

## Synthesis and characterization of lanthanide(III) complexes of 1-naphthoxy-, 2-naphthoxy- and 8-quinolinyloxyacetic acids

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Lanthanum(III), praseodymium(III), neodymium(III), samarium(III), gadolinium(III), terbium(III) and dysprosium(III) chelates of the type  $[M(RCOO)_3] \cdot 2H_2O$  with the ligands 1-naphthoxy-, 2-naphthoxy- and 8-quinolinyloxyacetic acids have been isolated and characterized on the basis of elemental analyses, spectral, magnetic and thermal data. The IR data show that the bonding of the carboxylato group to the metal ion is bidentate. A coordination number of six is suggested for the rare earth metal ions in these complexes.

In continuation of our work on 4-X-phenoxyacetato lanthanide(III) complexes<sup>1</sup>, we report in this paper the synthesis and characterisation of hitherto unknown chelates of 1-naphthoxy-, 2-naphthoxy- and 8-quinolinyloxyacetic acids of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III). The work has been attempted primarily with a view to study the effect of peri-H/lone pair interaction on meta-ligand covalency. It is pertinent to note that the higher acid strength of 1-naphthoic acid compared to 2-naphthoic acid is attributed to the steric effect of peri-H in the former<sup>2</sup>. Further, among the complexes of 1- and 2-naphthalenesulphonic acids, the 'proximity effect' of peri-H in 1-isomer complexes cause the  $-SO_2-$  group to deviate from the plane of the naphthyl ring which inhibits resonance of the sulphinato group with the naphthyl ring<sup>3</sup>. Therefore, it could be expected that among the lanthanide(III) complexes of 1- and 2-naphthoxyacetic acids, the effect of peri-H may be significant for the 1-isomer compared to the 2-isomer. In the case of 8-quinolinyloxyacetic acid, the peri-H has been replaced by the imine-N lone pair. Hence, it would be interesting to study how the steric/electronic effect of this lone pair affects the metal-ligand covalency in the complexes with lanthanide(III) ions.

### Materials and Methods

Rare-earth oxides, (99.9% purity) were obtained from Indian Rare Earths Ltd., Trivandrum. Lanthanide chlorides were prepared by dissolving the calculated amount of oxide in concentrated

hydrochloric acid and then evaporating to get the residue. The residue was dissolved in water and the chloride solution was used for the preparation of complexes. The ligands were prepared by the general procedure reported in the literature<sup>4</sup>. The complexes of 1- and 2-naphthoxyacetic acids were prepared as follows:

To a solution of naphthoxyacetic acid (2.02 g, 10 mmol) in aqueous acetone (1:1, 200 ml), drops of aqueous ammonia (1:6) were added to bring the pH to 6.5-7. The above solution was treated with lanthanide(III) chloride (3.33 mmol) in aqueous acetone (1:1, 50 ml). The complex settled was suction filtered, washed with aqueous acetone (1:1), dried in air and then *in vacuo* over anhydrous calcium chloride.

The lanthanide(III) chelates of 8-quinolinyloxyacetic acid were prepared as follows:

To a solution of sodium salt of 8-quinolinyloxyacetic acid (2.25 g, 10 mmol) in water (200 ml), was added a solution of lanthanide(III) chloride (3.33 mmol) in water (30 ml). The complex settled was suction filtered, washed with water, dried in air and then *in vacuo* over anhydrous calcium chloride.

The metal content of the complexes was estimated by incinerating them to the oxides. The conductivity measurements were made using a Toshniwal conductivity meter with a dip-type cell fitted with a platinised platinum electrode (cell constant, 0.734), using approximately  $1 \times 10^{-3}$  M solution of the complexes. The magnetic susceptibility measurements were carried out using solid samples on a simple Gouy type magnetic balance at room

temperature (303-308 K). The infrared spectra of all the complexes and sodium salts of the ligands were recorded as KBr pellets on a Perkin-Elmer 527 infrared spectrophotometer (200-4000  $\text{cm}^{-1}$ ). The electronic spectral measurements were made as nujol mulls on filter paper with a Shimadzu UV-visible spectrophotometer (UV-160).

