

**SYNTHESIS AND CHARACTERIZATION
OF LANTHANIDE(III) SCHIFF BASE
COMPLEXES DERIVED FROM CYSTEINE
AND BENZOIN**

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ABSTRACT

Six new complexes of the Schiff base ligand (HL) derived from benzoïn and cysteine with Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) of the type LnLCl₂(H₂O)₂ have been synthesized and characterized by elemental analyses, molar conductance, XPS, IR, thermal analysis, ¹H NMR and electronic spectra.

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INTRODUCTION

The coordination chemistry of lanthanides in biological systems¹⁻³ and the development of lanthanide shift reagents^{4,5} have aroused much interest. As no studies on lanthanide(III) complexes of benzoin and cysteine have been reported so far and in continuation of our earlier systematic investigation⁶ on lanthanide(III) coordination binding models by XPS spectra, we report here the synthesis and characterization of some of these new complexes of the Schiff base ligands (HL) derived from benzoin and cysteine (Fig. 1).

EXPERIMENTAL

Reagents and Solvents

Benzoin was A.R. grade, lanthanide chlorides (LnCl_3) were obtained by treating 0.5 mmol of Ln_2O_3 with 3.0 mmol of 1:1 hydrochloric acid. The resulting solution was filtered and evaporated to dryness. The white crystals were dried in a vacuum desiccator over CaCl_2 ; yields, 85%. All other reactants were of high purity and were used without any further purification.

Preparation of KL

The white compound KL (potassium salt of Schiff base) was obtained by mixing benzoin (0.032 mol, 6.73 g) with cysteine (0.032 mol, 5.0 g), and potassium hydroxide (0.032 mol, 1.8 g) in 100 mL EtOH. The mixture was refluxed for 2 h and precipitation occurred immediately on cooling the mixture. The crystals were filtered, recrystallized in EtOH two times and dried in a vacuum desiccator over CaCl_2 ; yield, 9.38 g (83%); m.p. 209.7–210.2 °C.

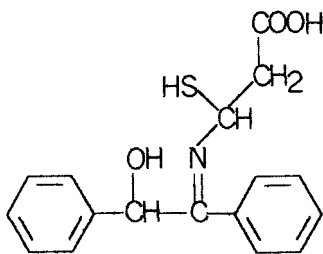


Figure 1. Structure of HL.

Preparation of Complexes $\text{LnLCl}_2(\text{H}_2\text{O})_2$

To a solution of 0.5 mmol lanthanide(III) chloride in 20 mL of absolute EtOH was added 0.35 g (0.1 mmol) of KL in 20 mL EtOH with stirring. The mixture was refluxed on a water bath for 1 h and then cooled to room temperature. The resulting precipitate was separated by filtration, washed with cold EtOH and finally dried at 110 °C for 1 h; yields, 75–85%.

Physical Measurements

The melting points of the ligand and complexes were determined with a Gallenkamp melting point apparatus. Microanalyses for C, H, N and S were carried out on a Perkin–Elmer 240C elemental analyzer. The content of Cl was determined by AgNO_3 titration. Lanthanides were determined volumetrically by EDTA titrations⁷ using xylenol orange as the indicator. The molar conductance of the complexes in methanol and in DMSO at 10^{-4} M concentration was measured with a DDS-IIA molar conductometer at room temperature as before⁸. The molar conductances are listed in Table I. The electronic spectra of the ligand and complexes were recorded in a Shimadzu UV-240 double-beam spectrophotometer using freshly prepared absolute methanol solutions of the samples. The infrared spectra (CsI pellets) were obtained on a NIC-5DX spectrophotometer in the 200–4000 cm^{-1} region. X-ray photoelectron spectra (XPS) were taken on a PHI-550 apparatus, using non-monochromatic Mg- $K\alpha$ radiation from an X-ray gun operated at 15 kV and 20 mA under a pressure of 10^{-9} mbar using the carbon 1s peak at 284.6 eV as standard. The samples were finely pulverized and spread on a gold holder as thin films. The hemispherical electrostatic analyzer was operated in the retarding mode with a pass energy of 20 eV. The accuracy of the measured BE value is ± 0.1 eV. The peak areas for semiquantitative analyses were determined using a linear background. Thermal analysis (TG and DTA) measurements were made in nitrogen atmosphere between room temperature and 800 °C using a Thermoflex TG-DTA meter. ^1H NMR spectra were measured on a Bruker AC 80 spectrometer using DMSO-d_6 as solvent.

