

Studies of XPS and ORD on Ternary Lanthanide Complexes of D-Camphor- β -sulfonic Acid and 1,10-Phenanthroline

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Received 7 January 2000

Nine new chiral ternary complexes of lanthanide with D-camphor- β -sulfonic acid and 1,10-phenanthroline formulated here as $\text{Ln}(\text{Phen})_2\text{L}_2\text{Cl}\cdot\text{H}_2\text{O}$ ($\text{Ln} = \text{La}(\text{III}), \text{Ce}(\text{III}), \text{Pr}(\text{III}), \text{Nd}(\text{III}), \text{Sm}(\text{III}), \text{Eu}(\text{III}), \text{Tb}(\text{III}), \text{Dy}(\text{III}), \text{and Ho}(\text{III})$, Phen = 1,10-phenanthroline, L = ion of D-camphor- β -sulfonic anion) have been synthesized and characterized by the elemental analysis, molar conductance, UV, IR, XPS, ORD, and fluorescence spectra. A chiral seven-coordinate structure has been proposed for these complexes.

The ternary rare earth complexes of camphor sulfonic acid and 1,10-phenanthroline have been reported in the previous works [1, 2]. In 1997 we have previously reported some lanthanide ternary complexes of D-camphoric acid and 1,10-phenanthroline [3]. This type complexes exhibit good bacteriostatic properties on *Bacillus subtilis*, *Staphylococcus*, and *Candida albicans*. Herein we report the synthesis and the characterization of nine new chiral ternary lanthanide complexes of D-camphor- β -sulfonate and 1,10-phenanthroline. Their structure and properties are discussed. The results of elemental analyses of complexes I—IX (Table 1) give the general formula $(\text{C}_{12}\text{H}_8\text{N}_2)_2\text{Ln}(\text{C}_{10}\text{H}_{15}\text{O}_3\text{S})_2\text{Cl}\cdot n\text{H}_2\text{O}$, when Ln = La (I), Ce (II), Pr (III), Nd (IV), Sm (V), Eu (VI), Tb (VII), trivalent ion, $n = 1$; and when Ln = Dy (VIII), Ho (IX), trivalent ion, $n = 0$. The complexes are well soluble in methanol and insoluble in ether, acetone, and THF. The molar conductivity of the complexes ($\Lambda_m = 6\text{--}8 \text{ S cm}^2 \text{ mol}^{-1}$, 25°C , $c = 1 \times 10^{-4} \text{ mol dm}^{-3}$) is very small and shows that they are non-electrolytes [4].

The UV spectra of these complexes are similar, but they are different from those of the ligands (Table 1). The absorption bands of the complexes are at about 275 nm, 295 nm, and 320 nm and are purple-shifted or red-shifted about 4–10 nm in comparison with those of the free ligands. This indicates that the nitrogen and the oxygen atoms are coordinated to the central ion Ln(III).

The assignments of some important absorption bands in IR spectra of the complexes are given in Table 2. The band at $\tilde{\nu}(\nu(\text{C}=\text{O})) = 1740 \text{ cm}^{-1}$ in the complexes remains almost unshifted in comparison with that in the ligand, which indicates that the carbonyl oxygen atoms are uncoordinated. Two stretching vibrations of $\nu_{\text{as}}(\text{SO}_3^-)$ and $\nu_{\text{s}}(\text{SO}_3^-)$ are

