

Synthesis & Absorption Spectral Studies of Praseodymium (III) & Neodymium (III) Complexes with Amino Acids

SUDHINDRA N. MISRA*, G. K. JOSHI† & M. P. BHUTRA‡
Department of Chemistry, University of Jodhpur, Jodhpur 342 001

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Amino acid complexes of Pr(III) and Nd(III) have been synthesized by the reaction of lanthanide(III) isopropoxides and the amino acids (glycine, alanine, valine, leucine, isoleucine, histidine, serine, 4-aminobutyric acid, methionine, tryptophane and cysteine) in 1 : 3 molar ratio. These sparingly soluble complexes of the type Ln (amino acid)₃ have been characterized on the basis of elemental analyses and electronic spectral data. The values of Slater-Condon (F_2, F_4, F_6) interelectronic repulsion and Lande' (ξ_{4f}) spin-orbit interaction parameters have been computed from the spectral data. The variation of these parameters in the complexes from the corresponding Pr³⁺ and Nd³⁺ free ion parameters is discussed. The average values of F_4/F_2 and F_6/F_2 have been found to be 0.139 and 0.0151 for Pr(III) complexes and 0.150 and 0.0150 for Nd(III) complexes, respectively. Using F_2 values, the nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$) have been calculated. The relative variation of covalent bonding in the complexes has been discussed.

THE absorption spectra of free or aquo ions of lanthanides in different chemical environments have been studied by several investigators¹⁻⁷. But work on anhydrous chelates of praseodymium and neodymium is scanty⁸⁻¹⁰. With a view to making a comparative study of various parameters of Pr(III) and Nd(III) complexes with amino acids, we report herein the synthesis and characterization of anhydrous amino acid chelates of Pr(III) and Nd(III). Calculation of various parameters like Slater-Condon (F_k), Lande' (ξ_{4f}), nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$) has also been carried out. The variation of these parameters and correlation of these with the nature of metal-ligand bonding have been discussed.

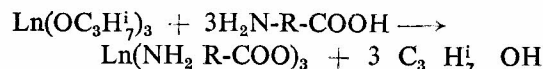
Materials and Methods

Synthesis of lanthanide isopropoxides — Isopropoxides of Pr(III) and Nd(III) were synthesized by a method reported earlier^{11,12}. The anhydrous trichloroacetate of Pr(III) or Nd(III) (prepared by heating the hydrated trichloroacetate *in vacuo* at 60°C for 6 hr) was reacted with sodium isopropoxide in 1:3 molar ratio in benzene when Pr(III) or Nd(III) isopropoxide was obtained in good yield.

Preparation of amino acid complexes of Pr(III) and Nd(III) — The complexes were prepared by the reaction of the lanthanide (Pr or Nd) isopropoxide with amino acid in the molar ratio (1:3) in benzene-isopropanol mixture. These were purified by repeated crystallization. The analytical data of the complexes have been summarized in Table 1.

Results and Discussion

Lanthanide(III) complexes have generated much interest among chemists and biochemists¹³⁻¹⁵. The lanthanide ions have been classified as class (A) acids having ionic sizes in the range 0.85-1.05 Å and thus these do not show much inclination towards coordination with ligands containing sulphur. The reactions of lanthanide isopropoxides with amino acids have been carried out in benzene medium, and these appear to follow the following type of equation :



The reaction scheme is supported by analytical data as well as IR spectral data. The reaction appears to be a bit slower than the reaction of lanthanide alkoxides with carboxylic and hydroxy carboxylic acids^{16,17}.

The amino acids used in the present study are monocarboxylic acids having different structural features. Histidine has pseudo-aromatic imidazole ring; tryptophan has indole unit; serine has a side chain oxygen (hydroxyl) atom; while cysteine and methionine have sulphur as a potential donor site. Although structural features of these amino acids are such that these may cause some hindrance to direct interaction with metal ion of the potential donor sites, the large ionic size of lanthanides and their tendency to form coordination polyhedra where coordination number of metal exceeds six may permit these ions to have some sort of interaction with sulphur, imidazole nitrogen, indole nitrogen and possibly with the side chain hydroxyl group of serine.

