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XPS and Chiroptical Studies on Lanthanide(III) Complexes of Hydroxylamine and Sodium D-Camphor-β-sulfonate

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ABSTRACT

Six new chiral complexes LnL₃ (Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III)) with an optically active Schiff base ligand (HL) derived from sodium D-camphor- β -sulfonate and hydroxylamine were synthesized and characterized by elemental analyses, molar conductance, IR, XPS (X-ray photoelectron spectroscopy), electronic spectra, ¹H NMR, magnetic susceptibility measurements and thermal methods. It was found that the complexes behave as non-electrolytes in CH₃OH and in DMSO and possess the stoichiometric ratio of Ln:C:N:O:S = 0.33:10.1:1.0:4.0:1.0 which is consistent with the analytical data. Their

1763

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dominant conformers were determined by CD spectra. A six-coordinated model is proposed for these complexes.

Key Words: Chiral; D-Camphor-b-sulfonate; Hydroxylamine; Non-electrolytes; CD spectra.

INTRODUCTION

Many Schiff bases and their metal complexes have been synthesized and attracted much attention.^[1-3] In our earlier papers,^[4,5] we reported the synthesis and properties of the chiral lanthanide complexes of D-camphor- β -sulfonic acid, but no lanthanide optically active Schiff base complexes derived from D-camphor- β -sulfonic acid and hydroxylamine have been reported so far. In continuation of our study on chiral complexes of lanthanides, we report here the synthesis and characterization of some complexes of this ligand (HL, Figure 1).

EXPERIMENTAL

Reagents and Solvents

All chemicals and solvents were analytically pure and used without further purification. Sodium D-camphor- β -sulfonate was purchased from Merck and used without further purification. Lanthanide chlorides were prepared as follow: the requisite amount of Ln₂O₃ was dissolved in a minimum amount of conc. HCl. The solution was concentrated by evaporation and the process was repeated thrice. Finally, the residue was dissolved in H₂O (5 mL) before use.

Preparation of NaL

To a solution of sodium D-camphor- β -sulfonate (5.0 g, 17.2 mmol) in 50 mL methanol was added hydroxylamine hydrochloride (1.2 g,



Figure 1. Structure of HL.

1764

17.2 mmol). The resulting solution was treated with 50% NaOH solution under stirring until the pH was adjusted to 5.0 and refluxed for 1 h. The yellowish precipitate thus obtained was separated by vacuum filtration and recrystallized from anhydrous methanol and finally dried at 110 °C for 1 h, yield 4.5 g (85%): m.p. 252–254 °C, $[\alpha]_{\rm D}^{20} = +84-86^{\circ}$ (c = 1.5 mol·L⁻¹, DMSO).

1765

Preparation of Complexes

A solution of NaL (0.81 g, 3 mmol) and the lanthanide(III) chloride (1 mmol) in 40 mL anhydrous ethanol was refluxed in a water bath for 1 h. After cooling to room temperature a precipitate was formed. The solid was collected by vacuum filtration and purified by column chromatography (Al₂O₃, acetone/EtOH [1/3 (v/v) as eluent]. The solvent was then evaporated under reduced pressure and the product dried at 110 °C for 1 h, yields 78–90%.

