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Lanthanide Chelate Complexes of Salicyloyl Hydrazide–Salicylaldehyde Schiff Base (SHSASB) and Anthranilic Acid–Salicylaldehyde Schiff Base (AASASB)

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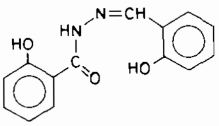
Abstract

New lanthanide complexes of salicylaldehyde-Schiff bases with salicyloyl hydrazide and anthranilic acid, were synthesized by a novel method consisting of refluxing the mixtures of Schiff base ligands and lanthanide trichloroacetate in acetone. Solid complexes of formulae $Ln(SHSASB)_3 \cdot 2H_2O$ and $Ln_2(AASASB)_3 \cdot 2H_2O$ where Ln = La–Yb and Y, were isolated. Proton NMR and IR spectra for the complexes reveal the bidentate binding of both the Schiff base ligands to the lanthanide ion. Electronic spectra along with the conductance data for the complexes indicate a coordination number of six for the lanthanide ion in the complexes of both the Schiff bases.

Introduction

Literature survey reveals that a majority of lanthanide Schiff base complexes have been studied in solution only but, recently, some progress has been made in isolation and study of solid schiff base complexes of lanthanides [1–6]. Synthesis of lanthanide-Schiff base complexes have been done by different procedures [2, 7–9]. Neutral N-salicylidene-anthranilic acid–lanthanide complexes have been prepared by the deprotonation of the –COOH group in the Schiff base by using pyridine and refluxing for about one hour and subsequent freezing for over two days [7]. On the other hand neutral 1:1 lanthanide complexes of Schiff bases (X-saltren) derived from substituted salicylaldehyde and tris-(2-amino ethyl)-amine, have been obtained by reacting the metal nitrates with the Schiff bases in the presence of sodium acetate under strictly anhydrous and reflux conditions, over night [8]. In an another method, the Schiff base and the lanthanide salt are refluxed in warm ethanol, for more than one hour, the resulting solution treated with ammonium hydroxide and the pH adjusted to 4–4.5 until the complex separates out [9]. However, the need for an elegant and direct method for the preparation of Schiff base complexes, wherein the hydrated lanthanide salts could be used, is very much felt. Accordingly, research in this direction was undertaken in our laboratory. Lanthanides, which are hard acids require hard bases to form stable complexes. One would expect that Schiff bases consisting of functional moieties such as the phenolic-OH or carboxylic groups juxta-posed suitably for chelation, will yield stable solid complexes with lanthanides. These functional moieties as $-O^-$ or $-COO^-$ which can readily coordinate to the lanthanide ions result in stable chelates. Thus the Schiffbases, SHSASB (I) and AASASB (II) were selected for the synthesis of their lanthanide chelates in the present work. Deprotonation during complexation has been nicely achieved by employing the lanthanide trichloroacetates, where the trichloroacetate ion forms the acid by abstracting the proton from the Schiff base. The isolated chelates have been characterized by analysis, electrolytic conductance, IR, ^{1}H NMR and electronic spectral data.



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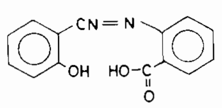

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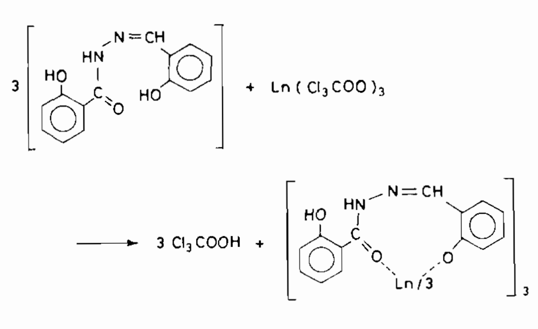

Experimental

Materials

Anthranilic acid was procured from Riedel De Haen A.G., Germany, and salicylaldehyde methyl

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salicylate and hydrazine hydrate from S.D. Chemicals, India. Lanthanide oxides (99.9% purity) were obtained from Indian Rare-earths, India.

Hydrated lanthanide trichloroacetates were prepared by dissolving the lanthanide oxide, in aqueous solution of trichloroacetic acid and evaporating the solution to dryness at room temperature. The solid was washed with chloroform three or four times, to remove the excess of trichloroacetic acid.

