	$^4L_{9/2} \rightarrow {}^4G_{5/2}$		
565[d]	$^4L_{9/2} \rightarrow {}^2G_{7/2}$	−0.13	
510	$^4L_{9/2} \rightarrow {}^2G_{9/2}$	−1.01	1.22
459	$^4L_{9/2} \rightarrow {}^4G_{11/2}$	0.64	0.14
353	$^4L_{9/2} \rightarrow {}^2I_{11/2}$	−0.75	−0.86
	Eu Transitions		
595	$^7F_1 \rightarrow {}^5D_0$	−3.15	0.71
535[b]	$^7F_1 \rightarrow {}^5D_1$	−0.284	0.33
524	$^7F_0 \rightarrow {}^5D_1$	−1.54	0.146
471	$^7F_1 \rightarrow {}^5D_2$	−1.05	0.99

[a] Calculated from free ion wave functions: (i) Wybourne, B. G., *J. Chem. Phys.*, **1961**, *34*, 279. (ii) Ofelt, G. S. *Ibid.* **1963**, *38*, 2171. [b] Absorption spectrum is not resolved and R_K's are determined from the sigmoid CD band. This unavoidable procedure is admittedly approximate and very probably leads to loss of CD band area through overlap of oppositely signed band. [c] CD is very small (see Figure 1B). [d] Absorption could not be resolved.

$\Delta J \geq 2$ transitions. This is only roughly borne out by Table I for Nd^{3+} transitions. The transition $^4I_{9/2} \rightarrow {}^2G_{7/2}$ (565 nm) is principally magnetic dipole allowed and hence stands out prominently over the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transitions in the CD spectrum, in contrast to the normal absorption spectrum. Particularly noteworthy is the high $R_K/D_K^{1/2}$ values for $^4I_{9/2} \rightarrow {}^4F_{9/2}$ (674-nm) transitions. For such transitions with high magnetic dipole moment, CD may be used as a diagonistic tool.

It is interesting to compare the CD spectra of principally magnetic-dipole-allowed Eu^{3+} $^7F_0 \rightarrow {}^5D_1$, $^7F_1 \rightarrow {}^5D_0$ and $^5D_1$ transitions with those of principally electric-dipole-allowed Nd^{3+} transitions. Some of the Nd^{3+} transitions such as $^4I_{9/2} \rightarrow {}^4F_{9/2}$, $^2G_{7/2}$ have $R_K D_K^{1/2}$ values as high as those of Eu^{3+} transitions. The high magnetic dipole contribution to some of the Nd^{3+} transitions should be carefully looked into in other nonoptically active Nd^{3+} crystals through a comparison of axial and polarized spectra.

A detailed calculation on the optical activity of $K_3Pr_2(NO_3)_9$ has been done and will be discussed elsewhere.

Acknowledgment. Thanks are due to Dr. A. C. Sen and Mr. D. S. Ray for discussion and to Mr. K. Bhattacharyya for experimental assistance.

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Effects of Pressure on the Reduction of $Co(NH_3)_5N_3^{2+}$ by Iron(II) in Dimethyl Sulfoxide

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In a recent paper[1] Watts et al. investigated the effects of solvent on the reduction of $Co(NH_3)_5N_3^{2+}$ by Fe(II). Similar to their earlier findings[2-4] for the reduction of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ by Fe(II), $\Delta H^\ddagger$ for the second-order rate constant increases from 63 to 80.5 kJ mol^{-1} and $\Delta S^\ddagger$ increases from −74 to −10 J K^{-1} mol^{-1} on changing the reaction medium from water to Me_2SO. The reduction of $Co(NH_3)_5N_3^{2+}$ by Fe(II) is believed to proceed according to an inner-sphere mechanism in Me_2SO and in water[1,5] as is the case for the reduction of $Co(NH_3)_5X^{2+}$ (X = Cl, Br, F).[2-4] The observed changes in the activation parameters are interpreted in terms of a change in the stereochemistry of the iron(II) atom from an octahedral to a tetrahedral geometry in the bridged intermediate.[1]

According to Stranks,[6] a positive volume of activation is expected for inner-sphere redox reactions primarily due to the expulsion of a solvent molecule upon forming the bridged intermediate. Indeed, Halpern et al.[7] reported a value of +14 cm^3 mol^{-1} at 25 °C for the title reaction in water. Along these lines it is expected[8] that $\Delta \bar{V}^\ddagger$ should be remarkably more positive for this reaction in Me_2SO since three solvent molecules are released when a bridged intermediate with a tetrahedral Fe(II) center is formed.

Experimental Section

$[Co(NH_3)_5N_3]Cl_2$ was prepared according to standard procedures[9] and converted into the perchlorate salt. UV-visible absorption spectra are in excellent agreement with those published elsewhere.[10,11] $[Fe(OH_2)_6](ClO_4)_2$ was used as source of Fe(II).[12] Chemicals of analytical reagent grade, freshly distilled Me_2SO, and doubly distilled water were used in all solutions. Kinetic runs were performed on a modified Zeiss PMQ II spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell,[13] under conditions very similar to those chosen by Watts et al.[1] The observed pseudo-first-order rate constants were calculated in the usual way, and such plots were linear for at least three to four half-lives of the reaction.

Results and Discussion

The results in Table I clearly illustrate that k_{obsd} and, therefore, the second-order rate constant k decrease with increasing pressure. Plots of ln k vs. pressure are linear, from which the volume of activation, $\Delta \bar{V}^\ddagger_{exptl}$, was calculated in the usual way. The reported rate constants at normal pressure are in close agreement with the values 2.7 × 10^{-2} and 7.1 × 10^{-2} M^{-1} s^{-1} (for water and Me_2SO, respectively) extrapolated from the activation parameters reported by Watts et al.[1] A similar agreement exists between $\Delta \bar{V}^\ddagger$ found for the redox reaction in water and that reported by Halpern et al.[7]

The volume of activation for an inner-sphere redox reaction is a composite of the volume change associated with the precursor formation ($\Delta \bar{V}_{PC}$) and the volume of activation for the electron-transfer step ($\Delta \bar{E}^\ddagger_{ET}$) such that

$$\Delta \bar{V}^\ddagger_{exptl} = \Delta \bar{V}_{PC} + \Delta \bar{V}^\ddagger_{ET}$$

A detailed discussion[8] has illustrated that two major contributions are expected to determine the magnitude of $\Delta \bar{V}_{PC}$ and, therefore, $\Delta \bar{V}^\ddagger_{exptl}$: first, a large volume increase due to the

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