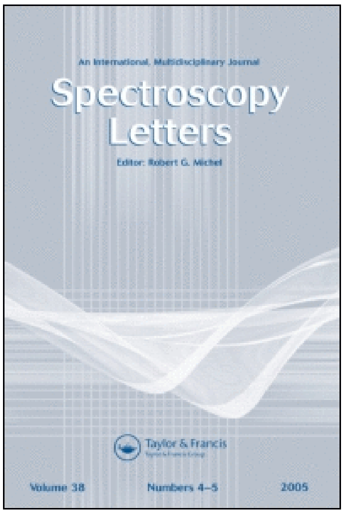

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Chiroptical Studies of Lanthanide (III) Complexes of Sulphur-Nitrogen-Oxygen Ligands Derived from l-Cysteine and Acetylbenzene

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Chiroptical Studies of Lanthanide (III) Complexes of Sulphur–Nitrogen–Oxygen Ligands Derived from L-Cysteine and Acetylbenzene

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ABSTRACT

L-cysteine and acetylbenzene react with La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+} and Ho^{3+} to yield new chiral complexes. They were characterized by chemical analyses, molar conductance, magnetic properties, CD, XPS, ^1H NMR, visible and IR spectra. It was found that the complexes behave as non-electrolytes in methanol solution, and possess the stoichiometric ratio of Ln:C:N:O:Cl=0.5:11.0:1.0:3.0:1.0 which is consistent with the analytical data. TGA data indicate that the complexes sustain weight loss in the 70–100°C region and possess crystallized

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water. Their dominant conformers were determined from CD spectra supported by ^{1}H NMR data.

Key Words: Acetylbenzene; Chiral complexes; L-Cysteine; Conformer.

INTRODUCTION

The coordination chemistry of lanthanide systems, use of lanthanide ions as structural probes in biological systems and the development of lanthanide shift reagents have aroused keen interest.[1,2] Chiral lanthanide systems continue to receive critical attention, and chiroptical studies on trivalent lanthanide complexes of imine acids are of interest.[3,4] In continuation of our study of chiral complexes of lanthanide,[5] we report here the synthesis and characterization of the lanthanide complexes of an optical Schiff base ligand (KL, Figure 1) derived from L-cysteine and acetylbenzene.

EXPERIMENTAL

Materials

The reagents used were of AR grade and were employed without further purification. The solvents were purified by literature procedures.

Lanthanide chlorides were prepared as follows: the requisite amount of Ln_2O_3 was dissolved in a minimum of conc. HCl. The solution was concentrated by evaporation, and the process was repeated three times. Finally the residue was dissolved in H_2O (5 cm^3) before use.

Physical Measurements

After destruction of organic matter with perchloric acid, the lanthanides were titrated with EDTA in the presence of a buffer solution (urotropine

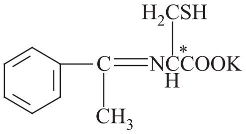

Figure 1. Structure of KL.

buffer pH 5.5) using xylenol orange as an indicator.[6] The C, H, N and S contents were microanalysed on a Perkin-Elmer 240C Elemental Analyzer.

Magnetic moments were measured at room temperature using a Gouy balance with $Hg[Co(CNS)_4]$ as calibrant. Thermal analyses were done under nitrogen between room temperature and 800°C using a thermoflex Q-1500D meter. Molar conductance, electronic spectra, IR spectra, XPS and the chiral properties of the complexes were investigated as in our early paper.[5] The purity of the complexes was checked by Thin Layer Chromatography (TLC) (silica gel G) using methanol (MeOH) solutions, with absolute ethanol (EtOH) as the eluent.

Preparation of the Ligand

The ligand was isolated as the potassium salt by boiling a mixture of acetylbenzene, L-cysteine and KOH under reflux (1:1:1 ratio) in dry EtOH. The products were recrystallized twice in MeOH, yield 48%, m.p.224–225.4°C.

Synthesis of the Complexes

To a solution of the ligand (2 mmol, 0.84 g) in EtOH ($10\,cm^3$), $LnCl_3$ (1 mmol) in water ($10\,cm^3$) was added with stirring, and the mixture heated under reflux for 30 min. The resultant solutions were concentrated and cooled to room temperature to yield the product. The final pH of the reaction mixture was ca. 5.5. Light yellow to white compounds were separated and filtered, washed with water/EtOH followed by EtOH, recrystallized from absolute EtOH, and dried in vacuo, with a yield of 25–30%.