Absorption spectral parameters — The electrostatic and magnetic interactions among 4f electrons can be

*Department of Chemistry, Govt. P.G. College, Nagaur 341 001.

†Department of Physics, University of Jodhpur, Jodhpur.

TABLE 1 — SYNTHESIS AND ANALYTICAL DATA OF LANTHANIDE AMINO ACID COMPLEXES

Reactants	Product and Colour	Found (Calc.), %	
		M	N
Pr(OPr ¹) ₃ (1.6 g) glycine (1.12 g)	Pr(glycinate) ₃ Green	38.3 (38.80)	11.3 (11.56)
Nd(OPr ¹) ₃ (1.62 g) Glycine (1.12 g)	Nd(glycinate) ₃	38.6 (39.38)	11.2 (11.47)
Pr(OPr ¹) ₃ (0.79 g) Alanine (0.66 g)	Pr(alaninate) ₃ Greenish-yellow	34.2 (34.77)	10.1 (10.36)
Nd(OPr ¹) ₃ (1.05 g) Alanine (0.86 g)	Nd(alaninate) ₃ Yellow	35.0 (35.32)	10.1 (10.28)
Pr(OPr ¹) ₃ (1.13 g) Valine (1.22 g)	Pr(valinate) ₃ Green	28.6 (28.79)	8.7 (8.58)
Nd(OPr ¹) ₃ (1.00 g) Valine (1.08 g)	Nd(valinate) ₃ Pink	29.5 (29.29)	8.6 (8.52)
Pr(OPr ¹) ₃ (0.78 g) Phenylalanine (1.20 g)	Pr(phenylalaninate) ₃ Greenish-yellow	22.5 (22.25)	—
Nd(OPr ¹) ₃ (0.83 g) Phenylalanine (1.27 g)	Nd(phenylalaninate) ₃ Yellowish-pink	22.7 (22.67)	—
Pr(OPr ¹) ₃ (1.0 g) Leucine (1.22 g)	Pr(leucinate) ₃ Greenish-yellow	26.3 (26.53)	7.7 (7.91)
Nd(OPr ¹) ₃ (0.86 g) Leucine (1.04 g)	Nd(leucinate) ₃ Pink	26.8 (27.00)	7.9 (7.86)
Pr(OPr ¹) (1.00 g) Isoleucine (1.21 g)	Pr(isoleucinate) ₃ Green	26.7 (26.53)	8.0 (7.91)
Nd(OPr ¹) ₃ (0.90 g) Isoleucine (1.08 g)	Nd(isoleucinate) ₃ Pink	27.1 (27.00)	7.9 (7.86)
Pr(OPr ¹) ₃ (0.68 g) Histidine (0.98 g)	Pr(histidinate) ₃ Yellowish-green	23.7 (23.36)	—
Nd(OPr ¹) ₃ (0.72 g) Histidine (1.03 g)	Nd(histidinate) ₃ Orange	24.2 (23.79)	—
Pr(OPr ¹) ₃ (1.0 g) Serine (0.98 g)	Pr(serinate) ₃ Green	31.0 (31.40)	9.3 (9.27)
Nd(OPr ¹) ₃ (0.88 g) Serine (1.00 g)	Nd(serinate) ₃ Pink	31.4 (31.63)	9.1 (9.20)
Pr(OPr ¹) ₃ (0.88 g) 2-Aminobutyric acid (0.85 g)	Pr(2-aminobutyrate) ₃ Green	31.3 (31.5)	9.5 (9.39)
Nd(OPr ¹) ₃ (0.80 g) 2-Aminobutyric acid (0.67 g)	Nd(2-aminobutyrate) ₃ Pink	32.0 (32.03)	9.4 (9.31)
Pr(OPr ¹) ₃ (0.70 g) 4-Aminobutyric acid (0.67 g)	Pr(4-aminobutyrate) ₃ Green	31.3 (31.50)	9.2 (9.39)
Nd(OPr ¹) ₃ (0.72 g) 4-Aminobutyric acid	Nd(4-aminobutyrate) ₃ Pink	31.7 (32.02)	9.2 (9.31)
Pr(OPr ¹) ₃ (1.11 g) Tryptophan (2.10 g)	Pr(tryptophanate) ₃ Green	19.00 (18.77)	—
Nd(OPr ¹) ₃ (1.05 g) Tryptophan (1.95 g)	Nd(tryptophanate) ₃ Pink	19.3 (19.13)	—
Pr(OPr ¹) ₃ (0.92 g) Methionine (1.00 g)	Pr(methioninate) ₃ Green	24.2 (24.06)	7.3 (7.17)
Nd(OPr ¹) ₃ (0.76 g) Methionine (1.08 g)	Nd(methioninate) ₃ Yellow	24.6 (24.49)	7.3 (7.13)
Pr(OPr ¹) ₃ (1.58 g) Cysteine (1.78 g)	Pr(cystenatate) ₃ Green	28.3 (28.13)	8.5 (8.38)
Nd(OPr ¹) ₃ (1.64 g) Cysteine (1.80 g)	Nd(cystenatate) ₃ Yellow	28.8 (28.61)	8.5 (8.32)