### Results and Discussion

The results of elemental analysis and magnetic moment data of these complexes are given in Table 1. All these complexes are amorphous and insoluble in water. They are soluble in DMF and are non-conducting in DMF as shown by the values of molar conductance which lie in the range of 3-6  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ .

The weight loss experiments carried out at different temperatures (isothermal heating) indicate that all the complexes begin to lose water at 80° and 90°C. Two water molecules are lost, suggesting the presence of lattice held nature of these molecules.

All lanthanum(III) complexes are diamagnetic. Other lanthanide(III) complexes are paramagnetic and the  $\mu_{\text{eff}}$  values are closer to their respective theoretical values, except for samarium(III). The magnetic moments of Sm(III) complexes do deviate from the theoretical value for reasons already known<sup>5</sup>. The magnetic moment values of all the complexes, presently studied, are shown in Table 1.

In the case of carboxylato complexes, attempts have been made to relate values of the carbon-oxygen stretching frequencies to the nature of the carboxylate coordination<sup>6</sup>. The unidentate coordination removes the equivalence of two oxygen atoms. If the carbon-oxygen bond orders are appreciably affected, a pseudo-ester configuration is obtained. This should increase  $\nu_{\text{as}}(\text{COO})$  and decrease  $\nu_{\text{s}}(\text{COO})$  thereby increasing the separation between the (COO) frequencies relative to the values for the free carboxylate ion, usually taken as those of the sodium or potassium salts<sup>7</sup>.

In the bidentate chelate coordination of the carboxylate group to the metal ions, two factors assume importance<sup>8</sup>. (i) Due to the depletion of the electron density from the carboxylate group by the metal ion both  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  frequencies are lowered. (ii) In bidentate chelation, the O-C-O angle is expected to decrease when the metal-oxygen bond becomes stronger. The valence force-field equations for  $\text{XY}_2$  system<sup>8</sup> and the calculations for the triatomic model<sup>8</sup>, have shown that a decrease in the O-C-O angle re-

Table 1 - Characterization data of Ln(III) complexes

Compound	Found (calc.), %				$\mu_{\text{eff}}$ (B.M.)
	Metal	C	H	N	
[La(ONAP) <sub>3</sub> ].2H <sub>2</sub> O	17.91 (17.85)	55.11 (55.53)	3.96 (3.98)	—	dia.
[Pr(ONAP) <sub>3</sub> ].2H <sub>2</sub> O	17.72 (18.06)	55.46 (55.39)	3.84 (3.97)	—	3.41
[Nd(ONAP) <sub>3</sub> ].2H <sub>2</sub> O	17.95 (18.41)	55.01 (55.15)	3.73 (3.95)	—	3.72
[Sm(ONAP) <sub>3</sub> ].2H <sub>2</sub> O	18.82 (19.05)	54.12 (54.72)	4.02 (3.92)	—	1.64
[Gd(ONAP) <sub>3</sub> ].2H <sub>2</sub> O	18.94 (19.75)	54.36 (54.25)	3.65 (3.89)	—	8.12
[Tb(ONAP) <sub>3</sub> ].2H <sub>2</sub> O	19.52 (19.92)	53.92 (54.14)	3.36 (3.88)	—	9.64
[Dy(ONAP) <sub>3</sub> ].2H <sub>2</sub> O	19.96 (20.27)	54.06 (53.90)	4.02 (3.87)	—	10.48
[La(TNAP) <sub>3</sub> ].2H <sub>2</sub> O	18.12 (17.85)	55.12 (55.53)	3.87 (3.98)	—	dia.
[Pr(TNAP) <sub>3</sub> ].2H <sub>2</sub> O	18.54 (18.06)	55.62 (55.39)	3.63 (3.97)	—	3.56
[Nd(TNAP) <sub>3</sub> ].2H <sub>2</sub> O	17.92 (18.41)	54.98 (55.15)	3.75 (3.95)	—	3.58
[Sm(TNAP) <sub>3</sub> ].2H <sub>2</sub> O	18.88 (19.05)	54.25 (54.72)	4.02 (3.92)	—	1.52
[Gd(TNAP) <sub>3</sub> ].2H <sub>2</sub> O	19.52 (19.75)	54.12 (54.25)	3.62 (3.89)	—	7.98
[Tb(TNAP) <sub>3</sub> ].2H <sub>2</sub> O	19.62 (19.92)	54.08 (54.14)	3.41 (3.88)	—	9.76
[Dy(TNAP) <sub>3</sub> ].2H <sub>2</sub> O	20.05 (20.27)	54.01 (53.90)	4.02 (3.87)	—	10.65
[La(EHQA) <sub>3</sub> ].2H <sub>2</sub> O	17.52 (17.79)	50.41 (50.71)	3.46 (3.58)	5.16 (5.38)	dia.
[Pr(EHQA) <sub>3</sub> ].2H <sub>2</sub> O	18.36 (18.00)	50.06 (50.58)	3.62 (3.58)	5.24 (5.36)	3.49
[Nd(EHQA) <sub>3</sub> ].2H <sub>2</sub> O	18.82 (18.34)	50.62 (50.37)	3.39 (3.56)	5.40 (5.34)	3.65
[Sm(EHQA) <sub>3</sub> ].2H <sub>2</sub> O	19.00 (18.98)	50.01 (49.97)	3.65 (3.53)	5.22 (5.30)	1.40
[Gd(EHQA) <sub>3</sub> ].2H <sub>2</sub> O	20.05 (19.67)	50.12 (49.55)	3.42 (3.50)	5.18 (5.25)	7.82
[Tb(EHQA) <sub>3</sub> ].2H <sub>2</sub> O	20.12 (19.84)	50.25 (49.44)	3.61 (3.49)	5.14 (5.24)	9.51
[Dy(EHQA) <sub>3</sub> ].2H <sub>2</sub> O	20.35 (20.20)	48.94 (49.22)	3.02 (3.48)	5.30 (5.22)	10.49