Physical Measurements

The C, H, N and S contents were determined microanalytically on a Perkin-Elmer 240C elemental analyzer. The lanthanide content was determined volumetrically by EDTA titration using xylenol orange as an indicator. The molar conductance of the complexes in MeOH and in DMSO at 0.001 mol/L concentration was measured with a Shanghai DDS-IIA molar conductor at 25 °C. Room-temperature magnetic susceptibility measurements were made by the Guoy method using $Hg[Co(CNS)_4]$ as calibrant. Diamagnetic corrections were calculated from Pascal's constants. Thermal analyses were made under nitrogen in the range from room temperature and 800 °C using a Thermoflex Q-1500D thermal analyzer. Electronic spectra of DMSO solutions of the complexes in the 200-700 nm region were recorded on a Shimazu 240 spectrophotometer. IR spectra (CsI pellets) were obtained on a Nicolet-5DX spectrophotometer in the 200-4000 cm⁻¹ region. XPS was taken on a Perkin-Elmer PHI-550 X-ray photoelectron spectrophotometer using Mg-K_{α} radiation. The samples were finely pulverized and spread on a gold holder as thin films. The background pressure of residual gases during the measurements was lower than 10^{-6} Pa. The hemispherical electrostatic analyzer was operated in the retarding mode with a pass energy of 20 eV. The accuracy of the measured binding energy (BE) is ± 0.1 eV. The peak areas for semiquantitative analyses were determined using a linear background. The C1s electron BE in benzene was used as an internal standard, BE = 284.6 eV. The ¹H NMR spectra were measured on a Bruker AC 80 spectrometer using DMSO-d₆ as solvent. The chiral properties of the complexes were investigated by circular dichroism (CD) spectra at 20 °C on a

Cary model 60 spectropolarimeter with a CD model 6001 accessary. The sample cell was 1 cm and the slit was programmed for a spectral band width of 1.5 nm. Cut-off was indicated when the dynode voltage reached 400 V. Spectral measurements began at 200 nm, and the molar ellipticity ($[\theta]$) values were adjusted to an enantiomeric excesses of 100%.

RESULTS AND DISCUSSION

The synthesis of the salt of the ligand is given in Figure 2.

The formation of the complexes occurs by the following representative equation:

 $3NaL + LnCl_3 \cdot xH_2O \xrightarrow{EtOH} LnL_3 + 3NaCl + xH_2O$

Physical and analytical data for the trivalent lanthanide complexes are given in Table 1. The complexes are air-stable and soluble in CH₃OH, chloroform, diethyl ether, EtOH, acetone, DMSO and dimethylformamide. Λ_M values in methanol and in DMSO indicate that the complexes behave as non-electrolytes in solution. But the Λ_M values in methanol are relatively higher than in DMSO, and it is found that the Λ_M values are constant with time at room temperature. This phenomenon indicates that the coordinated sphere or the coordination bond is stable in polar solvents and no replacement reactions occured. The thermal analyses revealed that all complexes are anhydrous.

Infrared Spectra

The main IR bands with their tentative assignments are listed in Table 2. The bands at $3380-3250 \text{ cm}^{-1}$ for the salt of the ligand and its complexes due to OH stretching frequencies remain almost unchanged, which indicates that the OH group is not coordinated to the lanthanide(III) ion. The salt of the Schiff base ligand exhibits a sharp band at 1640 cm⁻¹ due to v(C=N). On complexation, this band shifts to a lower energy by



Figure 2. Scheme for the synthesis of the sodium salt of the ligand (NaL).

1766

Compounds, empirical				Т	⁷ ound (c	alcd.) %	0				$\Lambda_{M}~(\mathrm{s} \cdot \mathrm{cm}^{-2} \cdot$
formulae; (formula weight)	Color	$\mu_{eff} \\ (B.M.)$	Ln	С	Н	Z	S	Yield (%)	M. p. (°C)	λ_{max} (log ϵ) ^a	mol ⁻¹) in CH ₃ OH /DMSO
NaL, C ₁₀ H ₁₆ NNaO ₄ S	Yellow			45.87	3.18	5.43	12.35	85	252- 254		
LaL ₃ , C ₃₀ H ₄₈ LaN ₃ O ₁₂ S ₃	White	Dia.	16.14	42.40	2.62	(00) 4.71	11.42	86	225	275	
(761.80)			(16.29)	(42.21)	(2.81)	(4.92)	(11.26)			(1.2)	
PrL_3 , $C_{30}H_{48}N_3O_{12}PrS_3$	Pale	2.68	16.40	41.30	2.96	4.79	11.36	82	211	268	9.0/2.2
(888.42)	yellow		(16.48)	(41.11)	(2.81)	(4.91)	(11.23)			(1.90)	
NdL ₃ , $C_{30}H_{48}N_3NdO_{12}S_3$	Red	3.45	16.85	41.33	2.65	4.75	11.27	80	236	260	8.0/2.8
(883.04)			(16.80)	(41.19)	(2.80)	(4.89)	(11.19)			(2.15)	
SmL ₃ , C ₃₀ H ₄₈ N ₃ O ₁₂ S ₃ Sm	Grey	1.80	17.33	41.44	2.97	4.65	11.31	90	228	259	9.5/3.1
(889.15)			(17.40)	(41.65)	(2.78)	(4.86)	(11.11)			(2.05)	
EuL_3 , $C_{30}H_{48}EuN_3O_{12}S_3$	White	3.50	17.60	41.66	2.63	4.67	11.25	87	237	262	8.4/3.8
(890.76)			(17.55)	(41.57)	(2.77)	(4.85)	(11.09)			(1.88)	
GdL ₃ , C ₃₀ H ₄₈ GdN ₃ O ₁₂ S ₃	Pale	7.82	18.22	41.51	2.94	4.69	11.25	78	209	261	8.1/2.8
(896.05)	yellow		(18.04)	(41.32)	(2.75)	(4.82)	(11.02)			(1.85)	