expressed in terms of electron repulsion integrals, Slater-Condon (F_k) and spin-orbit interaction (ζ_{4f}) parameters. The change in the value of F_k with respect to the free ion as a result of complexation is known as nephelauxetic effect and is expressed by nephelauxetic ratio (β), defined as,

$$\beta = F_k^c / F_k^f$$

where F_k^c and F_k^f refer to the parameters in complex and free ion respectively³.

The positions of free ion bands of Pr(III) and Nd(III) have been inferred from the crystal spectra of Pr(III) and Nd(III)¹⁸. Using these estimated zero order and partial derivative values, the free ion F_k 's, have been computed as discussed below.

An initial set of F_2, F_4, F_6 and ζ_{4f} values may be evaluated by expressing the band energy as Taylor series expansion. To a first approximation, the energy E_j of j th level is given by Eq. 1.

$$E_j(F_k, \zeta_{4f}) = E_{0j} + \sum_{k=2,4,6} (F_k^0, \zeta_{4f}^0) + \sum (\delta E_j / \delta F_k) \Delta F_k + (\delta E_j / \delta \zeta_{4f}) \Delta \zeta_{4f} \quad \dots (1)$$

where E_{0j} is the energy of zero order energy level;

the value of E_{0j} and partial derivatives $\frac{\delta E_j}{\delta F_k}, \frac{\delta E_j}{\delta \zeta_{4f}}$

for different levels (with respect to the free ion) are known. The observed E_j values can be written as :

$$E_j = E_{0j} + n_1 \Delta F_2 + n_2 \Delta F_4 + n_3 \Delta F_6 + n_4 \Delta \zeta_{4f}$$

$$\frac{E_j - E_{0j}}{n_1} = \Delta F_2 + \frac{n_2}{n_1} \Delta F_4 + \frac{n_3}{n_1} \Delta F_6 + \frac{n_4}{n_1} \Delta \zeta_{4f}$$

which is of the form,

$$Y = \frac{E_j - E_{0j}}{n_1}$$

$$Y = a + X_1 b_1 + X_2 b_2 + X_3 b_3 \quad \dots (2)$$

$$a = \Delta F_2; b_1 = \Delta F_4; b_2 = \Delta F_6; b_3 = \Delta \zeta_{4f}$$

and $X_1 = \frac{n_2}{n_1}, X_2 = n_3/n_1$ and $X_3 = n_4/n_1$

where n_1, n_2, n_3 and n_4 are the partial derivatives.