ONAPH = 1-Naphthoxyacetic acid, TNAPH = 2-naphthoxyacetic acid; EHQA = 8-Quinolinyloxyacetic acid

Table 2 – Electronic absorption data of Ln(III) complexes

Compound	$\nu_{\max}$ ( $\text{cm}^{-1}$ )	Nephelauxetic ratio ( $\beta$ )	Sinha parameter $\delta$ (%)	Bonding parameter ( $b^{1/2}$ )
Pr(ONAP) <sub>3</sub> ·2H <sub>2</sub> O	21186 <sup>a</sup>	0.9937	0.6340	0.0561
[Pr(TNAP) <sub>3</sub> ] <sub>3</sub> ·2H <sub>2</sub> O	21195 <sup>a</sup>	0.9941	0.5935	0.0543
[Pr(EHQA) <sub>3</sub> ] <sub>3</sub> ·2H <sub>2</sub> O	21142 <sup>a</sup>	0.9916	0.8471	0.0648
[Nd(ONAP) <sub>3</sub> ] <sub>3</sub> ·2H <sub>2</sub> O	17053 <sup>b</sup>	0.9857	1.4507	0.0846
[Nd(TNAP) <sub>3</sub> ] <sub>3</sub> ·2H <sub>2</sub> O	17059 <sup>b</sup>	0.9860	1.4198	0.0836
[Nd(EHQA) <sub>3</sub> ] <sub>3</sub> ·2H <sub>2</sub> O	17021 <sup>b</sup>	0.9838	1.6467	0.0900
[Sm(ONAP) <sub>3</sub> ] <sub>3</sub> ·2H <sub>2</sub> O	24272 <sup>c</sup>	0.9757	2.4905	0.1102
[Sm(TNAP) <sub>3</sub> ] <sub>3</sub> ·2H <sub>2</sub> O	24284 <sup>c</sup>	0.9762	2.4380	0.1091
[Sm(EHQA) <sub>3</sub> ] <sub>3</sub> ·2H <sub>2</sub> O		masked by ligand band		

<sup>a</sup>  $^3H_4 \rightarrow ^3P_1$ ; <sup>b</sup>  $^4I_{9/2} \rightarrow ^2G_{7/2}$ ,  $^4G_{5/2}$ ; <sup>c</sup>  $^6H_{5/2} \rightarrow ^6P_{3/2}$

sults in a decrease in the frequency separation,  $\Delta\nu$ , between the two (COO) frequencies.