^a ε = molar extinction coefficient (L·mol⁻¹·cm⁻¹).

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1767

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Compounds	v(OH)	v (C=N)	v _{as} (-SO ₃ -)	v _s (-SO ₃ -)	Δν (-SO ₃ -)	v (Ln–O)	v (Ln–N)
NaL	3365 br	1640 s	1185 s	1050 s	135		
LaL ₃	3358 br	1600 m	1211 s	1051 m	160	515 m	320 m
PrL ₃	3365 br	1602 m	1207 m	1052 m	155	510 w	325 m
NdL ₃	3360 br	1603 m	1210 s	1050 m	160	518 m	324 w
SmL ₃	3366 br	1602 m	1200 s	1045 w	155	514 m	318 w
EuL ₃	3372 br	1595 m	1206 s	1051 m	155	520 w	322 w
GdL ₃	3370 br	1600 m	1200 s	1047 m	153	513 w	321 w

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

as = sharp, m = medium, br = broad, w = weak.

1768

 $38-45 \text{ cm}^{-1}$, which might be due to a reduction in the electron density in the azomethine group owing to coordination of the nitrogen atom to the metal ion.^[6] The v_{as} and v_s modes of the $-SO_3-$ group appear at 1200– 1211 and 1045–1052 cm⁻¹, respectively, and the Δv value (155 cm⁻¹) is consistent with unidentate coordination. Furthermore, several new bands were observed at ca. 510 and 320 cm⁻¹, some may be tentatively assigned to v(Ln–O) and v(Ln–N) vibrations.^[7] Thus, it is apparent that the ligand is attached to the metal ion by two coordination sites involving the sulfonate oxygen and the azomethine nitrogen. The valence requirement of the metal ion and the infrared data indicate that the three molecules of the ligands are attached to the lanthanide(III) ion in a symmetric form.

Magnetic Moments and Electronic Spectral Studies

The paramagnetic behavior of the lanthanide(III) ion is consistent with the presence of unpaired electrons. The room temperature magnetic moments of the complexes in Table 1 show little deviation from the literature values^[8] or values calculated using the equation: $\mu_{eff} = \xi [J(J + 1)]^{1/2}\beta$, thereby indicating negligible participation of 4*f* electrons in bond formation.

