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Synthesis and Characterization of Open-ring Complexes Formed in the Reaction of Lanthanides(III) with Salicylaldehyde Schiff base Containing Pyridine and Amide Bridge

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Eleven new lanthanide(III) complexes have been prepared by the reaction of lanthanide chlorides and the salicylaldehyde Schiff base ligand (L) in ethanol solution. They have been characterized by elemental analysis, molar conductivity data, IR, UV and ^{1}H NMR. The measured results shows that lanthanide(III) is coordinated with the Schiff base by ratio of 1 : 1. The formula of the complexes is $[LnLH_2O]Cl_3$, where Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu.

Key Words: Lanthanide(III), Complex, Salicylaldehyde Schiff base.

INTRODUCTION

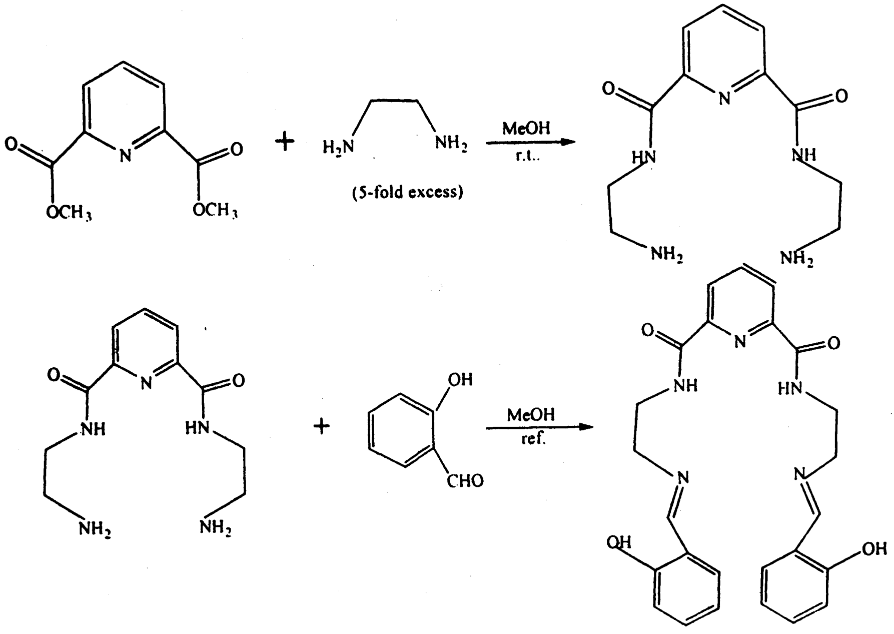
There is a continued interest in synthesizing complexes of lanthanides because of variable coordination numbers of lanthanides[1] and their potential applications in fundamental and applied sciences. For example, they can serve as NMR shift reagents[2–4], as luminescent chemosensors[5], as luminescent probes[6], in biomedical analysis[7–9], cancer phorotherapy[10], fluoroimmunoassay[6], etc. Meanwhile, salicylaldehyde Schiff bases have also attracted much attention due to their diverse biological activities, such as antimicrobial[11], antibacterial[12], antiviral[13], anticancer[14] activities etc. This paper studies the reaction of lanthanides and the salicylaldehyde Schiff base ligand (L) in the ethanol and synthesized eleven new lanthanide complexes. Their compositions and structures are corroborated by elemental analysis and various spectrum measurements.

EXPERIMENTAL

All chemicals and solvents used were purchased as AR grade and without further purification before use. The hydrated lanthanide chlorides were prepared by the reported method[15].

The elemental analyses (C, H, N) were done by MOD-1106 elemental autoanalyzer. Metal contents of the complexes were determined by EDTA titration using xylenol orange as an indicator. The IR spectra in the 4000–400 cm^{-1} range in KBr pellets were recorded on a Shimadzu FTIR 3000 instrument. The UV-Vis spectra in 200–700 nm range were recorded on a Shimadzu UV-160 A spectrophotometer in DMF solution. 1D ^{1}H NMR spectra were acquired on Variant Mercury-UX 300 MHz spectrophotometer for DMSO-d_6 solution, using TMS as internal standard. Molar conductivities were obtained on a DDSJ-308 type instrument for DMF as solvent at 25 ± 1°C.

The salicylaldehyde Schiff base ligand (**L**) was prepared by the reported method[16]. The synthesis route is shown in **Scheme**.



(L)

Scheme

General procedure for the preparation of complexes: Rare earth oxide was dissolved in HCl. Then the H_2O and the excess HCl were removed *in vacuo* to give $LnCl_3$ solid. To a solution of 0.23 g (0.5 mmol) **L** in 20 mL ethanol, 20 mL ethanol solution of $Ln(Cl)_3$ (0.5 mmol) was added and stirred for 24 h under reflux. Then the reaction mixture was cooled to room temperature and the yellow precipitate was filtered off, washed with ethanol three times and dried *in vacuo*, yield 34–87%.

