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Synthesis and Characterization of Some Polymeric Lanthanide(III) Complexes

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A series of polymeric complexes having general formula $[Ln_2(AA)_3L_4]_n$, where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III), AA = oxalato, L = pyridine-N-oxide or γ-picoline-N-oxide were synthesised in non-aqueous medium by suitable synthetic method. The polychelates were characterized on the basis of their elemental analyses, conductance, molecular weight, magnetic moment, infrared and electronic spectral data.

INTRODUCTION

Lanthanide ions are known to pose interesting bonding posibilities with various types of ligands. In persuit of our endeavour to investigate on preference and stabilization of coordination numbers and geometries, we report here synthesis of coordination polymer of oxalic acid with some lanthanides in presence of neutral oxygen donor ligands and the results of a study of their magnetic, conductivity and spectral behaviour.

EXPERIMENTAL

All chemicals used were of A.R. grade.

Synthesis of Ln(III) Polychelates

First ethanolic solutions of oxalic acid and pyridine-N-oxide/γ-picoline-N-oxide were mixed together. Then to the above mixture an ethanolic solution of metal nitrate was added and refluxed for 3–4 h on a water bath. Metal nitrate and oxalic acid were taken in the ratio of 2 : 3 and neutral oxygen donor ligand in excess. The compounds separated out on cooling were filtered through G_4 crucible, washed with ethanol, ether and dried in *vacuo*.

The metal contents were determined as metal oxides.[1] Microanalyses for carbon, hydrogen and nitrogen were performed at the Central Drug Research Institute, Lucknow. Magnetic susceptibilities of the complexes were determined by Gouy method[2] at room temperature. The conductance measurements were carried out at *ca.* 10^{-3} M nitrobenzene medium by systronics direct reading conductivity meter-303. Infra-red spectra were recorded on Shimadzu-408 and electronic spectra on Shimadzu-UV-160A spectrophotometers, respectively. The molecular weight measurements were carried out by Rast's method using biphenyl as solvent.

RESULTS AND DISCUSSION

The polychelates are insoluble in common organic solvents and possess high melting point. (> 250°C). The lower Δm values of 4.3–5.2 mhos in nitrobenzene medium indicate that the compounds are essentially non-electrolytes. Molecular weight of compound calculated per lanthanide ion was little less than the theoretical value. From analytical data (Table-1) it is evident that all polychelates have the general formula $[Ln_2(C_2O_4)L_4]_n$. The magnetic moment values show little deviation from Van Vleek values[3] indicating that 4f-electrons do not participate in bond formation. The magnetic moments of these complexes are within the normal predicted range.[4, 5]

TABLE-1
ANALYSES, COLOUR, MELTING POINT, MOLAR CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA OF COMPLEXES OF COORDINATED POLYMERS OF LANTHANIDE(III).

Compound (Colour)	% Analysis; Found (Calcd.)					M. wt. Found (Calcd.)
	Ln	N	C	H	μ_{eff} (B.M.)	
$[La_2(C_2O_4)_3(PyNO)_4]_n$ (White)	29.89 (30.13)	5.92 (6.07)	33.52 (33.86)	1.98 (2.19)	Diamag	900.73 (922.12)
$[La_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$ (White)	28.09 (28.40)	5.36 (5.73)	36.62 (36.83)	2.66 (2.89)	Diamag	950.86 (978.22)
$[Ce_2(C_2O_4)_3(PyNO)_4]_n$ (White)	30.04 (30.31)	5.88 (6.06)	33.42 (33.77)	2.01 (2.18)	2.33	900.25 (924.54)
$[Ce_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$ (Cream)	28.26 (28.57)	5.25 (5.71)	36.36 (36.74)	2.63 (2.88)	2.26	900.78 (980.64)
$[Pr_2(C_2O_4)_3(PyNO)_4]_n$ (White)	30.11 (30.43)	5.78 (6.05)	33.37 (33.72)	1.98 (2.18)	3.69	900.25 (926.12)
$[Pr_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$ (Greenish white)	28.32 (28.69)	5.37 (5.70)	36.27 (36.68)	2.56 (2.87)	3.66	900.56 (982.22)
$[Nd_2(C_2O_4)_3(PyNO)_4]_n$ (Pinkish white)	30.43 (30.93)	5.72 (6.01)	33.07 (33.48)	1.88 (2.16)	3.42	900.73 (932.78)
$[Nd_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$ (Pinkish white)	28.78 (29.17)	5.43 (5.67)	36.01 (36.43)	2.37 (2.85)	3.97	900.02 (988.92)
$[Sm_2(C_2O_4)_3(PyNO)_4]_n$ (Cream)	31.56 (31.83)	5.59 (5.93)	32.78 (33.04)	1.78 (2.13)	2.63	900.78 (945.10)
$[Sm_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$ (Cream)	29.71 (30.04)	5.49 (5.60)	35.67 (35.99)	2.73 (2.82)	1.99	925.68 (1001.20)
$[Gd_2(C_2O_4)_3(PyNO)_4]_n$ (White)	32.39 (32.80)	5.36 (5.85)	32.29 (32.57)	1.76 (2.10)	7.27	900.71 (958.82)
$[Gd_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$ (White)	30.59 (30.99)	5.29 (5.52)	35.11 (35.50)	2.36 (2.78)	7.38	935.62 (1014.92)