The electronic spectra of the complexes are similar, but are different from that of the salt of the ligand (Table 1). A strong peak was observed at ca. 275 nm attributed to $\pi - \pi^*$ transition of the group -C=N. Compared with the salt of the ligand, a blue-shift of about 7–16 nm was observed, which indicates bond formation between the lanthanide(III) ion and the ligand.^[7]

XPS Spectra

The results of the XPS semi-quantitative analyses of the complexes are in agreement with the elemental analysis data (Table 3, Figure 3). The N1s

	Table 3.	The binding en	lergy values of the ligand Na	aL and complex	tes LnL ₃ (eV).	
Compounds	C1s(-C=N)	N1s	01s	S2p	Ln3d	Ln:C:N:O:S
NaL	281.3	399.6	530.5, 533.3	165.6		
LaL_3	281.6	401.1	530.6, 532.2, 533.0	165.5	835.9	0.33:10.1:1.0:4.0:1.0
PrL_3	281.8	401.0	530.5, 532.2, 533.3	165.3	933.3	0.33:10.0:1.1:4.0:1.1
NdL ₃	281.5	400.5	530.4, 532.4, 533.2	165.2	984.5	0.33:10.1:1.0:4.1:1.0
SmL_3	281.8	401.2	530.1, 532.3, 533.5	165.5	1084.1	0.32:10.1:1.2:4.1:1.0
EuL_3	281.6	400.8	530.2, 532.3, 533.4	165.4	1136.2	0.33:10.0:1.1:4.0:0.9
GdL_3	281.6	400.5	530.3, 532.7, 533.5	165.6	1191.4	0.33:10.0:1.0:4.0:1.0

1769





Figure 3. XPS spectra of NaL (1) and the complex EuL_3 (2).

electron spectra of the complexes are symmetric and their deconvolution revealed that one band was observed at ca. 401.5 eV which is related to the salt of the ligand at 399.6 eV and is due to the C=N group. It was found that after coordination the N1s BE value of C=N group shifted up about 1.2 eV which indicates that the nitrogen atom in the C=N group coordinates to the central metal ion and then leads to a decrease of the electron density on the nitrogen atom, and its strength ratio is close to 3:1 which indicates the three coordinated ligands are in an identical chemical environment. Another piece of information supporting the coordination of the nitrogen atom in the C=N group is the C1s (C=N) BE which shows a small shift from 281.3 to 281.8 eV in the complexes compared with that of the salt of the ligand, indicating that the azomethine nitrogen is coordinated to the metal ion. The S2p spectrum is also symmetric and bands at 165.5 eV for the salt of the ligand and at 165.4 eV for the complexes were observed which can be assigned to the sulfur atom of the SO₃ group. A fact that the S2p binding energy remained unchanged indicates that the sulfur atom in the SO₃ group does not coordinate to the lanthanide ion. The O1s electron spectra of the complexes were in an asymmetric form and three bands were observed at ca. 533.3, 532.2 and 530.4 eV. In comparison, the two asymmetric bands of the salt of the ligand at 533.0 and 530.5 eV

1770

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assigned to the SO₃ group and OH group indicate that three chemical environments arose from coordination. In view of the relative strength of the bands at 532.2 eV and 530.4 eV (2:1), it can be deduced that the SO₃ group coordinates to the metal ion through an oxygen atom in a unidentate form and the OH group does not coordinate to lanthanide ion due to the O1s BE value for the OH group (530.5eV) almost unchanged. On the basis of the above discussions it may be concluded that the three ligands coordinate to the lanthanide ion in a chemically identical coordination mode. The atomic molar percentages in the complexes have also been examined. It was found that the complexes possess the stoichiometric ratio of Ln:C:N:O:S = 0.33:10.1:1.0:4.0: 1.0, which is consistent with the analyses data.

1771

¹H NMR Spectra

The ¹H NMR spectra of the complexes show that only one set of signals was observed for the hydrogen of the N–OH group and the hydrogen signal is shielded relative to the salt of the ligand by ca. 0.3-0.55 ppm (1H, s) (Table 4). Most of the other types of hydrogens (e.g., $-CH_3$, $-CH_2$ -, $-CH_2$) are also shielded to a varying extent. Although coordination usually involves deshielding of ligand hydrogens (especially of coordinating groups) due to a decrease of electron density, a rigid chelate

