of formation of the complex $[CuL_3]^{2+}$ is 0.5 kcal mol^{-1} less negative than that of $[CuL_2]^{2+}$. This difference is rather smaller than would be predicted from the data available for methylated ethylenediamines. On the other hand, the free energy of formation is 1.0 kcal mol^{-1} more negative than that of $[CuL_2]^{2+}$ rather than 0.6 kcal mol^{-1} less negative, which would be predicted on the same basis. In terms of the macrocyclic effect, we can now compare the enthalpic and entropic contributions to the macrocyclic free energy. The macrocyclic complex can be seen to be 1 kcal mol^{-1} less stable than previously determined with reference to a nonsubstituted reference ligand, with a small increase in the enthalpic contribution of 0.5 kcal mol^{-1} and a decrease in the entropic contribution $(T\Delta S^\circ)$ of 1.5 kcal mol^{-1}.

It would be dangerous to draw too many conclusions or read too much significance into these results since the differences reported with the N-substituted reference ligand are small and are at the limit of the experimental method. **We can, however, satisfactorily conclude that the original choice of reference ligands for the tetraaza macrocycles, namely, the series of nonsubstituted linear polyamines similar to L_2, was entirely appropriate.** It is not therefore necessary to modify the interpretation of the macrocyclic effect which has been made on the basis of these earlier results, namely, in terms of a favorable entropy contribution and an enthalpy contribution which varies with the relative matching of the metal ion to the ligand in terms of size, geometric requirements, and chemical affinity. What is perhaps more surprising is that the effect of alkylation of the nitrogens does not result in such a large difference in ΔH° and ΔG° as was observed for ethylenediamine and highlights the dangers of making comparisons of this type. It is most likely that the almost identical values of ΔH° for $[CuL_2]^{2+}$ and $[CuL_3]^{2+}$ result from the very similar structures and bond distances within the two complexes since the "bite" of ligands containing four nitrogen donors linked by two adjacent ethylenic bridges seems too small to accommodate most transition metals and results in the type of structures already discussed for $[CuL_1]^{2+}$ and $[CuL_2]^{2+}$.

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Circular Dichroism Spectra and Stereoselective Formation of Some Complexes of the Type [Co(phen)₂(am)]²⁺

Akira Tatehata

In the series of the complexes $[Co(phen)_{3-x}(am)_x]^{n+}$ (where phen is 1,10-phenanthroline and am is an α-amino acid anion, $x = 0$–3), the circular dichroism (CD) spectra of this series of complexes except for $x = 1$, that is, $[Co(phen)_3]^{3+}$ $(x = 0)$,[1,2] $[Co(phen)(am)_2]^+$ $(x = 2)$,[3,4] and $[Co(am)_3]$ $(x = 3)$,[5-9] have

been studied extensively. We have now completed the series. In the present work, some of the new complexes $[Co(phen)_2(am)]^{2+}$ have been prepared and separated into the optical isomers. The amino acids studied were glycine, (S)-alanine, (S)-phenylalanine, (S)-leucine, $(2S,3S)$-isoleucine, and (S)-valine. The CD spectra and the stereoselectivity in the formation of the diastereoisomers of the $[Co(phen)_2(S$-am$)]^{2+}$ have been discussed, being compared with those of the corresponding ethylenediamine complexes $[Co(en)_2(S$-am$)]^{2+}$. A coordinated amino acid in the $[Co(en)_2(S$-am$)]^{2+}$ had been considered to have little stereoselectivity owing to the planarity of the chelate ring. However, it has been found that in $[Co(phen)_2(S$-am$)]^{2+}$, the great stereoselectivity in the formation of the diastereoisomers was observed and an inverse relationship for the preferred absolute configuration exists between the phenanthroline complexes and the corresponding ethylenediamine complexes.