Pyridine-N-oxide and substituted pyridine-N-oxide form complexes with varied stoichiometries. In case of pyridine-N-oxide an empirical correlation is estab-

lished[6] between N—O and C—N bond lengths in both H-bonding and the metal complexex, which leads to a decrease of N—O π bond order from 35% in the free N-oxide to *ca.* 14 % in the metal complexes. The infra-red spectra of the compounds are very informative. The bonding of N-oxide ligands to the metal ion is usually discussed from three fundamental vibrations, *viz.*, ν(N—O), δ(N—O) and γ(C—H) of the ligand in the free state and on complexation. It has been reported[7-9] that on complexation the ν(N—O) undergoes considerable negative shift, with no significant change for δ(N—O). The γ(C—H) will have either small positive or negative shift or will be at the same position. The strong absorption bands at *ca.* 1250, 855 and 740 cm^{-1} in the infrared spectra of free N-oxide (Nujol mulls) are assigned to the above three fundamental vibrations. The ν(N—O) stretching frequency in the complexes under report (Table-2) occurs in the range 1225–1210 cm^{-1}. The shifting of this band from 1250 cm^{-1} in the free ligand to the lower frequency is attributed to a change in the (N—O) bond order as a result of oxygen-metal coordination.[8-10] The δ(N—O) bending vibration in all these complexes occurs in the range 800–790 cm^{-1}. Hence the δ(N—O) shows a negative shift in all the complexes. This negative shift suggests that the mass effect due to coordinated metal ion on δ(N—O) is outweighing the effect due to coordination.[11] The γ(C—H) vibration of the ligand has also undergone positive shift in some compounds and some cases remain unchanged. The diagnostic spectra for tetradentate oxalato anion is simple. Because of its high symmetry [D_{2h} (planar) or D_{2d} (twisted)] it exhibits only two ν(CO)[12] bands. In these complexes one of the ν(CO) stretching frequencies occurs in the range of 1600–1590 cm^{-1} and another in the range of 1315–1300 due to tetradentate coordination.

TABLE-2
INFRARED SPECTRAL DATA OF COORDINATED POLYMERS OF LANTHANIDE(III) (in cm^{-1})

Compound	Oxalic acid, ν(CO)		PyNO/ γ-PicNO		
			ν(N—O)	δ(N—O)	γ(C—H)
$[La_2(C_2O_4)_3(PyNO)_4]_n$	1590	1300	1215	800	740
$[La_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$	1590	1300	1215	830	740
$[Ce_2(C_2O_4)_3(PyNO)_4]_n$	1590	1300	1215	800	740
$[Ce_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$	1590	1300	1215	830	740
$[Pr_2(C_2O_4)_3(PyNO)_4]_n$	1600	1305	1210	800	750
$[Pr_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$	1600	1300	1225	830	760
$[Nd_2(C_2O_4)_3(PyNO)_4]_n$	1600	1305	1210	800	750
$[Nd_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$	1600	1300	1225	830	760
$[Sm_2(C_2O_4)_3(PyNO)_4]_n$	1600	1305	1225	790	740
$[Sm_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$	1600	1310	1210	820	750
$[Gd_2(C_2O_4)_3(PyNO)_4]_n$	1600	1305	1225	790	740
$[Gd_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$	1600	1310	1210	820	750

