

Synthesis & Characterization of Phenoxyacetates of Lanthanoids

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Lanthanum (III), praseodymium (III), neodymium (III), samarium (III), gadolinium (III), terbium (III) and dysprosium (III) phenoxyacetates and 4-X-phenoxyacetates (X = chloro, methyl, methoxy and nitro) of the type $M[L_3H_2O].H_2O$ 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 carboxylate group to the metal ion is bidentate. A coordination number of seven is suggested for the rare earth metal ions in the complexes.

The different modes of bonding of phenoxyacetates in their complexes with many first transition metal ions and uranyl ion have been established¹. The cerium (III) and uranium (IV) phenoxyacetates have also been reported². The present work deals with the preparation and characterization of phenoxy and 4-substituted phenoxyacetates of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III).

The ligands were prepared as reported in the literature^{3,4}. The complexes were prepared by adding a solution of the ligand (3 mmol) in ethanol at pH 6.5-7 to an aqueous solution of the rare earth chloride (1 mmol). The precipitated metal(III) phenoxyacetates were suction-filtered, washed with water followed by ethanol and dried *in vacuo* over anhydrous $CaCl_2$.

The analytical data of the complexes, given in Table 1, conform to the general formula, $M(RCOO)_3.2H_2O$. The magnetic moments of the complexes are quite close to the literature values⁵. Electronic spectra of the phenoxyacetates of Pr, Nd and Sm in the visible region indicated red-shift of the bands. The magnitude of red shift (nephelauxetic effect) is dependent on the change in the interelectronic repulsion parameter. The nephelauxetic (β), the percentage covalency parameter (δ) and the bonding parameter ($b^{1/2}$) for the complexes of Pr(III), Nd(III) and Sm(III) with *p*-methylphenoxyacetate ($p-CH_3C_6H_4OCH_2COO^-$) were calculated using well known equations. The β , δ and $b^{1/2}$ values, respectively are: Pr(III) chelate, 0.994, 0.6036, 0.0547; Nd(III) chelate, 0.986, 1.4198, 0.0836; and Sm(III) chelate, 0.9757, 2.4905, 0.1102. The β -values are less than one and the positive values of covalency parameter (δ) indicate that the nature of bonding between the metal ion and the ligand is covalent as compared to that in lanthanide aquo complexes. The

Table 1—Elemental Analyses of the Rare Earth Complexes,
 $[M(4-X-C_6H_4OCH_2COO)_3.H_2O].H_2O$

X	Found (calc), %		
	M	C	H
M = La(III)			
OCH ₃	19.12 (19.34)	44.76 (45.15)	4.19 (4.31)
CH ₃	20.21 (20.72)	47.56 (48.38)	4.41 (4.62)
H	21.92 (22.11)	45.13 (45.88)	3.64 (3.97)
Cl	18.86 (18.99)	40.02 (39.38)	3.05 (3.00)
NO ₂	17.53 (18.20)	37.02 (37.77)	3.04 (2.88)
M = Pr(III)			
OCH ₃	18.91 (19.56)	44.41 (45.02)	4.12 (4.30)
CH ₃	20.42 (20.96)	47.56 (48.24)	4.83 (4.61)
H	21.54 (22.36)	46.25 (45.74)	3.05 (3.96)
Cl	18.62 (19.21)	40.21 (39.27)	2.12 (3.00)
NO ₂	18.72 (18.41)	36.95 (37.67)	3.01 (2.87)
M = Nd(III)			
OCH ₃	19.11 (19.93)	45.12 (44.81)	4.45 (4.28)
CH ₃	22.12 (21.35)	48.91 (48.00)	4.65 (4.58)
H	22.51 (22.77)	45.12 (45.50)	4.02 (3.94)
Cl	18.74 (19.58)	38.76 (39.09)	3.02 (2.98)
NO ₂	19.00 (18.76)	36.62 (37.50)	2.74 (2.86)
M = Sm(III)			
OCH ₃	19.82 (20.61)	43.95 (44.44)	4.65 (4.24)
CH ₃	21.29 (22.06)	46.82 (47.56)	4.35 (4.54)
H	23.41 (23.51)	44.63 (45.06)	4.02 (3.91)
Cl	20.45 (20.24)	38.25 (38.77)	2.63 (2.96)
NO ₂	20.02 (19.41)	36.51 (37.20)	2.34 (2.84)
M = Gd(III)			
OCH ₃	21.12 (21.35)	43.69 (44.02)	4.01 (4.20)

(Contd)

Table 1—Elemental Analyses of the Rare Earth Complexes,
 $[M(4-X-C_6H_4OCH_2COO)_3 \cdot H_2O] \cdot H_2O$ —Contd.