RESULTS AND DISCUSSION

The formation of the complexes may be shown by the following representative equation:



Table I. Elemental Analysis and Physical Properties of the Ligand and Complexes

Compounds (Empirical formula, formula weight)	Found (Calc.) %							Decomp. Temp. °C	% Yield	$\lambda_{\text{max}}(\log \epsilon)$	Λ_{M} (S·cm ² ·mol ⁻¹) in MeOH/DMSO
	Ln	C	H	N	S	Cl					
KL	—	57.60	4.57	3.98	9.05			380	83	224 (2.5)	
(C ₁₇ H ₁₆ NO ₃ SK, 353.34)	—	(57.59)	(4.56)	(3.96)	(9.06)					315 (1.8)	
LaCl ₂ (H ₂ O) ₂	24.78	36.45	3.57	2.49	5.70	12.67		228	82	321 (1.75)	10.5/3.1
(C ₁₇ H ₂₀ Cl ₂ NO ₃ SLa, 560.15)	(24.79)	(36.44)	(3.60)	(2.50)	(5.71)	(12.67)					
PrCl ₂ (H ₂ O) ₂	25.06	36.34	3.57	2.47	5.71	12.64		221	76	320 (1.70)	8.0/2.6
(C ₁₇ H ₂₀ Cl ₂ NO ₃ SPr, 562.15)	(25.06)	(36.31)	(3.58)	(2.49)	(5.69)	(12.63)					
NdCl ₂ (H ₂ O) ₂	25.48	36.08	3.54	2.48	5.64	12.53		225	85	332 (1.80)	9.0/2.0
(C ₁₇ H ₂₀ Cl ₂ NO ₃ SNd, 565.48)	(25.50)	(36.10)	(3.56)	(2.48)	(5.66)	(12.55)					
SmCl ₂ (H ₂ O) ₂	26.29	35.69	3.54	2.44	5.62	12.43		230	79	327 (1.75)	9.2/2.2
(C ₁₇ H ₂₀ Cl ₂ NO ₃ SSm, 571.59)	(26.31)	(35.71)	(3.53)	(2.45)	(5.60)	(12.42)					
EuCl ₂ (H ₂ O) ₂	26.50	35.62	3.54	2.45	5.60	12.35		223	75	335 (1.80)	9.5/3.2
(C ₁₇ H ₂₀ Cl ₂ NO ₃ SEu, 573.2)	(26.51)	(35.61)	(3.52)	(2.44)	(5.58)	(12.38)					
GdCl ₂ (H ₂ O) ₂	27.20	35.26	3.45	2.44	5.52	12.24		228	80	325 (1.90)	9.2/2.1
(C ₁₇ H ₂₀ Cl ₂ NO ₃ SGd, 578.49)	(27.18)	(35.28)	(3.48)	(2.42)	(5.53)	(12.27)					