RESULTS AND DISCUSSION

The physical properties and analytical data for the trivalent lanthanide complexes are given in Table 1. The complexes are air stable and insoluble in ether, moderately soluble in methanol, ethanol and acetone and soluble in DMSO and DMF. Λ_M values in methanolic solution indicate that the complexes behave as non-electrolytes.[7]

IR Spectra

The main IR bands with their tentative assignments are listed in Table 2. The ν(C═N) mode due to the coordinated azomethine group is split into several components as expected, with the main band lying at

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Table 1. Elemental analysis and physical properties of the complexes.

Compound	Found (calcd.) %					μ_{eff} B.M	TGA total mass loss %	λ_{max} (log ε)	Λ_M $S \cdot cm^2 \cdot mol^{-1}$
	Ln	C	H	N	S				
KL		50.4	4.5	5.8	12.4			230(2.8);255(2.2);	
		(50.6)	(4.6)	(5.4)	(12.3)			275(3.2)	
$LaL_2 \cdot 2H_2O$	22.1	42.6	4.0	4.1	10.1	dia	67.8	224(2.9);258(2.3);	18
	(22.5)	(42.8)	(4.2)	(4.5)	(10.4)			268(3.4);321(1.8);	
								355(2.2)	
$PrL_2 \cdot 2H_2O$	23.1	43.0	4.4	4.3	9.8	2.86	67.4	222(2.9);257(2.4);	16
	(22.8)	(42.7)	(4.2)	(4.5)	(10.3)			263(3.4);320(1.8);	
								355(2.2)	
$NdL_2 \cdot 2H_2O$	23.3	42.7	4.0	4.6	10.2	3.41	67.0	225(2.9);258(2.3);	21
	(23.2)	(42.4)	(4.2)	(4.5)	(10.3)			264(3.4);324(1.8);	
								53(2.2)	

$SmL_2 \cdot 2H_2O$	23.5 (23.9)	42.2 (42.0)	3.7 (4.1)	4.2 (4.5)	10.6 (10.2)	1.58	66.5	221(2.9);257(2.2); 265(3.4);323(1.9); 354(2.2)	17
$EuL_2 \cdot 2H_2O$	24.5 (24.1)	41.7 (41.9)	3.9 (4.1)	4.8 (4.4)	9.8 (10.2)	3.45	66.4	222(2.9);258(2.2); 266(3.4);320(2.0); 357(2.2)	19
$GdL_2 \cdot 2H_2O$	24.4 (24.8)	41.5 (41.6)	4.5 (4.1)	4.6 (4.4)	10.4 (10.1)	7.68	65.7	224(2.9);258(2.3); 268(3.4);321(1.8); 356(2.2)	22
$TbL_2 \cdot 2H_2O$	25.7 (25.0)	41.6 (41.4)	3.8 (4.1)	3.9 (4.4)	9.6 (10.0)	9.40	65.5	224(2.9);258(2.3); 266(3.4);321(1.7); 355(2.4)	20
$HoL_2 \cdot 2H_2O$	26.2 (25.7)	41.4 (41.0)	3.5 (4.0)	3.8 (4.4)	9.9 (10.0)	10.39	64.8	224(2.9);258(2.3); 268(3.4);321(1.6); 355(2.1)	23

Table 2. Principal IR bands of the ligand and the complexes (cm^{-1}).

Compound	ν(O–H)	ν(C═N)	$\nu_{as}(-CO_2)$	$\nu_s(-CO_2)$	Δν	ν(Ln–N)	ν(Ln–S)	ν(Ln–O)
KL	3360br	1640	1562	1428	134			
$LaL_2 \cdot 2H_2O$	3435br	1615	1570	1375	195	238	340	515
$PrL_2 \cdot 2H_2O$	3415br	1612	1577	1379	198	243	334	510
$NdL_2 \cdot 2H_2O$	3421br	1613	1578	1374	204	253	342	516
$SmL_2 \cdot 2H_2O$	3438br	1621	1580	1379	201	252	335	516
$EuL_2 \cdot 2H_2O$	3409br	1615	1585	1388	197	245	339	514
$GdL_2 \cdot 2H_2O$	3422br	1622	1580	1379	201	252	335	520
$TbL_2 \cdot 2H_2O$	3410br	1625	1576	1381	195	255	339	509
$HoL_2 \cdot 2H_2O$	3432br	1620	1580	1370	210	246	341	513