RESULTS AND DISCUSSION

All complexes are light yellow crystals and insoluble in ethanol, acetone and ether but soluble in methanol, DMF and DMSO. They are stable to air and light. The elemental analysis data are presented in Table-1 which correspond to the formula $LnC_{25}H_{27}N_5O_5Cl_3$. The yields of the complexes are given in Table-3.

Various important bands and their assignments are given in Table-2. The IR spectra of the eleven complexes are similar indicating the presence of the same ligand throughout the series. The considerable shift to lower frequency of the amide I (from 1667 to 1637–1632 cm^{-1}) and the weaker vibration of amide II in the complexes indicate that the N atom of the amide coordinates to the metal. The band at 1633 cm^{-1} assignable to $\nu(C{=}N)$ appears at a lower value and folds with the amide I as result of coordination of the azomethine N atoms to metal[17]. In the free ligand, the characteristic bands of pyridine occur at 1574 cm^{-1} (pyridine deformation), 1045 cm^{-1} (pyridine-ring breathing mode), respectively. However, these bands in the complexes appear at lower frequency values (1563–1555 cm^{-1}, 1021–1006 cm^{-1}). This change suggests coordination of the N atom of the pyridine ring to the metal[18]. In the complexes, in the ranges of 582–564 and 445–416 cm^{-1} are observed two new bands, which are contributable to $\nu(N{-}M)$ and $\nu(O{-}M)$, respectively. The appearance of a broad band in the regions of 3394–3364 cm^{-1} and two weak bands at *ca.* 740 and ca. 660 cm^{-1} indicate the presence of the coordinated water molecule in the complexes.

TABLE-1
ELEMENTAL ANALYSIS DATA FOR THE COMPLEXES

Complex	Analysis (%)							
	M		C		H		N	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$[LaLH_2O]Cl_3$	19.10	19.25	41.35	41.55	3.69	3.74	9.78	9.70
$[NdLH_2O]Cl_3$	20.02	19.80	41.15	41.27	3.52	3.71	9.51	9.63
$[SmLH_2O]Cl_3$	20.59	20.46	40.55	40.93	3.82	3.68	9.69	9.55
$[EuLH_2O]Cl_3$	20.48	20.68	40.69	40.82	3.56	3.67	9.38	9.52
$[GdLH_2O]Cl_3$	23.50	23.08	39.75	39.58	3.43	3.56	9.02	9.23
$[DyLH_2O]Cl_3$	21.40	21.78	40.36	40.21	3.74	3.62	9.52	9.38
$[HoLH_2O]Cl_3$	22.28	22.06	40.03	40.11	3.50	3.61	9.48	9.36
$[ErLH_2O]Cl_3$	22.62	22.27	40.18	40.00	3.69	3.60	9.21	9.33
$[TmLH_2O]Cl_3$	22.87	22.50	39.61	39.95	3.51	3.60	9.48	9.32
$[YbLH_2O]Cl_3$	23.46	22.88	39.95	39.68	3.46	3.57	9.37	9.26
$[LuLH_2O]Cl_3$	23.72	22.98	39.89	39.63	3.71	3.56	9.01	9.25

The UV spectral data are presented in Table-3. In the UV spectra of the ligand only one strong band is observed, which is λ 273 nm. This band is due to the superimposition of K bands of two conjugated systems (a) and (b). This band appears at 266 nm (λ_1) in the complexes, shifting to higher frequency by *ca.* 7

nm because of electrons transfer on coordination[19]. In all complexes, the increase of ε_1 and the appearance of a new band (λ_2) in the regions of 316–318 nm, which is assignable to electrons transfer between the ligand and metal[19], also confirm the coordination between the ligand and metal ions.

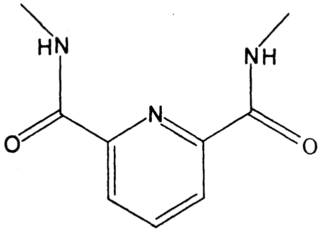
The molar conductivity data of the complexes are given in Table-3. The molar conductance values for the complexes in DMF are higher than that of 1 : 2 electrolyte in the same solvent[20], indicating Cl^- does not coordinate to metal.