The complexes are soluble in water, chloroform, ether, EtOH, acetone and dimethylformamide (DMF). The colors of aqueous solutions are dependent on the pH value. Between pH = 1–5 yellow solutions were observed, and at pH = 6–7.5 colorless turbid solutions were produced. The molar conductance values in methanol and in DMSO indicate that the complexes are non-electrolytes in solution^{8,9}, but in methanol the molar conductance values are relatively higher than those in DMSO and this may be attributed to methanol coordination. To confirm this result, longer time molar conductance values have been examined. It was found that the change of the molar conductance values with time increased for about 2 h at room temperature and then the data become constant. These phenomena indicate that the coordinated sphere or the coordination bond model may be changed due to replacement by small polar molecules. The TG-DTA diagrams of all complexes are similar and indicate that the complexes sustain weight loss in the 120–140 °C region and mass loss was observed at *ca.* 200 °C, then the complexes continue to decompose exothermally at 350, 520 and 630 °C and the decomposition is completed at about 780 °C. Water of crystallization (extraspheric water) is usually lost over the 70–110 °C range while water of coordination (intraspheric water) is eliminated at higher temperature (120–150 °C). Together with the corresponding weight losses (water) it can be concluded that the two water molecules in all complexes are coordinated.

Infrared Spectra

The IR spectra of the potassium salt of the ligand (KL) and its complexes are complicated. However, attempts have been made to identify some important bands that furnish information regarding the mode of bonding. The main IR bands with their tentative assignments are listed in Table II. The broad band between 3414 and 3386 cm^{-1} due to the stretching modes of $\nu(\text{OH})$ of the ligand remains almost unchanged but becomes stronger in the complexes, which indicates that the hydroxyl group remains uncoordinated. Two stretching vibration of CO_2^- , $\nu_{\text{as}}(\text{CO}_2^-)$ and $\nu_{\text{s}}(\text{CO}_2^-)$ in the spectra of the complexes are observed at *ca.* 1580 and 1406 cm^{-1} with the difference $\Delta\nu(\text{CO}_2^-) = 174 \text{ cm}^{-1}$. Compared with the ligand, the two bands at 1566 and 1400 cm^{-1} having the difference $\Delta\nu(\text{CO}_2^-) = 166 \text{ cm}^{-1}$ suggested that the CO_2^- group is coordinated with the metal ion in unidentate form. The band at 1625 cm^{-1} in the ligand attributed to the $\nu(\text{C}=\text{N})$ stretching vibration shifts to lower frequencies at 1600–1605 cm^{-1} after complexation indicating coordination of the nitrogen atom in the C=N group to the metal ion. Furthermore, several new bands observed in the far-IR spectra at *ca.* 510, 318, 270 and 225 cm^{-1} in the complexes are assigned

Table II. Principal IR Bands of the Ligand and Complexes (cm^{-1})

Compounds	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu_{\text{as}}(\text{CO}_2^-)$	$\nu_{\text{s}}(\text{CO}_2^-)$	$\Delta\nu(\text{CO}_2^-)$	$\nu(\text{Ln}-\text{O})$	$\nu(\text{Ln}-\text{N})$	$\nu(\text{Ln}-\text{Cl})$	$\nu(\text{Ln}-\text{S})$
KL	3400 m	1625 s	1566 s	1400 s	166				
La $\text{LCl}_2(\text{H}_2\text{O})_2$	3410 s	1602 m	1580 s	1407 s	173	512 m	320 m	270 m	225 m
Pr $\text{LCl}_2(\text{H}_2\text{O})_2$	3406 s	1600 m	1583 m	1408 s	175	511 w	317 m	268 m	223 w
Nd $\text{LCl}_2(\text{H}_2\text{O})_2$	3414 s	1600 m	1580 s	1408 s	172	510 m	318 w	271 m	222 w
Sm $\text{LCl}_2(\text{H}_2\text{O})_2$	3408 s	1605 m	1580 s	1404 s	176	512 m	316 w	273 m	224 m
Eu $\text{LCl}_2(\text{H}_2\text{O})_2$	3413 s	1603 m	1582 s	1408 s	174	510 m	319 m	272 m	225 sh, m
Gd $\text{LCl}_2(\text{H}_2\text{O})_2$	3409 s	1602 m	1581 s	1409 s	172	514 w	318 w	270 m	221 w

to $\nu(\text{Ln-O})$, $\nu(\text{Ln-N})$, $\nu(\text{Ln-Cl})$ and $\nu(\text{Ln-S})$ stretching modes, respectively. All of the complexes exhibit an intense sharp band at 3440 cm^{-1} in the aqueous stretching region, suggesting that the water molecules in the complexes are in the coordinated form, which is consistent with the thermal analysis. On the basis of the discussion referred to above, it is possible to conclude that the ligand is attached to the metal ion by the carboxyl oxygen, nitrogen and sulfur atoms. Other groups coordinated to the metal ion are chlorine ion and oxygen atom in water, and seven-coordinated complexes are formed.