observed at about 1200 cm^{-1} and 1046 cm^{-1} and the difference $\Delta\tilde{\nu}$ equals $155\text{--}157 \text{ cm}^{-1}$. Comparing with the ligand (NaL) in which two bands are at 1196 cm^{-1} and 1042 cm^{-1} and the difference $\Delta\tilde{\nu}$ equals 154 cm^{-1} , this shows that the ligand L is coordinated to the Ln(III) ion with an SO_3^- group in an unidentate form [5]. The band at 1620 cm^{-1} in the free ligand (Phen) is attributed to the $\nu(\text{C}=\text{N})$ stretching vibration which is shifted to lower frequency at about 1600 cm^{-1} in these complexes. The stretching vibration of 1,10-phenanthroline ring is shifted from 1355 cm^{-1} in the ligand to 1346 cm^{-1} in the complexes indicating that the nitrogen atoms are coordinated to the central ion. Furthermore, three new bands are observed at about 510 cm^{-1} , 320 cm^{-1} , and 270 cm^{-1} in the complexes assigned to $\nu(\text{Ln}-\text{O})$, $\nu(\text{Ln}-\text{N})$, and $\nu(\text{Ln}-\text{Cl})$, respectively. This supports the idea that the three types of ligands are all coordinated to the central ion Ln(III) [6, 7].

The XPS spectra of complexes and ligands are measured in powder at room temperature. It is found that the data of atomic mole % of the complexes are very close to the results of elemental analyses. The binding energy (BE) data of N 1s, S 2p, Cl 2p, and Ln $3d_{5/2}$ for the complexes and ligands are shown in Table 3. Since the binding energies of the core electrons of lanthanide metals depend upon the charge of atom and therefore upon its valence, the oxidation state of the atoms can cause the overlapping of XPS peak position. This turns out that the BE values of Ln(III) $3d_{5/2}$ are about 0.8–3.2 eV higher than in the simple compounds of metals (e.g. La 834 eV, Pr 930 eV, Eu 1136 eV, Tb 1244 eV, Dy 1295 eV, etc.) [8], and are approximately the same as those of Ln(III) ions in the literature [9]. This report shows that the oxidation state of lanthanide in the complexes is 3. There is only one symmetry peak of the XPS spectra of the

Table 1. Analytical Data and Some Properties of the Ligands and the Complexes

Compound	M_r	$\{\Lambda_m\}^*$	UV λ_{\max}/nm	$w_i(\text{found})/\%$ $(w_i(\text{calc.})/\%)$				ORD $\{\alpha\}^{20}/^\circ$
				Ln	C	N	H	
Phen	180.20		291, 235					
NaL	238.28		285					3.0
<i>I</i>	983.38	6	275, 295, 320	14.04 (14.13)	53.80 (53.74)	5.53 (5.70)	5.10 (4.92)	3.4 + 86.0
<i>II</i>	984.58	7	275, 293, 318	14.20 (14.23)	53.77 (53.67)	5.54 (5.69)	4.83 (4.91)	3.2 + 87.1
<i>III</i>	985.38	8	276, 290, 315	14.23 (14.30)	53.66 (53.63)	5.60 (5.69)	4.84 (4.91)	2.8 + 89.0
<i>IV</i>	988.71	6	276, 295, 316	14.60 (14.59)	53.61 (53.45)	5.65 (5.67)	4.92 (4.89)	2.7 + 94.8
<i>V</i>	994.83	7	278, 295, 318	15.22 (15.11)	53.35 (53.12)	5.55 (5.63)	4.90 (4.86)	2.6 + 104.5
<i>VI</i>	996.43	6	278, 295, 320	15.16 (15.25)	53.20 (53.04)	5.58 (5.62)	4.77 (4.86)	2.5 + 113.6
<i>VII</i>	1003.39	8	278, 297, 320	15.79 (15.84)	52.87 (52.67)	5.52 (5.58)	4.53 (4.82)	2.6 + 135.2
<i>VIII</i>	988.95	7	275, 295, 318	16.44 (16.43)	53.32 (53.43)	5.57 (5.67)	4.70 (4.69)	2.5 + 129.2
<i>IX</i>	991.38	6	275, 294, 318	16.63 (16.65)	53.30 (53.31)	5.55 (5.65)	4.77 (4.68)	2.4 + 126.3

* $\Lambda_m(25^\circ\text{C}, c = 1 \times 10^{-4} \text{ mol dm}^{-3}, \text{ in THF})/(\text{S cm}^2 \text{ mol}^{-1})$. ** $c(\text{in DMF}) \cdot 10^{-4}/(\text{mol dm}^{-3})$.