Experimental Section

Reagents. Amino acids were purchased from Nippon Rikagaku Yakuhin Co., Tokyo, except for glycine and (S)-alanine, which were obtained from Wako Pure Chemical Industries, Ltd. The reported specific rotations at 589 nm were as follows: (S)-alanine, +14.0–+15.0° in 6 N HCl; (S)-phenylalanine, −34.3° in water; (S)-leucine, +15.2° in 6 N HCl; $(2S,3S)$-isoleucine, +40.9° in 6 N HCl; (S)-valine, +27.5° in 6 N HCl.

Preparation and Separation of Isomers. The (amino acido)bis(phenanthroline)cobalt(III) ions $[Co(phen)_2(am)]^{2+}$ were prepared by the method of Ito et al. with the modification using methanol as a solvent.[10] The amino acid (2 mmol, 0.15 g for glycine) was dissolved in methanol (50 mL) containing an equimolar amount of sodium ethylate (2 mmol, 0.14 g). Solid *cis*-[Co(phen)₂Cl₂]Cl·3H₂O (1.7 mmol, 1.0 g) was added to the solution. The mixture was kept on a water bath at 40 °C for 3 h with stirring. The resulting orange red solution was diluted with water and passed through a CM-Sephadex column (ϕ 2.7 × 35 cm) to remove the reaction byproducts. The desired complex (orange red, 2+ charged species) was collected by elution with a 0.3 M NaCl solution. Half of the solution containing the desired complex was poured into a column (ϕ 2.7 × 130 cm) of SP-Sephadex C-25 and eluted with a 0.08 M Na₂[Sb₂(L-tart)₂] solution for the glycinato complex. The elution for the optically active (S)-amino acido complexes was carried out with a 0.1 M Na₂SO₄ solution. In every case the adsorbed orange red complex separated into two bands. So that the elution curves could be obtained, the eluate was divided into fractions of 15 mL each by an automatic fraction collector and the absorbance at the maximum wavelength of the first absorption band of the isomer was plotted against the eluate volume. First the $(+)_D$ isomer was eluted and then the $(-)_D$ isomer followed. The eluates of these two bands were diluted separately about ten times with water, and then the solution was passed through an SP-Sephadex short column (ϕ 2.5 × 5 cm) in each case. The complex on the exchanger was eluted with a 1 M NaCl solution. Sodium perchlorate solution was added to this eluate, and the solution was kept in a refrigerator. Orange red crystals were filtered off, washed with an ethanol–water (1:1) solution and then ethanol, and recrystallized from water and air-dried at room temperature.

Measurements. The absorption spectra were obtained on a Shimadzu MPS-50L recording spectrophotometer. The optical rotations were measured with a Union automatic polarimeter PM-101 in a 1-cm cell. The CD spectra were recorded on a JASCO J-40 CS spectropolarimeter with 1-cm or 1-mm cells. These measurements were carried out in aqueous solutions at room temperature. The 90-MHz ^{1}H NMR spectra were measured at about 35 °C on a Varian EM-390