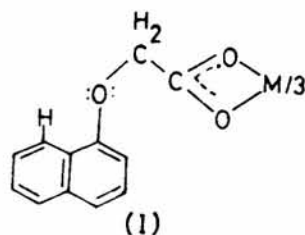
These two factors act in the opposite direction for the  $\nu_s(\text{COO})$  but in the same direction for the  $\nu_{as}(\text{COO})$ . Thus in a bidentate chelate mode of coordination of the carboxylate group, the  $\nu_{as}(\text{COO})$  frequency decreases and the  $\nu_s(\text{COO})$  frequency either increases or remains the same compared to that in the sodium salt.

The potassium salt of 1-naphthoxyacetic acid exhibits  $\nu_{as}(\text{COO})$  at  $1590\text{ cm}^{-1}$  and  $\nu_s(\text{COO})$  at  $1420\text{ cm}^{-1}$ ; the lanthanide complexes of the above acid exhibit these absorptions in the range of  $1565\text{--}1575\text{ cm}^{-1}$  and  $1430\text{--}1437\text{ cm}^{-1}$  respectively. While the  $\nu_{as}(\text{COO})$  and  $\nu_s(\text{COO})$  of potassium salt of 2-naphthoxyacetic acid appear at  $1590$  and  $1420\text{ cm}^{-1}$ , the lanthanide complexes of this acid absorb in the range of  $1572\text{--}1585\text{ cm}^{-1}$  and  $1423\text{--}1430\text{ cm}^{-1}$  respectively. The sodium salt of 8-quinolinylxyacetic acid exhibits  $\nu_{as}(\text{COO})$  at  $1605\text{ cm}^{-1}$  and  $\nu_s(\text{COO})$  at  $1405\text{ cm}^{-1}$ , whereas these absorptions occur in the range of  $1580\text{--}1590\text{ cm}^{-1}$  and  $1412\text{--}1420\text{ cm}^{-1}$  respectively for its lanthanide complexes. The magnitude of difference between the  $\nu_{as}(\text{COO})$  and  $\nu_s(\text{COO})$  values, suggests bidentate chelate mode of carboxylate coordination for these complexes. All the complexes exhibit a broad band  $\sim 3400\text{ cm}^{-1}$  suggesting the presence of water molecules in these complexes.

The electronic absorption data for the complexes are presented in Table 2. The electronic transition  $^3H_4 \rightarrow ^3P_1$  exhibits red-shift for all the Pr(III) complexes. A relatively higher red-shift is shown by the complex of 8-quinolinylxyacetic acid. The bonding parameters  $\beta$ ,  $\delta$  and  $b^{1/2}$  have

been calculated for this transition using the well-known equations.

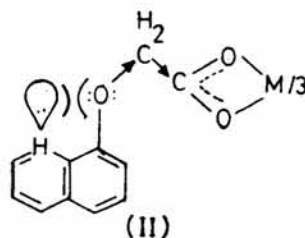
The bonding parameter ( $b^{1/2}$ ) value of tris-(2-naphthoxyacetato)Pr(III) dihydrate is the same as that of tris(phenoxyacetato)quoPr(III) monohydrate<sup>1</sup>. This shows that the mesomeric interaction due to the lone pair on ether-O is perhaps the same in both the cases. The bonding parameter ( $b^{1/2}$ ) value of tris(1-naphthoxyacetato)Pr(III) dihydrate is slightly greater than that of tris(phenoxyacetato)quoPr(III) monohydrate. This may be due to the interaction of peri-H and ether-O.



Since mesomeric interaction of ether-O with aromatic ring is affected, the electron density in the carboxylate ring may increase compared to phenoxyacetate complex and thus the bonding parameter i.e. M–L covalency may increase in the tris(1-naphthoxyacetato)Pr(III) dihydrate complex.