TABLE-2

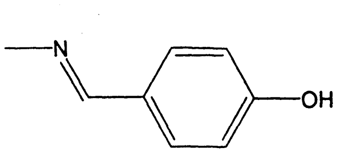
KEY INFRARED SPECTRAL BANDS (cm^{-1}) OF THE LIGAND AND THE COMPLEXES

Complex	ν (H_2O, OH)	ν (NH)	ν (amide I)	ν (C=N)	ν (amide II)	νPh (C—OH)	Pyridine ring	ν (N—M)	ν (O—M)
L	3360	3312	1649	1633	1531	1287	1574, 1045	—	—
$[LaLH_2O]Cl_3$	3372 (br)	3220	1632 (br)		1534	1282	1558, 1012	575	429
$[NdLH_2O]Cl_3$	3382 (br)	3218	1633 (br)		1535	1283	1560, 1015	577	445
$[SmLH_2O]Cl_3$	3363 (br)	3221	1632 (br)		1536	1273	1555, 1011	564	438
$[EuLH_2O]Cl_3$	3381 (br)	3225	1635 (br)		1537	1284	1562, 1021	582	418
$[GdLH_2O]Cl_3$	3383 (br)	3185	1635 (br)		1537	1285	1562, 1018	575	420
$[DyLH_2O]Cl_3$	3368 (br)	3220	1637 (br)		1532	1283	1555, 1009	569	419
$[HoLH_2O]Cl_3$	3364 (br)	3210	1636 (br)		1538	1287	1563, 1019	582	427
$[ErLH_2O]Cl_3$	3364 (br)	3219	1634 (br)		1540	1277	1560, 1006	579	423
$[TmLH_2O]Cl_3$	3378 (br)	3220	1632 (br)		1536	1283	1560, 1011	574	416
$[YbLH_2O]Cl_3$	3385 (br)	3218	1636 (br)		1539	1286	1563, 1019	581	423
$[LuLH_2O]Cl_3$	3394 (br)	3221	1632 (br)		1535	1278	1555, 1021	574	417

The ^1H NMR data of the ligand and Ho complex are shown in Table-4. Their ^1H NMR spectra exhibit all the expected signals with the desired integral ratio and support the postulated molecular structure. The downfield shift of the proton signal of —CH=N— and the pyridine indicates that the N atoms of —CH=N— and pyridine coordinate to the metal ion[21], while the upfield shift of —CONH— signal explains coordination of the N atom of amide to the metal.



(a)



(b)

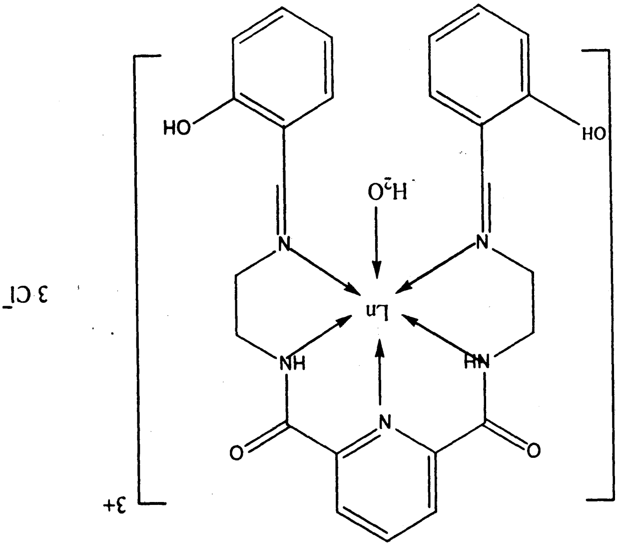
TABLE-3
YIELDS, UV SPECTRA (λ_1, ε_1, λ_2, ε_2) AND MOLAR CONDUCTIVITY (Λ_m) DATA FOR THE COMPLEXES

Complex	Yield (%)	Λ_m (s cm^2 mol^{-1})	λ_1 (nm)	ε_1	λ_2 (nm)	ε_2
$[LaLH_2O]Cl_3$	34.50	235	266	5640	316	3584
$[NdLH_2O]Cl_3$	67.60	225	266	6285	316	4261
$[SmLH_2O]Cl_3$	67.02	231	266	5830	316	4236
$[EuLH_2O]Cl_3$	58.51	220	266	7028	316	4638
$[GdLH_2O]Cl_3$	53.97	217	266	7654	316	5264
$[DyLH_2O]Cl_3$	65.90	222	266	6392	316	4338
$[HoLH_2O]Cl_3$	82.10	214	266	7085	316	4446
$[ErLH_2O]Cl_3$	81.84	217	266	10943	316	5443
$[TmLH_2O]Cl_3$	87.10	240	266	11713	316	5287
$[YbLH_2O]Cl_3$	81.20	245	266	11000	316	5116
$[LuLH_2O]Cl_3$	72.89	246	266	13742	316	5948

TABLE-4
^{1}H NMR DATA OF THE LIGAND AND Ho COMPLEX

Compound	Ph—OH	PyH	CO—NH	—N═CH	PhH	CH_2
L	13.56 (s, 2H)	8.37 (d, 2H)	8.25 (br, 2H)	7.33 (s, 2H)	7.26 (d, 2H)	3.85 (t, 4H)
		8.01 (t, 1H)			7.16 (q, 2H)	3.84 (q, 4H)
					6.87 (m, 4H)	
Ho Complex	13.28 (s, 2H)	8.55 (d, 2H)	8.14 (br, 2H)	7.98 (s, 2H)	7.32 (t, 4H)	3.78 (s, 4H)
		8.14 (br, 1H)			6.81 (s, 4H)	3.65 (d, 4H)

Thus, based on the result of elemental analysis, molar conductance measurements, UV, IR, ^{1}H NMR study, the following structure is suggested for the complexes:



Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu

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