For each observation (for a level) the equation of the type (2) can be obtained. The values of b_1, b_2, b_3 can be obtained using partial and multiple regression methods¹⁹. From these, the values of F_k and other parameters are obtained (Tables 2 and 3). The reported values of zero order energies and partial derivatives with respect to F_k and ζ_{4f} parameters for Pr(III) are given⁴.

In the present study of Pr(III) and Nd(III) complexes, it has been observed (Tables 2, 3) that the values of F_k and ζ_{4f} are less as compared to the corresponding parameters of free ion. These obser-

TABLE 2 — COMPUTED VALUES OF VARIOUS ENERGY INTERACTION PARAMETERS OF PRASEODYMIUM COMPLEXES

Complexes	F_2	F_4	F_6	ζ_{4f}	$\beta = \frac{F_2^c}{F_2^f}$	b_1^{\ddagger}	F_4/F_2	F_6/F_2
Pr ³⁺ free ion	332.09	44.46	4.58	741.0	1.000	—	0.1334	0.0138
Pr(glycinate) ₃	313.8	43.3	4.74	738.0	0.9744	0.113	0.1378	0.0152
Pr(alanine) ₃	312.4	43.13	4.72	736.5	0.9700	0.116	0.1380	0.0151
Pr(2-aminobutyrate) ₃	312.37	43.14	4.72	736.4	0.9698	0.116	0.1381	0.0151
Pr(valinate) ₃	312.2	43.0	4.67	735.0	0.9688	0.117	0.1378	0.0149
Pr(phenylalaninate) ₃	311.6	43.0	4.71	739.0	0.9675	0.127	0.1380	0.0151
Pr(leucinate) ₃	311.04	42.9	4.70	738.0	0.9669	0.128	0.1379	0.0151
Pr(4-aminobutyrate) ₃	311.0	43.0	4.70	735.3	0.9666	0.129	0.1380	0.0151
Pr(isoleucinate) ₃	310.10	42.8	4.68	739.6	0.9632	0.1358	0.1380	0.0151
Pr(histidine) ₃	309.6	42.78	4.69	734.0	0.9612	0.139	0.1382	0.0151
Pr(methionine) ₃	308.6	42.6	4.66	732.6	0.9581	0.144	0.1380	0.0151
Pr(tryptophanate) ₃	307.3	42.4	4.64	719.9	0.9537	0.152	0.1380	0.0157
Pr(cysteinate) ₃	307.0	42.4	4.64	719.6	0.9534	0.153	0.1381	0.0151

TABLE 3 — COMPUTED VALUES OF VARIOUS ENERGY INTERACTION PARAMETERS OF NEODYMIUM COMPLEXES

Nd ³⁺ Complexes	F_2	F_4	F_6	ζ_{4f}	$\beta = \frac{F_2^c}{F_2^f}$	b_1^{\ddagger}	F_4/F_2	F_6/F_2
Nd ³⁺ free ion	331.16	50.71	5.15	884.0	1.000	—	0.1531	0.0155
Nd(glycinate) ₃	326.75	49.83	4.91	866.0	0.9867	0.0812	0.1526	0.0160
Nd(alanine) ₃	326.5	50.40	2.90	861.0	0.9860	0.0837	0.1542	0.0159
Nd(serinate) ₃	325.0	48.84	4.59	878.8	0.9814	0.096	0.1507	0.0151
Nd(2-aminobutyrate) ₃	324.9	48.96	4.60	880.0	0.9812	0.097	0.1507	0.0151
Nd(valinate) ₃	324.2	49.62	4.52	870.0	0.9790	0.1025	0.1530	0.0153
Nd(phenylalaninate) ₃	323.6	48.40	4.51	868.0	0.9770	0.1070	0.1455	0.0145
Nd(4-aminobutyrate) ₃	323.8	48.2	4.71	860.0	0.9770	0.1070	0.1490	0.0145
Nd(leucinate) ₃	323.4	48.6	4.70	858	0.9755	0.1082	0.1535	0.0160
Nd(isoleucinate) ₃	322.6	48.3	4.76	851	0.9712	0.120	0.1498	0.0148
Nd(methionine) ₃	321.5	47.2	4.80	848.0	0.9707	0.1214	0.1468	0.0150
Nd(histidine) ₃	321.0	47.2	4.80	846.0	0.9693	0.1240	0.1468	0.0150
Nd(tryptophanate) ₃	321.0	47.2	4.80	846.0	0.9693	0.1240	0.1468	0.0150
Nd(cysteinate) ₃	321.0	47.2	4.80	846.0	0.9693	0.1240	0.1468	0.0150