Salicyloyl hydrazide was prepared by refluxing methyl salicylate (1 mol) and hydrazide hydrate (1.1 mol) in about 100 ml of alcohol for one hour. The precipitated salicyloyl hydrazide was filtered at the pump, then washed with a minimum amount of alcohol.

SHSASB was prepared by mixing a hot solution of salicyloyl hydrazide (1 mol) in 75 ml of alcohol and hot salicylaldehyde (1 mol) with stirring. The precipitated Schiff base was filtered at the pump, washed with alcohol and recrystallised from alcohol, m.p. 275 ℃ (Lit. 277 ℃).

AASASB was synthesised by adding 1 mol of hot salicylaldehyde to a hot solution of 1 mol anthranilic acid and stirring the mixture. The solution was concentrated and cooled when crystals of the Schiff base separated out. This was filtered at the pump, washed with alcohol and recrystallised from alcohol, m.p. 206 ℃ (Lit. 207 ℃).

Synthesis of the Complexes

1 mmol of the metal salt was dissolved in 15 ml acetone. This was added to a mixture of SHSASB (4 mmol) and acetone (200 ml) and the resulting mixture warmed on a water bath. The clear solution formed was refluxed over the water bath for 5–6 h. The complex separated was filtered through a sintered crucible, washed 3–4 times with hot acetone and dried over P_2O_5 in a vacuum desiccator.

To a solution of AASASB (4 mmol) in acetone (200 ml) a solution of hydrated lanthanide trichloroacetate (1 mmol) in acetone (15 ml) was added and the mixture was refluxed over water bath for 5 h. The separated complex was filtered through a sintered crucible, washed 3–4 times with hot acetone to remove any ligand present, and the pure complex dried over P_2O_5 in a vacuum desiccator.

Analyses

The complex was decomposed by repeated treatment with concentrated nitric acid, pH adjusted to 5, and then titrated against standard EDTA solution using xylenol orange as indicator [10].

Conductance and Spectral Studies

Conductance measurements of AASASB complexes in DMF solutions and of SHSASB complexes in DMSO solutions were made using the Siemens conductivity bridge with an immersion type (LTA) cell, calibrated with standard KCl solution. Infrared spectra in nujol mulls, were obtained on a Perkin-Elmer model-397 spectrophotometer, in the region 600–4000 cm^{-1}. The proton NMR spectra for diamagnetic complexes and the ligands in DMSO-d_6 solutions were recorded on Varian 80-MHz and Bruker WH-270 spectrometers, operating in the Fourier transform mode. TMS was used as internal reference. The electronic spectra for Nd^{+3} and Ho^{+3} complexes in the solid state (nujol mulls) in the visible region, were obtained on Shimdzu double beam spectrophotometer UV-210A in the reflectance mode. Because of poor solubility in DMSO, electronic spectra in solution could not be obtained.

Discussion

Stoichiometries of the Complexes

The complexes are nonhygroscopic and insoluble in solvents like methanol, acetonitrile and chloroform, but sparingly soluble in DMSO and DMF. The analytical and molar conductance data for the complexes are presented in Tables I and II respectively. They analyse for the general formulae $Ln(SHSASB)_3\cdot 2H_2O$ and $Ln_2(AASASB)_3\cdot 2H_2O$ where Ln = La–Yb

TABLE I. Analytical and Molar Conductance Data for the Lanthanide–AASASB Complexes.

Complex	Metal %		$\Lambda_m{}^a$
	Found	Calculated	
$La[La(AASASB)_3]\cdot 2H_2O$	26.83	26.95	81.59
$Nd[Nd(AASASB)_3]\cdot 2H_2O$	27.84	27.70	61.45
$Ho[Ho(AASASB)_3]\cdot 2H_2O$	30.61	30.46	66.15
$Er[Er(AASASB)_3]\cdot 2H_2O$	30.64	30.76	94.47
$Yb[Yb(AASASB)_3]\cdot 2H_2O$	31.51	31.49	85.57
$Y[Y(AASASB)_3]\cdot 2H_2O$	19.26	19.11	61.85

[a] Molar conductance in DMF ohm^{-1} cm^2 mol^{-1}.

TABLE II. Analytical and Molar Conductance Data for the Lanthanide–SHSASB Complexes.