Electronic and ^1H NMR Spectra

The electronic spectra of KL in MeOH show two bands at 224 and 315 nm that are attributed to $\pi \rightarrow \pi^*$ transitions of the phenyl ring and C=N bond, but in the complexes the latter band shifted to 320–335 nm (Table I) indicating that the N atom coordinates to the lanthanide(III) ion. The band at 224 nm was almost unchanged.

To obtain further insight into the coordination model, ^1H NMR spectra have been recorded. The ^1H NMR spectrum of KL displays signals at 1.78, 6.04 and 7.10–8.01 ppm, assignable to -SH, -OH and aromatic protons, respectively. The observed downfield shifts of the -SH signal to *ca.* 1.54 ppm in the spectra of the complexes are indicative of involvement of the sulfur atom in coordination. The deshielding is due mainly to the -SH group being distant from the crowded coordination sphere. The new band at *ca.* 5.02 ppm in the spectrum of the complexes indicated the coordination of water.

X-Ray Photoelectron Spectra (XPS)

In order to obtain further insight into the nature of bonding, XP spectra of the complexes and the ligand were recorded in powder form at room temperature. The results of the XPS semi-quantitative analyses of the complexes are in agreement with the elemental analysis data and are given in Table III and Fig. 2. The values for the Ln 3d or 4d electron binding energy (BE) in the complexes are approximately the same and support the oxidation number of three. The N 1s and S 2p electron spectra of the complexes are symmetric and their deconvolution revealed that relative to the free ligand, the N 1s and S 2p BEs are all shifted higher. This may be explained as due to the decrease of the electron density after coordination to the lanthanide(III) ion and it is consistent with the electronic spectral date. The

Table III. The Binding Energy (eV) of the Ligand and Complexes LnLCl₂(H₂O)₂

Compounds	N 1s	O 1s	S 2p	Cl 2p	Ln	Atomic ratio Ln/C/N/O/S/Cl
KL	400.5	531.6 (OH), 533.2 (COO)	164.5			
	400.9	531.6 (OH), 532.4 (H ₂ O), 533.0 (-C-O ⁻ , 533.4 (-C=O))	164.8	198.2	835.7	1.0:16.8:1.0:5.1:1.0:2.0
PrLCl ₂ (H ₂ O) ₂	401.1	531.6 (OH), 532.4 (H ₂ O), 533.0 (-C-O ⁻ , 533.4 (-C=O))	164.8	198.2	933.0	1.0:17.0:1.0:5.0:1.0:2.0
	401.5	531.5 (OH), 532.5 (H ₂ O), 532.9 (-C-O ⁻ , 533.4 (-C=O))	164.8	198.3	984.7	0.99:17.1:1.0:5.0:1.0:2.0
SmLCl ₂ (H ₂ O) ₂	401.6	531.5 (OH), 532.6 (H ₂ O), 533.1 (-C-O ⁻ , 533.6 (-C=O))	164.8	198.4	1083.8	1.0:16.9:1.02:5.1:1.0:2.0
	401.3	531.4 (OH), 532.5 (H ₂ O), 533.1 (-C-O ⁻ , 533.5 (-C=O))	164.8	198.3	1136.2	0.98:17.1:1.0:5.0:1.0:2.0
GdLCl ₂ (H ₂ O) ₂	401.5	531.6 (OH), 532.3 (H ₂ O), 533.0 (-C-O ⁻ , 533.5 (-C=O))	164.8	198.2	1016.5	0.98:16.8:1.0:5.1:1.0:2.0
				198.1		