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Table I. Elemental Analyses, Specific Rotations, and Formation Ratios of the Isomers
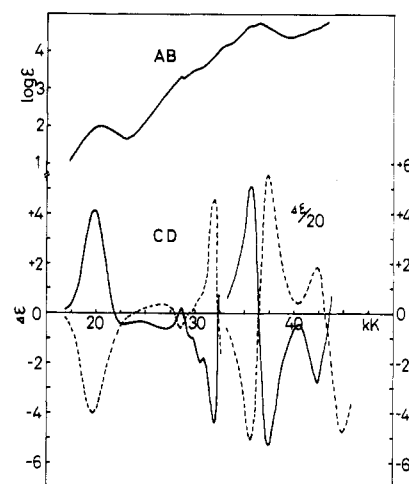
no.	complex	calcd C	calcd H	calcd N	found C	found H	found N	$[\alpha]_D$, deg	Λ/Δ
1	$(+)_D$-[Co(phen)$_2$(Gly)](ClO$_4$)$_2$·H$_2$O	43.96	3.12	9.86	43.79	2.90	9.86	+768	1.0
2	$(-)_D$-[Co(phen)$_2$(Gly)](ClO$_4$)$_2$·H$_2$O	43.96	3.12	9.86	43.56	2.78	9.83	−762	
3	$(+)_D$-[Co(phen)$_2$(S-Ala)](ClO$_4$)$_2$·2H$_2$O	43.68	3.53	9.43	43.65	3.03	9.43	+510	2.1
4	$(-)_D$-[Co(phen)$_2$(S-Ala)](ClO$_4$)$_2$·3H$_2$O	42.65	3.71	9.21	42.33	2.90	9.16	−600	
5	$(+)_D$-[Co(phen)$_2$(S-Phe)](ClO$_4$)$_2$	50.66	3.35	8.95	50.34	3.29	8.99	+532	3.0
6	$(-)_D$-[Co(phen)$_2$(S-Phe)](ClO$_4$)$_2$·2H$_2$O	48.43	3.69	8.56	48.37	3.28	8.54	−673	
7	$(+)_D$-[Co(phen)$_2$(S-Leu)](ClO$_4$)$_2$·3H$_2$O	44.90	4.27	8.73	44.93	3.71	8.75	+605	2.8
8	$(-)_D$-[Co(phen)$_2$(S-Leu)](ClO$_4$)$_2$·2H$_2$O	45.93	4.16	8.93	45.51	3.79	8.81	−637	
9	$(+)_D$-[Co(phen)$_2$(2S,3S-Ile)](ClO$_4$)$_2$·3H$_2$O	44.90	4.27	8.73	45.15	3.70	8.71	+613	5.1
10	$(-)_D$-[Co(phen)$_2$(2S,3S-Ile)](ClO$_4$)$_2$·3H$_2$O	44.90	4.27	8.73	44.92	3.65	8.82	−751	
11	$(+)_D$-[Co(phen)$_2$(S-Val)](ClO$_4$)$_2$·2H$_2$O	45.21	3.93	9.09	45.61	3.61	9.21	+627	5.4
12	$(-)_D$-[Co(phen)$_2$(S-Val)](ClO$_4$)$_2$·3H$_2$O	44.18	4.09	8.88	44.25	3.47	8.93	−764	
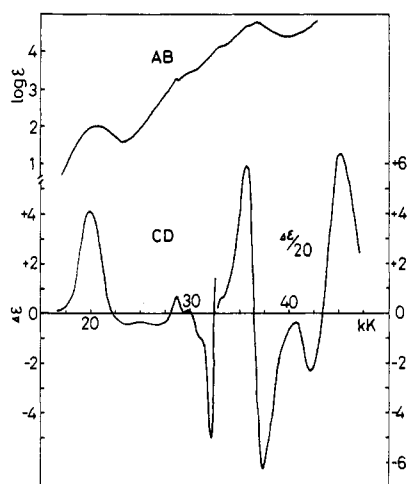
Figure 1. AB and CD spectra for $(+)_D$-[Co(phen)$_2$(Gly)]$^{2+}$.

Figure 2. AB and CD spectra for $(+)_D$-[Co(phen)$_2$(S-Phe)]$^{2+}$ (—) and the CD spectrum for $(-)_D$-[Co(phen)$_2$(S-Phe)]$^{2+}$ (---).

spectrometer in D$_2$O solutions containing sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal standard. So that a sufficient solubility of the complex for the measurement of ^{1}H NMR spectra could be obtained, the perchlorates were converted to the chlorides by using anion-exchange resin (Dowex 1-X8, 100–200 mesh, Cl form).