Complex	Metal %		$\Lambda_m{}^a$
	Found	Calculated	
$La(SHSASB)_3\cdot 2H_2O$	14.67	14.78	10.47
$Nd(SHSASB)_3\cdot 2H_2O$	15.14	15.26	7.35
$Ho(SHSASB)_3\cdot 2H_2O$	17.15	17.08	8.05
$Er(SHSASB)_3\cdot 2H_2O$	17.20	17.28	7.94
$Yb(SHSASB)_3\cdot 2H_2O$	17.89	17.77	7.46
$Y(SHSASB)_3\cdot 2H_2O$	9.84	9.99	10.82

[a] Molar conductance in DMSO ohm^{-1} cm^2 mol^{-1}.

TABLE III. Important Infrared Frequencies (in cm^{-1}) and their Assignments for AASASB and its Lanthanide Complexes.

AASASB	La	Nd	Ho	Er	Yb	Y	Assignments
–	3300w	3350w	3350w	3350w	3350w	3350w	Sym. and antisym. stretch of H_2O
1690m	1595s	1590m	1590s	1590s	1590s	1590s	ν_{COO}
1620s	1620s	1620s	1619s	1619s	1619s	1620s	$\nu_{C=N}$
1185w	1160m	1165m	1148m	1148m	1145m	1150m	ν_{C-O}(phenolic)
770w	–	–	–	–	–	–	OH out of plane (phenolic)

TABLE IV. Important Infrared Frequencies (in cm^{-1}) and their Assignments for SHSASB[a] and its Lanthanide Complexes.

SHSASB	La	Nd	Ho	Er	Yb	Y	Assignments
3200bw	3600–3206bw	3600–3200bw	3600–3200bw	3600–3200bw	3600–3200bw	3600–3200bw	Sym. and antisym. stretch of H_2O and NH
2625bw	2625vw	2625vw	2625vw	2625vw	2625vw	2625vw	ν_{O-H} (phenolic)
2575bw	2575vw	2575vw	2575vw	2575vw	2575vw	2575vw	
1640s	1525s	1530s	1530s	1530s	1540s	1530s	Amide-I
1618vs	1615vs	1618vs	1615vs	1612vs	1615vs	1615vs	$\nu_{C=N}$[a] ν_{N-H}
1560s	1580s	1585s	1580s	1580s	1585s	1585s	Amide-II
1158m	1155m	1155m	1155m	1155m	1155m	1155m	ν_{C-O} (phenolic)
785w	785w	785w	785w	785w	785w	785w	O–H out of plane (phenolic)
670w	700w	700w	700w	700w	700w	700w	N–H out of plane
650w	665w	665w	665w	670w	670w	675w	

[a] Assignments have been made as per the reported assignments by Dua S. K. *et al.* [16].

and Y. Molar conductance values for the complexes of SHSASB in DMSO and the complexes of AASASB in DMF indicate that the former are non-electrolytes in DMSO and the latter 1:1 electrolytes in DMF [11].

Infrared Spectra

Important spectral data for the Schiff base ligands and their complexes are presented in Tables III and IV. Bidentate binding of the ligands to the lanthanide ion is clearly revealed by the IR spectra. The AASASB complexes show a decrease by 95–105 cm^{-1} (1585–1595 cm^{-1}) and 25–40 cm^{-1} (1145–1160 cm^{-1}) in $\nu_{C=O}$ (1690 cm^{-1}) and ν_{C-O} phenolic (1185 cm^{-1}), respectively, of the free ligand, thereby showing the coordination of both carboxylic and phenolic oxygen to the lanthanide ion. The SHSASB complexes indicate a decrease of 100 cm^{-1} (1540 cm^{-1}) in the amide I band of the ligand occurring at 1640 cm^{-1} pointing to the coordination of the C=O group. The intensity of ν_{O-H} of the ligand at 2625–2575 cm^{-1} region diminishes very much in the spectra for the complexes, showing deprotonation of one of the two OH groups in the ligand, during complexation. The amide II (1560 cm^{-1}) band of the ligand shifts to higher frequencies, 1580 cm^{-1} in the spectra of the complexes, revealing the flow of electron density from the amide carbonyl group to the metal ion.