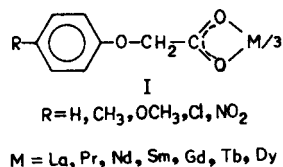
X	Found (calc), %		
	M	C	H
CH ₃	22.36	46.25	4.13
	(22.83)	(47.09)	(4.50)
H	23.98	44.25	3.92
	(24.32)	(44.58)	(3.86)
Cl	21.12	38.65	3.63
	(20.97)	(38.42)	(2.93)
NO ₂	19.76	36.19	2.92
	(20.12)	(36.88)	(2.81)
M = Tb(III)			
OCH ₃	21.12	43.63	4.08
	(21.52)	(43.92)	(4.20)
CH ₃	22.84	47.41	4.86
	(23.02)	(46.98)	(4.49)
H	24.17	44.15	3.96
	(24.52)	(44.47)	(3.85)
Cl	21.46	38.63	3.47
	(21.15)	(38.33)	(2.92)
NO ₂	19.84	36.14	2.92
	(20.29)	(36.80)	(2.80)
M = Dy(III)			
OCH ₃	21.76	44.01	4.06
	(21.90)	(43.71)	(4.18)
CH ₃	23.15	46.12	4.85
	(23.42)	(46.74)	(4.46)
H	25.35	43.84	3.02
	(24.93)	(44.22)	(3.83)
Cl	20.84	38.37	3.08
	(21.52)	(38.15)	(2.91)
NO ₂	20.93	37.11	3.62
	(20.65)	(36.63)	(2.79)

smaller values of bonding parameter ($b^{1/2}$) suggests that 4f-orbitals are slightly involved in bonding.

The IR spectra of the complexes exhibit two characteristic ν OH modes around 3600 and 3400 cm^{-1} suggesting that the two water molecules in the complexes are present as lattice-held water and coordinated water respectively. This is supported by the fact that the lattice-held water is lost at 100°C on isothermal heating for 4-5 hr. The IR spectra of the heated samples exhibit only one ν OH mode around 3400 cm^{-1} . The monoquo complexes when exposed to air reconvert themselves into the dihydrate, suggesting that the dihydrate is the more stable form.

The IR spectra of the complexes exhibit ν_{as} COO in the range 1595-1585 cm^{-1} and ν_s COO in the range

1519-1493 cm^{-1} . The corresponding vibrations for the potassium salt appear at 1610 and 1488 cm^{-1} respectively. The decrease in ν_{as} COO and increase in the ν_s COO mode observed in comparison to those of the corresponding potassium salts lend support to bidentate coordination of carboxyl group leading to a symmetric chelate structure (I) for the complexes.



Interestingly $\Delta\nu = (\nu_{as}COO^- - \nu_sCOO^-)$ for all the complexes studied presently vary with the nature of the substituent in the aromatic ring and, in general, follow the trend: $OCH_3 < CH_3 < H < Cl < NO_2$. The corresponding $\Delta\nu$ values in the case of La(III) complexes are: 54, 56, 70, 89 and 94 cm^{-1} . A similar trend is noticeable for other rare earth complexes synthesised presently. It may be noted that the electron attracting nitro group causes a significant shift in the $\nu_{as}COO^-$ mode to higher wavenumber, the ν_sCOO^- remaining almost unaltered. The electron releasing methoxy group increases ν_sCOO^- without affecting the $\nu_{as}COO^-$ much. In the *p*-nitrophenoxyacetates, the phenoxy oxygen will gain a positive charge due to mesomeric interaction. This in turn will pull out the electron density from $-C=O$: oxygen as a result of which $C=O$ bond order will increase which is reflected in an increase in $\nu_{as}COO^-$ mode. But in the case of *p*-methoxy- or *p*-methylphenoxyacetate such a contribution is absent. Hence the $\nu_{as}COO^-$ is not affected much with respect to the parent compound.

From the above studies, the rare earth phenoxyacetates can be represented as $[M(RCOO)_3 \cdot H_2O] \cdot H_2O$ with a coordination number of seven for the metal ion.

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