The visible spectral bands of lanthanides are hypersensitive to stereochemistry.[13] The absorption bands of Pr(III), Nd(III) and Sm(III) (Table-3) in the visible and near UV region appear due to transition from the ground levels $^3H_4$, $^4I_{9/2}$, and $^6H_{5/2}$ to the excited J-levels of 4f-configuration respectively. The spectra of the complexes show a shift of the spectral bands towards lower energy as compared to those of the aquo ions[14, 15] due to nephelauxetic effect. The observed red shift indicates the participation of a metal 4f and ligand orbitals in formation of covalent bonding.[16, 17]

TABLE-3
ELECTRONIC ABSORPTION SPECTRAL DATA OF LANTHANIDE(III) POLYMER COMPLEXES

Compound	λ_{max} (cm^{-1})	Transitions	Calculated parameters			
			$\bar{\beta}$	δ (%)	$b^{1/2}$	η
$[Pr_2(C_2O_4)_3(PyNO)_4]_n$	23809	$^3H_4 \rightarrow {}^3P_2$				
	20408	$\rightarrow {}^3P_0$	0.9938	0.624	0.056	0.0031
	16393	$\rightarrow {}^1D_2$				
$[Pr_2(C_2O_4)_3(\gamma\text{-PicNO})_4]_n$	25641	$^3H_4 \rightarrow {}^3P_2$				
	20618	$\rightarrow {}^3P_0$	0.9938	0.624	0.0557	0.0031
	16666	$\rightarrow {}^1D_2$				
$[Nd_2(C_2O_4)_3(PyNO)_4]_n$	22470	$^4I_{9/2} \rightarrow {}^2P_{1/2}$	0.9933	0.675	0.058	0.0034
	20000	$\rightarrow {}^2G_{9/2}$				
	18518	$\rightarrow {}^4G_{7/2}$				
	17152	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$				
$[Ng_2(C_2O_4)_3(\gamma\text{–PicNO})_4]_n$	24390	$^4I_{9/2} \rightarrow {}^2P_{1/2}$				
	21276	$\rightarrow {}^2G_{9/2}$				
	17094	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.9949	0.513	0.051	0.0026
	13333	$\rightarrow {}^4F_{7/2}$				
$[Sm_2(C_2O_4)_3(PyNO)_4]_n$	24390	$^6H_{3/2} \rightarrow {}^6P_{3/2}$				
	20500	$\rightarrow {}^4G_{7/2}$				
	19100	$\rightarrow {}^4F_{3/2}$				
	14705	$\rightarrow {}^6D_{7/2}$	0.9956	0.440	0.047	0.0022
$[Sm_2(C_2O_4)_3(\gamma\text{–PicNO})_4]_n$	25000	$^7F_6 \rightarrow {}^5D_3$	0.9925	0.756	0.061	0.0039
	20505	$^6H_{5/2} \rightarrow {}^4G_{7/2}$				
	17766	$\rightarrow {}^4G_{5/2}$				

The bonding parameter ($b^{1/2}$) which measures the amount of metal 4f and ligand orbitals mixing and covalency angular overlap parameter (η) which is also related to nephelauxetic ratio (β), are calculated by using the relations,[18, 19]

$$\beta = \frac{\bar{\nu}\ \text{complex}}{\bar{\nu}\ \text{aquo}}$$

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

$$\eta = \frac{1 - \beta^{1/2}}{\beta^{1/2}}$$

and

$$\delta\ \% = \left[\frac{1 - \beta}{\beta}\right] \times 100$$

In all the Pr(III), Nd(III) and Sm(III) complexes the positive and very small values of $b^{1/2}$ indicate poor covalency of the complexes. Here the values of δ % are found much below 1.5 (Table-3) which also suggests[20, 21] weak covalent bonding as well as weak metal-ligand interactions. The reported series of compounds are tentatively assigned eight coordinated polymeric configurations.

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