Proton NMR Spectra

Further evidence for the coordination of the ligands to the lanthanide ion is provided by the proton NMR spectra for lanthanum complexes of the two Schiff base ligands. The spectral data are given in Table V. In the ^1H NMR spectra of the lanthanum–AASASB complex, the signals for protons of both –COOH and –OH of the ligand vanish, clearly confirming the complexation of the ligand with the lanthanide ion after deprotonation. In the spectra of the ligand SHSASB, of the two proton signals, one appears as broad and the other as a sharp signal corresponding to salicylaldehyde and salicyloyl hydrazide –OH groups respectively. These signals are absent in the NMR spectra of SHSASB–lanthanum complex. The absence of salicylaldehyde –OH signal is evidently due to the coordination of this oxygen to the metal ion after deprotonation. The salicyloyl hydrazide –OH is expected to shift upfield as a consequence of the bonding of the amide C=O group to the lanthanide ion. This signal is probably masked by the aromatic proton signals.

TABLE V. Proton NMR Spectral Data for AASASB[a], SHSASB and their Lanthanum Complexes in DMSO-d_6. (Chemical Shifts are in 'δ' (ppm) w.r.t. TMS).

Compound	Carboxylic OH	Phenolic OH (strong H-bonded)	Phenolic OH (weak H-bonded)	Aromatic H
AASASB	10.966	–	10.23	6.6–7.9
$La_2(AASASB)_3 \cdot 2H_2O$	–	–	–	6.2–7.7
SHSASB	–	12.00	11.266	6.2–7.9
$La(SHSASB)_3 2H_2O$	–	–	–	6.2–7.8

[a]Assignments have been made as per values reported by F. De Sa Gilberto *et al.* [2].

TABLE VI. Electronic Spectral Data for Nd^{+3} and Ho^{+3} Complexes of AASASB and SHSASB.

Nd^{+3}				Ho^{+3}			
AASASB		SHSASB		AASASB		SHSASB	
J level	Energy (kilokaisers)	*J* level	Energy (kilokaisers)	*J* level	Energy (kilokaisers)	*J* level	Energy (kilokaisers)
$^4G_{5/2}, ^2G_{7/2}$	17.0252	$^4G_{5/2}, ^2G_{7/2}$	17.0647	$^5G_5$	23.6970	$^5S_2, ^5F_4$	18.2621
$^4F_{9/2}$	14.5771	$^4G_{7/2}$	18.9392	$^5F_3$	20.4916	$^5F_5$	15.3522
$\beta = 0.9804$		$\beta = 0.9841$		$\beta = 0.9914$		$\beta = 0.9927$	
$\delta = 2.0021$		$\delta = 1.6980$		$\delta = 0.8667$		$\delta = 0.7344$	

Electronic Spectra

The electronic spectral data for Nd^{+3} and Ho^{+3} complexes of both the Schiff base ligands along with their *J* levels are given in Table VI. The sharp f–f bands exhibit red-shifts with respect to the aquo ions. This is a consequence of complex formation and has been found in many lanthanide complexes [12]. These red shifts have been ascribed to nephelauxetic effect [13], and result from the changes in the interelectronic repulsion parameters of the complexes. The nephelauxetic red shift could well be used as a measure of covalency in the metal–ligand bond [13]. Sinha [14] has proposed a δ-scale to express qualitatively the covalent character of the Ln^{+3}–ligand bond in the complexes of lanthanides. It is expressed by the percentage relation:

$$\delta(\%) = |(1 - \beta)/\beta| \times 100$$

β is the average value of the ratio $\nu_{complex}/\nu_{aquo}$ where $\nu_{complex}$ and ν_{aquo} are the energies of absorption expressed in kilokaisers. The δ-values for the present complexes are positive suggesting thereby a certain amount of covalency in the ligand–metal bond in the complexes of both the ligands. Karraker [15] after a systematic sutdy of the various β-diketone complexes of lanthanides, found that the shapes of the electronic spectral bands varied with the coordination number around the lanthanide ion. The band shapes of the $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ band for Nd^{+3} complexes and $^5G_6 \leftarrow {}^5I_8$ band for Ho^{+3} complexes of both the Schiff base ligands, are similar to the corresponding electronic spectral band shapes for six coordinate complexes reported [15].

Conclusion

The various available data, as discussed above, clearly reveal a six coordinate geometry around the lanthanide ion in their complexes with SHSASB and AASASB Schiff base ligands.

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