Compounds Chemical shift (δ , ppm) NaL 12.2 (s, -SO₃H, 1H), 9.82 (s, N-OH, 1H), 1.71 (s, -CH < 1H), 1.22 (m, J = 1.2Hz, $-CH_2 - 8H$), 0.83–1.15 $(t, J = 5.5Hz, -CH_3, 6H)$ LaL₃ 9.52 (s, N-OH, 1H), 1.68 (s, -CH<, 1H), 1.21 $(m, J = 1.1Hz, -CH_2, 8H), 0.80-1.13 (t, J = 5.8Hz, -CH_3, 6H)$ 9.50 (s, N-OH, 1H), 1.71 (s, -CH<, 1H), 1.20 (m, J = 1.3Hz, PrL₃ -CH₂-, 8H), 0.82-1.15 (t, J = 5.7Hz, -CH₃, 6H) NdL₃ 9.27(s, N-OH, 1H), 1.70 (s, -CH<, 1H), 1.21 (m, J = 1.5Hz, $-CH_2$ -, 8H), 0.81-1.09 (t, J = 6.0Hz, $-CH_3$, 6H) SmL₃ 9.32 (s, N-OH, 1H), 1.74 (s, -CH<, 1H), 1.23 (m, J = 1.2Hz, $-CH_2$ -, 8H), 0.82-1.13 (t, J = 6.1Hz, $-CH_3$, 6H) EuL₃ 9.42 (s, N-OH, 1H), 1.70 (s, -CH<, 1H), 1.21 (m, J = 1.3Hz, $-CH_2-$, 8H), 0.82-1.11 (t, J = 6.0Hz, $-CH_3$, 6H) GdL₃ 9.58 (s, N–OH, 1H), 1.72 (s, -CH < 1H), 1.22 (m, J = 1.2Hz, $-CH_2-$, 8H), 0.80–1.14 (t, J = 5.9Hz, $-CH_3$, 6H)

Table 4. ¹H NMR data of NaL and the complexes (DMSO- d_6).

Compounds	Conc. (DMSO, $mol \cdot L^{-1}$)	$\left[\theta\right]^a \times 10^{-3}$	$\Delta\epsilon^{\rm b}$	$\lambda_{max} \ (nm)^{c}$	
NaL	1.5	8.21	2.6	282	+ 84-86
LaL ₃	1.6	7.1	2.1	285	+ 162.4
PrL ₃	1.5	7.0	2.4	280	+ 168.6
NdL ₃	1.5	7.3	2.4	278	+ 164.3
SmL ₃	1.4	6.6	2.0	269	+ 144.8
EuL ₃	1.6	7.2	2.3	270	+ 139.8
GdL_3	1.5	7.0	2.1	282	+ 182.2

Table 5. CD spectra data of NaL and the complexes.

 ${}^{a}\theta$ = molar ellipticity value.

1772

 ${}^{b}\varepsilon$ = molar extinction coefficient.

 $^{c}\lambda_{max}$ = the maximum absorption wavelength.

 ${}^{d}\alpha$ = specific rotatory degree.

structure (here octahedral) can cause anisotropic magnetic effects leading to the observed shielding.^[9]

CD Spectra

A distinct Cotton effect in the CD spectra of the complexes was observed (Table 5, Figure 4). The peak at ca.280 nm of the complexes is diagnostic of the preferred conformation. In terms of the camphor chirality rule, the conformer with the (S)-absolute configuration is dominant for dichroic absorption similar to a positive effect in the salt of the ligand. The



Figure 4. CD spectra of the salt of the ligand and the complexes.



Figure 5. Suggested bonding model of LnL₃.

overall electronic situation is much the same in all these cases, as indicated by the almost identical electronic spectra, and the complexes show a smaller Cotton effect than the ligand.^[10]

CONCLUSION

On the basis of the above discussions, it is found that in the complexes of the type LnL_3 , the ligand is attached to the metal ion at two coordination sites involving sulfonate oxygen and azomethine nitrogen. The three ligands are coordinated to the lanthanide metal ion in a symmetry form and an octahedral structure is proposed for these complexes (Figure 5).

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1774

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