ca. 1625–1610 cm^{-1} as compared to the ν(C=N) mode of the free ligand at 1640 cm^{-1};[8] the νas and νs modes of the $-CO_2$ group appear at 1570–1585 cm^{-1} and 1370–1388 cm^{-1} respectively, the Δν value (νas − νs= 195∼210 cm^{-1}) being consistent with unidentate carboxylate coordination;[9] the absence of any ν(SH) mode indicates complete deprotonation of the two imine acid residues. Thus three (C=N, $-CO_2$ and thiol sulphur) groups attached to the chiral C-atom are used as an ONS donor set to the metal ion. The low frequency spectra (600–200 cm^{-1}) of all these complexes have several common features with the main bands appearing in the regions 515–500 cm^{-1}, 450–420 cm^{-1}, 345–330 cm^{-1}, 310–280 cm^{-1} and 250–230 cm^{-1} indicating these lanthanide (III) ions to be in similar coordination environments (nature and number of donor groups). The bands in the region 450–420 cm^{-1} are mainly ligand(or chelate ring) deformation modes and some of them may be coupled with ν(Ln–O), ν(Ln–N) and/ or ν(Ln–S) mode. All complexes exhibit a broad band at 3440 cm^{-1} suggesting the presence of uncoordinated water being consistent with the TGA data, thereby leading to an overall coordination number of six.

Magnetic Moments

For most of the complexes the theoretical magnetic moments are given by: $\mu_J = g\beta[J(J+1)]^{1/2}$, while the magnetism of $Sm^{3+}(4f^5)$ and $Eu^{3+}(4f^6)$ ions is satisfactorily explained by the medium multiplet width case which is comparable to kT[μ_{eff} (Calcd.) = 1.3 B.M and 3.4 B.M.at 300 K]. The magnetic moments of other complexes are slightly lower than the calculated values. The lower magnetic moments of the complexes may arise from the presence of an anti-ferromagnetic interaction and from lower symmetry components, possibly because these complexes possess binuclear structure.[10]

^{1}HNMR Spectra

^{1}HNMR data of the lanthanide complexes indicate that in most cases only one set of signals is observed for the NCH– hydrogen (3.68 ppm) and other functional groups, indicating that the two ligand residues in these complexes (Ln: L ratio 1:2) are in identical chemical environments on the NMR scale. The NCH– hydrogen signals is shielded relative to the free ligand by ca. 0.7–0.35 ppm; most of the other types of hydrogen (e.g., $-CH_3$ (1.58 ppm), $-CH_2-$(3.24 ppm), etc.) are also shielded by varying amounts. Although coordination usually involves deshielding of ligand hydrogens (especially of coordinating groups) due to removal of electron density, a rigid chelate structure (essentially octahedral) can cause anisotropic magnetic effects leading to the observed shielding.[11]

XP Spectra

XP spectra of the complexes and ligand were recorded in the powder form at room temperature (298 K). The results of the XPS semiquantitative analyses and the atomic molar ratio of Ln:C:N:O:S is ca 0.5:11.1: 1.1:3.0:1.0 of the complexes are in agreement with the elemental analysis data and given in Table 3. The lanthanide 3d electron binding energy is close to the central atom charge and therefore to its valence.[12] Only one symmetric sulphur 2p peak was observed at 162.3 eV for all the complexes similar to the ligand but about 0.8 eV higher, this behavior suggested that the two ligands are in a chemically identical coordination mode. The N1s electron spectra of the complexes are asymmetric and the BE values are shifted up ca. 1.21 ∼ .6 eV indicates that the azomethine nitrogen is coordinated to the metal ion and the two coordinated nitrogen atoms are in a symmetric form. The O1s electron spectra of the complexes are in a asymmetric form and the BE values are at ca. 533.2 and 532.5 eV related to symmetric band of free ligand at 532.5 eV indicate that two chemical environment was produced after coordination,[13,14] a further assignment indicates that the peak with the higher BE value belongs to the $C{-}O^-$ group and the peak with the lower BE value belongs to C═O of the $-CO_2$ group, it can be deduced that the $-CO_2-$ group coordinated with metal ion through oxygen atom in an unidentate form. This assignment is supported by the determination of the C1s binding energy of the group.

Electronic Spectra and CD Spectra

The electronic spectra of the complexes (Table 1) reveal the presence of most of the ligand bands.[3] The bands observed at ca. 275, 230, 255 nm are attributed to C═N, C═O and benzene ring respectively. The benzene ring absorption red shifts at ca. 2–3 nm and the C=N and C=O purple shifts of 6–12 and 5–10 nm indicate the bond formation of these complexes. Two new bands are observed at ca. 320 and 355 nm, these characteristics may be related to electronic transitions based mainly on the ligand moieties and, in a few cases, ligand-to-metal charge transfer bands may also be present.

The diagnostic negative CD (Figure 2) band at 280–290 nm indicates the presence of the dominant conformer with negative (i.e., left handed)

Table 3. The binding energies (eV) of the ligand and its complexes.