variations are in conformity with the general trend that on complexation central metal ion orbital expands. This is expected to decrease the interelectronic repulsion and spin-orbit interaction parameters. The average values of ζ_{4f} for Pr(III) and Nd(III) complexes are ~ 731 and 871 cm^{-1} which are of smaller magnitude than those computed using Hartree-Fock method¹⁸ [980 and 1130 cm^{-1} for Pr(III) and Nd(III) respectively]. However, these values do not differ much from these of aquo ion and satisfy the relation,

$$\zeta_{4f} = 142z - 7648 \quad \dots (3)$$

suggested¹⁸ for lanthanide ions where z is the atomic number of the lanthanide.

In Pr(III) and Nd(III) complexes, $4f$ orbitals do participate in bonding. The amount of $4f$ ligand mixing is represented by parameter $b^{\frac{1}{2}}$ known as bonding parameter. This parameter is related to the nephelauxetic ratio (β) by the relation,

$$b^{1/2} = [(1 - \beta)/2]^{\frac{1}{2}}$$

Nephelauxetic ratio and bonding — The complexes of praseodymium and neodymium have been arranged in the increasing orders of bonding parameter ($b^{\frac{1}{2}}$), nephelauxetic effect ($1-\beta$) and decreasing magnitude of F_2 parameter. Tables 2 and 3 indicate that the amino acid chelates which do not have sulphur atom have higher values of F_2 parameter while methionine and cysteine yield chelates with minimum values of F_2 and maximum values of $b^{1/2}$ and $1-\beta$. This suggests that the presence of sulphur causes increased covalency in the metal-ligand bond. The presence of $d\pi$ orbitals on sulphur may increase the mixing of ligand orbitals with the $4f$ orbital on lanthanide.

Though histidine does not contain sulphur atom, yet we find sufficient decrease in the inter-electronic repulsion (F_2) and spin-orbit interaction (ζ_{4f}) parameters for its complexes. This decrease can be easily understood from the structure of histidine itself. Histidine molecule has imidazole nitrogen as a coordinating sites, in addition to the amino nitrogen and carboxylic hydroxy group. During complexation, it is the imidazole nitrogen that preferentially participates in coordination and thus the presence of pseudo-aromatic imidazole ring in the chelate ring increases the covalency.

Tryptophan complexes of Pr(III) and Nd(III) also show sufficient decrease in the F_2 and ζ_{4f} parameters. Tryptophan like histidine has an indole unit.

Its presence in the chelate ring causes sufficient decrease in interelectronic repulsion and spin-orbit interaction parameters. This finds further support when we compare the magnitudes of these parameters in alanine and phenyl-alanine derivatives. The lowering of these parameters is greater in the latter derivative which possesses an extra phenyl ring.

While comparing the data for 2-amino- and 4-aminobutric acid complexes we find larger lowering of F_2 and ζ_{4f} in the latter series of complexes. The chelate ring formed in the latter derivatives will be larger and would contribute towards larger decrease in F_2 and ζ_{4f} .

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