Results and Discussion

The preparation of [Co(phen)$_2$(am)]$^{2+}$ by the reaction of [Co(phen)$_2$Cl$_2$]Cl with the amino acid anion was carried out in methanol solution. The yield of the desired complex in the reaction mixtures was considerably greater in methanol solution than that in aqueous solution. Results of the elemental analyses, specific rotation, and formation ratios of the isomers are summarized in Table I. The absorption (AB) and the CD spectra of some of the isomers are shown in Figures 1 and 2, and their numerical data are given in Table II. The AB spectra of all the complexes of the type [Co(phen)$_2$(am)]$^{2+}$ show only one band in the first absorption band region ($^1A_{1g}$ → $^1T_{1g}$ transition for O_h parentage) and some intense ultraviolet absorption bands characteristic of the phenanthroline ligands. The features of the AB spectra are similar to those of the spectra of L- or D-tartrato-[11] and D-malatobis(phenanthroline) complex[12] reported previously. The CD spectra in the d–d transition region show the major CD band in the $^1T_{1g}$ region and the weak CD band in the $^1T_{2g}$ region, in analogy with [Co(en)$_2$(am)]$^{2+}$ complexes.[19,20] The CD spectra in the phenanthroline π–π^* transition region exhibit the typical exciton bands of (phen)$_2$ complexes at about 35–37 × 10^3 cm^{-1}, where they have two intense CD peaks of opposite sign.[1,11-14]
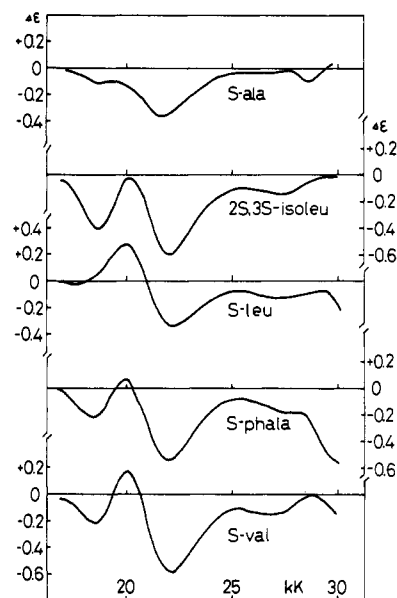
Figure 3. Vicinal effect curves of [Co(phen)$_2$(S-am)]$^{2+}$, where S-am is (S)-alanine, (2S,3S)-isoleucine, (S)-leucine, (S)-phenylalanine, and (S)-valine.

Each $(+)_D$ isomer of the [Co(phen)$_2$(am)]$^{2+}$ has a positive dominant CD peak in the T_{1g} region and a positive and a negative CD peak from the lower frequency side in the exciton region of phenanthroline, indicating the Λ configuration.[15]

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Table II. Absorption and CD Spectra of the Isomers (10^3 cm^{-1})

complex no.[a]	AB $\bar{\nu}_{max}$ (ϵ)	CD[b] $\bar{\nu}_{ext}$ ($\Delta\epsilon$)
1	20.41 (98)	19.88 (+4.06)
	28.57 (1920)	
	29.85 sh (2760)	
	32.79 sh (12 800)	
	35.71 sh (48 200)	35.71 (+118.4)
	36.56 (55 400)	37.31 (−126.1)
3	20.41 (99)	19.80 (+3.10)
	28.49 (1900)	
	29.85 sh (2780)	
	32.79 sh (12 600)	
	35.71 sh (46 700)	35.71 (+72.6)
	36.50 (53 300)	37.31 (−80.9)
4	20.41 (104)	19.84 (−3.34)
	28.49 (1910)	
	29.85 sh (2810)	
	32.79 sh (12 800)	
	35.71 sh (47 000)	35.71 (−96.9)
	36.50 (53 800)	37.31 (+107.7)
5	20.33 (96)	19.76 (+4.12)
	28.49 (1990)	
	29.85 sh (3000)	
	32.79 sh (13 000)	
	35.71 sh (45 600)	35.59 (+101.5)
	36.36 (49 200)	37.31 (−106.2)
6	20.37 (90)	19.65 (−4.01)
	28.49 (1950)	
	29.85 sh (2900)	
	32.79 sh (12 300)	
	35.71 sh (45 700)	35.59 (−101.1)
	36.36 (49 500)	37.31 (+110.3)
7	20.41 (98)	19.84 (+4.38)
	28.49 (1910)	
	29.85 sh (2800)	
	32.79 sh (12 700)	
	35.71 sh (46 400)	35.71 (+108.0)
	36.50 (52 900)	37.24 (−120.4)
8	20.41 (101)	19.80 (−3.82)
	28.49 (1930)	
	29.85 sh (2840)	
	32.79 sh (12 800)	
	35.71 sh (46 800)	35.71 (−97.2)
	36.50 (53 300)	37.31 (+108.2)
9	20.37 (100)	19.86 (+4.40)
	28.41 (1930)	
	29.85 sh (2840)	
	32.79 sh (13 100)	
	35.71 sh (47 200)	35.71 (+109.7)
	36.43 (53 200)	37.31 (−119.1)
10	20.37 (103)	19.65 (−4.60)
	28.49 (1960)	
	29.85 sh (2850)	
	32.97 sh (12 800)	
	35.71 sh (46 700)	35.65 (−109.3)
	36.50 (53 100)	37.31 (+115.6)
11	20.33 (101)	19.84 (+4.57)
	28.41 (1970)	
	29.85 sh (2910)	
	32.79 sh (13 200)	
	35.71 sh (48 200)	35.71 (+108.1)
	36.50 (54 600)	37.31 (−121.3)
12	20.33 (102)	19.69 (−4.30)
	28.57 (1930)	
	29.85 sh (2770)	
	32.79 sh (12 300)	
	35.71 sh (45 300)	35.71 (−96.8)
	36.56 (51 600)	37.45 (+104.4)