Table 2. Some Infrared Spectral Data of the Ligands and the Complexes

Compound	$\tilde{\nu}/\text{cm}^{-1}$							
	$\nu(\text{C—O})$	$\nu(\text{C—H})$	$\nu_{\text{as}}(\text{SO}_3^-)$	$\nu_{\text{s}}(\text{SO}_3^-)$	$\Delta\tilde{\nu}/\text{cm}^{-1}$	$\nu(\text{Ln—O})$	$\nu(\text{Ln—N})$	$\nu(\text{Ln—Cl})$
Phen		1620 s						
NaL	1740 s		1196 s	1040 s	156			
<i>I</i>	1740 s	1600 s	1205 s	1048 s	157	512 m	320 w	270 w
<i>II</i>	1741 s	1596 s	1204 s	1048 s	156	512 m	322 w	271 w
<i>III</i>	1741 s	1590 s	1205 s	1048 s	157	510 m	320 w	270 w
<i>IV</i>	1741 s	1590 s	1204 s	1048 s	156	512 m	320 w	270 w
<i>V</i>	1740 s	1588 s	1202 s	1046 s	156	513 m	319 w	270 w
<i>VI</i>	1741 s	1585 s	1201 s	1046 s	155	514 m	320 w	269 w
<i>VII</i>	1741 s	1585 s	1203 s	1047 s	156	514 m	318 w	268 w
<i>VIII</i>	1740 s	1584 s	1204 s	1050 s	154	512 m	320 w	271 w
<i>IX</i>	1740 s	1580 s	1201 s	1048 s	153	512 m	318 w	270 w

N 1s and S 2p in the complexes, respectively, and also in the free ligands, showing the identical chemical environment of nitrogens in each ligand Phen. In contrast to the free ligand Phen, the BE data of N 1s shifted in the complexes and so did the BE data of S 2p slightly. This evidence corresponds to the UV spectral data and supports the result of coordination. The XPS spectra of the O 1s in the complexes and in the ligand exhibit a broad band. After deconvolution, this asymmetry band can be resolved into two components with the intensity ratio 1:3 corresponding to two kinds of oxygen in the different chemical environments in which the weaker component with a lower BE value at ca. 531.5 eV is almost unchanged which concerns the carbonyl oxygen and the intense compo-

nent with a higher BE value at ca. 532.7 eV shifted towards lower energy range about 0.4–1.0 eV can be assigned to the coordinated oxygen of sulfonic group SO_3^- .

A strong red fluorescence of the solid complexes *VI* ($\text{Eu}(\text{Phen})_2\text{L}_2\text{Cl} \cdot \text{H}_2\text{O}$) was observed under the ultraviolet lamp ($\lambda = 254 \text{ nm}$), but a very weak fluorescence and a broad band in the solution ($c = 1 \times 10^{-5} \text{ mol dm}^{-3}$ in DMF) of the complexes are observed at 404 nm ($\epsilon = 550 \text{ m}^2 \text{ mol}^{-1}$) of E_{em} , at 345 nm ($\epsilon = 515 \text{ m}^2 \text{ mol}^{-1}$) of E_{ex} . The characteristic absorption bands of complexes *VII* ($\text{Tb}(\text{Phen})_2\text{L}_2\text{Cl} \cdot \text{H}_2\text{O}$) in DMF ($c = 1 \times 10^{-5} \text{ mol dm}^{-3}$) appear at 404 nm ($E_{\text{em}}, \epsilon = 710 \text{ m}^2 \text{ mol}^{-1}$) and 364 nm ($E_{\text{ex}}, \epsilon = 720 \text{ m}^2 \text{ mol}^{-1}$). This indicates that the fluorescence