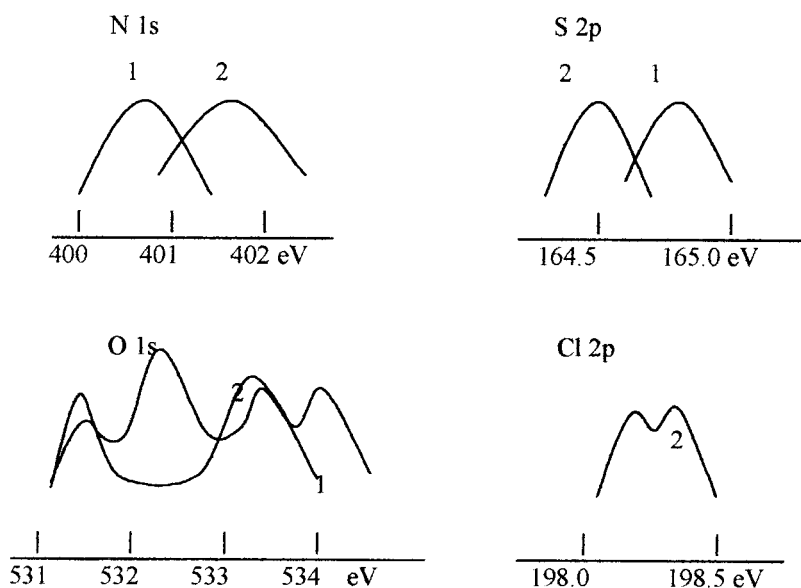


Figure 2. XPS spectra of the ligand (1) and complexes $\text{SmLCl}_2(\text{H}_2\text{O})_2$ (2).

Cl 2p spectra of the complexes are asymmetric and the relative intensity of the peaks on deconvolution is about 1:1, indicating that the two coordinated Cl atoms are in different chemical environments.

The O 1s electron spectra of the complexes are in a very asymmetric shape. Compared with the ligand bands at 531.6 and 532.5 eV attributed to hydroxyl -OH and symmetric carboxylic oxygen atoms, the BE values of the complexes appear at *ca.* 531.5, 532.4, 533.2 and 533.6 eV and may be assigned to hydroxyl -OH, H_2O , -COO^- (coordinated -C-O^-) and -COO^- (-C=O), respectively which indicates that four chemical environments were produced after coordination. Combined with the relative intensity of the bands which equals 1:2:1:1, it can be deduced that two water molecules coordinated to the lanthanide ion and the COO^- group coordinate with the central metal ion through an oxygen atom in a unidentate form, but the hydroxyl -OH does not take part in coordination with the lanthanide(III) ion¹¹.

The atomic ratios of the complexes also have been examined. It was found that the complexes possess the stoichiometric ratio of $\text{Ln:C:N:O:S:Cl} = 0.98:16.8:1.0:5.1:1.0:2.0$ which is consistent with the elemental analyses data.

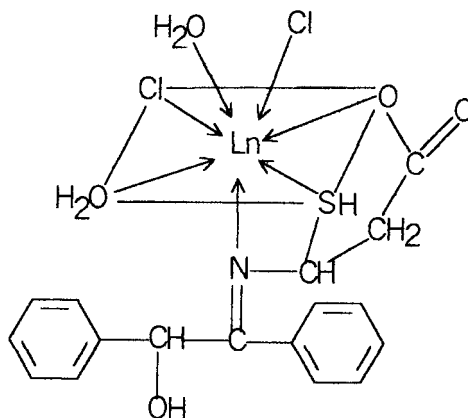


Figure 3. Suggested binding model of $\text{LnLCl}_2(\text{H}_2\text{O})_2$.

CONCLUSION

On the basis of the above discussions a seven-coordinated capped-octahedral structure is suggested for the complexes as shown in Fig. 3.

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