The bonding parameter ( $b^{1/2}$ ) of tris-(8-quinolinylxyacetato)Pr(III) dihydrate is higher as compared to tris-(1-naphthoxyacetato)Pr(III) dihydrate. This cannot be explained on the basis of steric effect. Here, the lone pair is either equal to or insignificantly smaller than hydrogen in size<sup>9</sup>. Hence, this may be accounted as probably due to the electronic repulsion between the lone pair on N and the lone pair on ether-O. This repulsion in turn may push electron density on the oxygen into the carboxylate group thereby increasing the M–L covalency for tris-(8-quinolinylxyacetato)Pr(III) dihydrate.

The hypersensitive transition  $^4I_{9/2} \rightarrow ^4G_{5/2}$ ,  $^2G_{7/2}$  has been used for the calculation of bonding parameters for all the Nd(III) complexes. The bonding parameter ( $b^{1/2}$ ) value of [Nd(TNAP)<sub>3</sub>]<sub>3</sub>·2H<sub>2</sub>O



is 0.0836 which is identical with the value obtained for tris(phenoxyacetato)aquoneodymium(III) monohydrate<sup>1</sup>. It could be seen that the M-L covalency is relatively large for Nd(III) complex of 8-quinolinylxyacetic acid and the reasons are obvious as in Pr(III) complex. The absorption spectra of the Nd(III) complexes suggest the coordination number six for all these complexes.

The electronic transition used for calculation of bonding parameters is  ${}^6H_{5/2} \rightarrow {}^6P_{3/2}$ . The above transition occurs at  $24272 \text{ cm}^{-1}$  for  $[\text{Sm}(\text{ONAP})_3] \cdot 2\text{H}_2\text{O}$  and at  $24284 \text{ cm}^{-1}$  for  $[\text{Sm}(\text{TNAP})_3] \cdot 2\text{H}_2\text{O}$ . This transition is masked by ligand absorption in the complex  $[\text{Sm}(\text{EHQA})_3] \cdot 2\text{H}_2\text{O}$ .

The bonding parameter ( $b^{1/2}$ ) value obtained for tris(2-naphthoxyacetato)samarium(III) dihydrate is the same as that obtained for tris(phenoxyacetato)aquosamarium(III)-monohydrate<sup>1</sup>.

As the size of the cation is decreased, an increased M-L covalency is expected for Ln(III) cations. The bonding parameter ( $b^{1/2}$ ) values for  $[\text{Pr}(\text{ONAP})_3] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Nd}(\text{ONAP})_3] \cdot 2\text{H}_2\text{O}$  and  $[\text{Sm}(\text{ONAP})_3] \cdot 2\text{H}_2\text{O}$  are found to be 0.0561, 0.0846 and 0.1102 respectively indicating the M-L covalency order,  $\text{Sm(III)} > \text{Nd(III)} > \text{Pr(III)}$ . The same trend is observed for the complexes of 2-naphthoxyacetic acid and 8-quinolinylxyacetic acid.

From the above studies, the composition of the rare earth complexes can be represented as  $[\text{M}(\text{RCOO})_3] \cdot 2\text{H}_2\text{O}$  with a coordination number of six for the metal ion. A coordination number 6 is reflected in the hypersensitive transition of Nd(III) chelates and in the thermal studies of all these chelates. The  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  values of all the complexes indicate bidentate chelate mode of carboxylate coordination. The non-ionic nature of the complexes is revealed by the lower

molar conductance values in DMF. The formula is supported by elemental analysis for all the complexes studied.

The metal-ligand covalency is found to be enhanced in the complexes of 1-naphthoxyacetic acid when compared to phenoxyacetic acid<sup>1</sup>. This may be due to the steric effect of *peri*-H, as it may affect the mesomeric interaction of ether oxygen with aromatic ring. Interestingly, complexes of 8-quinolinylxyacetic acid exhibit even greater metal-ligand covalency. This cannot be accounted in terms of steric effect and may be probably due to the interaction of imine N lone pair and ether-O; the net result of this interaction may lead to the increased electron density of the carboxylate group.

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