Table 3. The Data of XPS Spectra of the Complexes and the Ligands

Compound	BE/eV					X_i /mole %						
	N 1s	S 2p	O 1s	Cl 2p	Ln 3d _{5/2}	Ln	C	N	O	S	Cl	
Phen	401.2											
NaL		165.8	531.7	533.1								
I	399.5	165.6	531.6	532.7	198.4	835.8	1.1	44.0	4.0	6.2	2.0	1.0
II	399.4	165.7	531.6	533.0	198.4	881.8	1.0	44.2	4.0	6.1	2.1	1.0
III	399.5	165.5	531.4	532.3	198.3	933.2	1.1	44.3	4.0	5.8	1.9	1.0
IV	399.4	165.4	531.5	532.6	198.3	990.2	0.9	43.8	4.1	6.0	2.0	1.0
V	399.4	165.4	531.4	532.5	198.2	1081.3	1.0	44.1	4.0	6.0	2.0	1.0
VI	399.4	165.6	531.3	532.2	198.2	1136.8	1.1	44.4	4.0	5.9	1.9	1.0
VII	399.4	165.5	531.3	532.1	198.1	1246.2	0.9	44.0	4.0	6.0	2.1	1.0
VIII	399.4	165.5	531.4	532.1	198.1	1297.5	1.0	44.5	4.2	5.9	2.1	1.0
IX	399.4	165.5	531.3	532.3	198.2	1190.6	0.9	43.8	4.1	6.1	2.1	1.0

is due to the interaction of Phen with L. The results were confirmed by the determination of the solution ($c = 1 \times 10^{-5}$ mol dm⁻³ in DMF) of the gel prepared from Phen and L in the mole ratio 1:1.

The distinct positive Cotton effect on the ORD spectra of the complexes and of ligand (NaL) was obtained (Table 1). The positive value at about 280 nm of the complexes is diagnostic. This gives an *S* absolute configuration which is dominant for dichroic absorption and similar to a positive effect in the ligand [10].

EXPERIMENTAL

The reagents and solvents used were of anal. grade and purified according to the reported methods. Lanthanide(III) chlorides were made from the lanthanide oxides and hydrochloric acid. Sodium D-camphor- β -sulfonate was prepared from sodium hydroxide and the acid (HL) in stoichiometric ratio.

The IR spectra were recorded on a 170 SX FTIR spectrophotometer as CsI pellets in the range of $\tilde{\nu} = 200$ –4000 cm⁻¹. The UV spectra were recorded on a DJ-240 UV VIS spectrophotometer using DMF as a solvent. Elemental analyses were done using an Erba 1106 elemental analyzer. Conductivity measurements were performed with a DDS-11A conductometer using DMF as a solvent. X-Ray photoelectron spectra were measured on a PHI-550 spectrometer using the MgK α radiation ($h\nu = 1253.6$ eV). A Cary Model 60 spectropolarimeter with a CD model 6001 accessory was used to obtain the data of circular dichroism at 20°C in the range of $\lambda = 200$ –700 nm. The fluorescence spectra were recorded on a 3070 E spectrometer.

Ln(Phen)₂Cl₃

To a solution of 1,10-phenanthroline (2 mmol) in anhydrous ethanol (30 cm³) a solution of lanthanide chloride (1 mmol of LnCl₃, Ln = La³⁺ (I), Ce³⁺ (II), Pr³⁺ (III), Nd³⁺ (IV), Sm³⁺ (V), Eu³⁺ (VI), Tb³⁺ (VII), Dy³⁺ (VIII), Ho³⁺ (IX) ion) in anhydrous

ethanol (10 cm³) was added. After refluxing for 1 h the white precipitate was filtered, washed with anhydrous ethanol three times and dried *in vacuo* (10.7 kPa) at 80°C. The white precipitate was compound Ln(phen)₂Cl₃ and its yield was about 80%–90%.

Complexes I–IX

To a solution of compound Ln(Phen)₂Cl₃ (1 mmol) in absolute methanol (30 cm³) a solution of sodium D-camphor- β -sulfonate (3 mmol) in absolute methanol (20 cm³) was added dropwise. After refluxing for 1 h the white precipitate was filtered, washed with absolute methanol and diethyl ether three times, respectively and dried *in vacuo* (10.7 kPa) at 80°C for 2 h. The products are complexes I–IX and their yields are about 80%.

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