^{a} Complex no. is the same as those in Table I. ^{b} The only data for the $^1T_{1g}$ region and the long-axis polarized $\pi-\pi^*$ band region of the phenanthroline are given.

The reverse is found for $(-)_D$ isomers, indicative of the Δ configuration. The configurational and the vicinal effect curves

under the T_{1g} band were evaluated from the CD spectra of diastereomeric pair of an (S)-amino acid complex by a conventional method.[19] The configurational CD curves of the (S)-amino acid complexes well coincide with the observed curve for the corresponding glycinato complex. The vicinal CD curves of the [Co(phen)$_2$(S-am)]$^{2+}$ show three components with a −,+,− sign pattern (Figure 3). The contributions to the observed CD spectra of the vicinal effect are quite small for the amino acid complexes not only of the ethylenediamine systems but of the phenanthroline systems; unlike the hydroxy acid complexes, where the vicinal effects are very significant and comparable in intensity to the configurational effects.[11,12,16] The amino acid tetrammine series[17,18] and ethylenediamine series[19,20] have been extensively studied. From these studies, it has been shown that (S)-amino acids in tetragonal or rhombic complexes impose a negative Cotton effect on the transition with A_{2g} (D_{4h} parentage) and give rise to two nondegenerate transitions of opposite sign corresponding to the E_g (D_{4h}) band.[15] This was realized also in the phenanthroline complexes of the present work as shown already. Therefore, it can be considered that the chelate ring of the (S)-amino acid anion in the [Co(phen)$_2$(S-am)]$^{2+}$ is not greatly displaced from planarity like those of the [Co(NH$_3$)$_4$(S-am)]$^{2+}$ and the [Co(en)$_2$(S-am)]$^{2+}$. Because of the planarity, (S)-amino acids coordinated in the [Co(en)$_2$(S-am)]$^{2+}$ had, then, been considered to have only a small stereoselectivity between the Λ and the Δ isomer.[19,20] Buckingham and his co-workers reported the equilibrium ratio of the Λ to the Δ isomer of [Co(en)$_2$(S-ala)]$^{2+}$ and [Co(en)$_2$(S-val)]$^{2+}$, that is, $\Lambda/\Delta = 1.0$ for the (S)-alanine complex and $\Lambda/\Delta = 1/1.7$ for the (S)-valine complex.[21] We have been determined the equilibrium ratio of the Λ to the Δ isomer of [Co(phen)$_2$(S-am)]$^{2+}$. The reaction mixture under a variety of reaction times (1–5 h) with use of, for example, the (S)-valine complex was applied to a column of SP-Sephadex C-25 as described earlier, and the formation ratio between the diastereoisomers was calculated from the area of the elution bands and the molar extinction coefficients at the first absorption band maxima. The diastereoisomers were found to be sufficiently at equilibrium within 3 h at 40 °C. The stereoselectivity which occurred in the phenanthroline complexes reported here was greater than that in the corresponding ethylenediamine complexes, that is, $\Lambda/\Delta = 2.1$ for the (S)-alanine complex and $\Lambda/\Delta = 5.4$ for the (S)-valine complex (Table I). Furthermore, the preferred configuration was inverted between the phenanthroline complex and the ethylenediamine complex. In the case of the ethylenediamine complexes, it has been pointed out that conformational calculations give only a small energy difference between two diastereoisomers and that there exists also a possibility that slightly different solvation energies for the two ions decide the isomeric stability.[21] On the other hand, for every diastereomeric pair of the phenanthroline complexes in the present work, the Λ isomer was observed to be more preferable to the Δ isomer. Molecular models reveal that the substituent group on the amino acid chelate ring prefers the stable equatorial positions and has some repulsive interactions with α-position hydrogen atom of the neighboring phenanthroline. The repulsive interactions in the phenanthroline complex differ significantly from the corresponding ethylenediamine complex and may control the preferred absolute