Compound	N1s	O1s	S 2p	C1s(−CO$_2$)	Ln 3d$_{5/2}$	Ln:C:N:O:S
KL	399.3	532.5	162.3	288.6		
$LaL_2 \cdot 2H_2O$	400.5	533.6,532.8	162.9	288.4	836.2	0.5:11.0:1.0:3.0:1.0
$PrL_2 \cdot 2H_2O$	401.1	533.5,532.6	163.0	288.3	933.5	0.5:11.1:1.1:3.0:0.9
$NdL_2 \cdot 2H_2O$	401.2	533.4,532.7	163.1	288.3	984.5	0.5:11.2:1.0:3.1:1.1
$SmL_2 \cdot 2H_2O$	400.8	533.7,532.6	163.2	288.2	1084.2	0.5:11.1:1.1:2.9:1.0
$EuL_2 \cdot 2H_2O$	400.4	533.6,532.5	163.1	288.0	1136.4	0.5:11.2:1.1:3.0:0.9
$GdL_2 \cdot 2H_2O$	400.2	533.3,532.5	162.9	288.4	1191.2	0.5:11.0:1.0:3.0:1.0
$TbL_2 \cdot 2H_2O$	400.5	533.8,532.7	163.0	288.3	1245.3	0.5:11.0:1.0:3.1:0.9
$HoL_2 \cdot 2H_2O$	400.6	533.7,532.5	162.8	288.1	4d 162.5	0.5:11.0:1.5:1.4:1.0

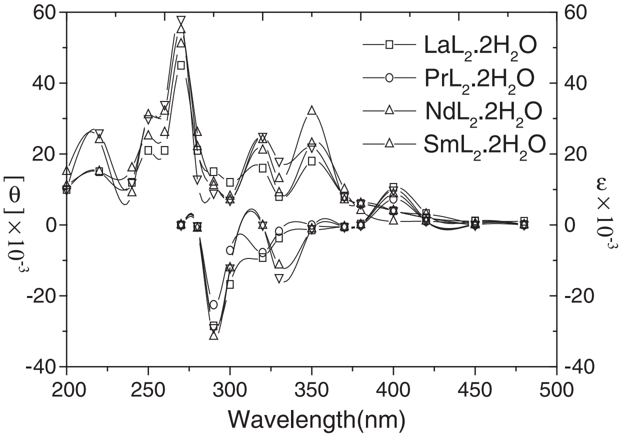

Figure 2. CD and electronic spectra of the complexes ($LaL_2 \cdot 2H_2O$(□), $PrL_2 \cdot 2H_2O$ (○), $NdL_2 \cdot 2H_2O$(△) and $SmL_2 \cdot 2H_2O$(▽)).

chirality.[3] An additional positive CD maximum is observed at 400nm for which no corresponding band is seen in the electronic spectral curve (it is obscured by other strong bands, such as intraligand bands, ligand-to-metal charge transfer bands, etc.). A 4*f*→5*d* type of transition cannot be ruled out and may be traced to the difference in electronic configurations between the lanthanum(III) ion, having a closed shell configuration, and the other trivalent lanthanide ions with two or more electrons in the 4*f* sub-level.[15] The negative Cotton effect at ca. 325–330nm in all these complexes (compared to a positive effect in the ligand), is ascribed to a charge transfer transition from a ligand pπ orbital to a 5d orbital of the lanthanide(III) ion, and may be related to the distortion of the chelate ring system.

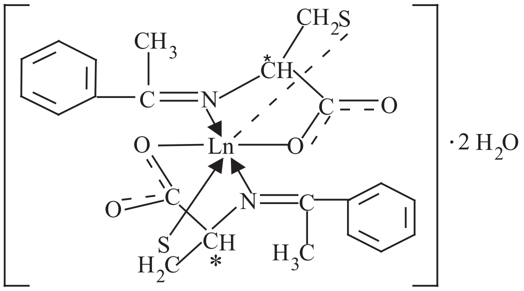

Figure 3. Possible binding model of complexes.

The chiroptical inference drawn may be relevant to those cases where lanthanide (III) ions could be used as probes for amine-containing chiral biomolecules.

Thermal Analyses

TGA data (ca. 5°C/min.; air) indicate that the complexes sustain weight loss in the 70–100°C region. Water of crystallization (extraspheric water) is usually lost over 70–110°C range while water of coordination (intraspheric water) is eliminated at higher temperature (120–150°C), the corresponding weight losses (water) are satisfactory.

On the basis of the above discussion a six-coordinated binding model is suggested for the complexes (Figure 3).

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