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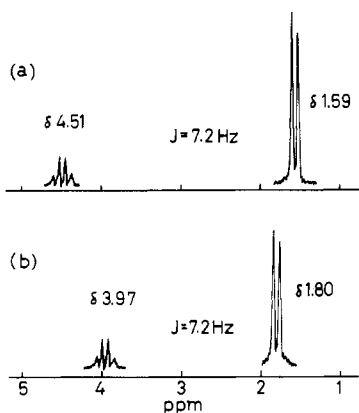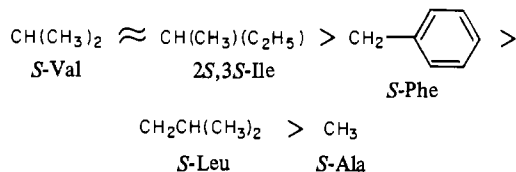(21) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 5133 (1967).

Figure 4. ¹H NMR spectra of the (a) Λ- and (b) Δ-[Co(phen)₂(S-Ala)]²⁺ in D₂O 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

$$CH(CH_3)_2 \approx CH(CH_3)(C_2H_5) > CH_2\text{—}\langle\text{phenyl}\rangle >$$
$$S\text{-Val} \qquad\qquad 2S,3S\text{-Ile} \qquad\qquad\qquad S\text{-Phe}$$

$$CH_2CH(CH_3)_2 > CH_3$$
$$S\text{-Leu} \qquad\quad S\text{-Ala}$$

The stereoselectivity of the (S)-phenylalanine and the (S)-leucine complex was smaller than that of the (2S,3S)-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 ¹H NMR spectra of the Λ- and the Δ-[Co(phen)₂(S-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 ¹H 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-Ala)₂(bpy)]⁺ complexes.³ Further study of the bis(phenanthroline) com-

plexes 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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Circular Dichroism of Eu³⁺ and Nd³⁺ in a K₃Nd₂(NO₃)₉ Single Crystal

Prabir K. Chatterjee and Mihir Chowdhury*

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 crystals³,⁴ where the optical activity originates from the asymmetric environment of the Ln³⁺ ion. Encouraged by the success of the spectra–environment correlation⁵⁻⁷ 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 Ln³⁺ double nitrates (Ln, = Pr, Nd, Sm).

This paper reports the low-resolution CD and absorption spectra of doped Nd³⁺ crystals primarily with a view to verify the expectations of Richardson⁸ regarding low-resolution lanthanide optical activity. In order to compare the CD of the Nd³⁺ transition, which are commonly considered as electric-dipole allowed, with that of primarily magnetic-dipole-allowed Eu³⁺ transitions having an identical environment, we have grown and studied a single crystal of K₃Nd₂(NO₃)₉ with Eu³⁺ as dopant.

The anhydrous double nitrate has the general formula K₃Ln₂(NO₃)₉ where Ln is Pr, Nd, or Sm. The crystal system is cubic and has the unusual space group P4₃32. 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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