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Synthesis and Characterisation of Lanthanide Complexes of Schiff Bases Derived from 2,6-Diacetyl Pyridine Monoxime and Diamino Benzene

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The La, Pr, Nd, Sm, Eu and Gd complexes of bis-(2,6-diacetyl pyridine monoxime) 1,2-diamino benzene (L_1) and bis-(2,6-diacetyl pyridine monoxime) 1,3-diamino benzene (L_2) with chloride as counter ions have been synthesised through the metal template effect. They are formulated as $[Ln(DAPMB)_2Cl_2]Cl$ (DAPMB = Schiff bases) on the basis of UV-VIS, IR ^1H NMR spectroscpic data, magnetic susceptibility measurement and elemental anlaysis.

INTRODUCTION

Interest in the study of monoxime has been growing because of their physiological activity, coordinative capability and application in analytical chemistry[1–3].

Although the dioxime as well as monoxime complexes of various transition metals have been studied[4–8], no work, to our best of knowledge, has been published on the coordinating ability of monoxime ligands with the >C=N—O—H moiety towards the lanthanides.

As a continuation of our systematic investigation of the macrocyclic and acyclic complexes formed in the reaction of the lanthanides with 2,6-diacetyl-pyridine monoxime and various diamines, we have examined the chelating behaviour of 2,6-diacetyl pyridine 1,2-diamino benzene towards the lanthanides and the correlation of the type of counter ion and the preparations with the stoichiometry and the filling of the coordiantion sphere of the complexes.

We report here the synthesis and characterization of a new hexadentate nitrogen donor, bis-(2,6-diacetylpyridine monoxime) 1,2-diaminobenzene and 1,3-diamino benzene complexes with some trivalent lanthanide metal ions like La(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III).

EXPERIMENTAL

The reagent 2,6-diacetylpyridine (Aldrich), hydrated metal chlorides (Indian Rare Earths Ltd, Kerala), diaminobenzene (Aldrich) and hydroxylamine hydrochloride (E. Merck) were used as obtained. The ligand bis-(2,6-diacetyl pyridine monoxime) 1,2-diamino benzene was prepared following the literature procedure[7–9].

Preparation of complexes

The ligand DAPMB in ethanol was added to an ethanolic solution of lanthanide chloride (1 : 1) and refluxed on water bath for 6 h. The solvent was then removed under reduced pressure until crystallization point was reached and the solution mixture was cooled in a refrigerator for 2 days. The solid coloured complexes obtained were filtered and washed with cold ethanol. The complexes were crystallized from ethanol to get pure compounds.

As reported by various researchers[10–12] lanthanide ions to be effective as template ions in the synthesis of many macrocyclic complexes derived from 2,6-diacetyl pyridine monoxime and diamino benzene, we prepared complexes also through template reaction of 2,6-diacetyl pyridine monoxime (0.02 mol); 1,3-diamino benzene (0.01 mol) and lanthanide chloride (0.01 mol) in ethanol. The reaction mixture was refluxed. The product was obtained on cooling the mixture at room temperature which was subsequently washed with alcohol and finally with ether and recrystallised from absolute alcohol.

The metal chloride and other contents in the complexes were estimated by the known methods[13].

The molar conductance of the complexes was determined on a WTW conductivity meter. The magnetic susceptibility measurements were made on a Cahn-Faraday electrobalance using $Hg[Co(NCS)_4]$ as a calibrant. Diamagnetic coorection was done using Pascal's constants[14]. The IR spectra of the complexes and lignad were recorded on a Perkin-Elmer spectrophotometer using KBr pellets. The electronic spectra were recorded on a Shimadzu-160A spectrophotometer. NMR spectra of the complexes were recorded on a Jeol FX90Q spectrometer in DMSO-d_6 solution using TMS as internal reference. Emission spectra of complexes were recorded on a Perkin-Elmer MPF-44B fluorescence spectrophotometer.

RESULTS AND DISCUSSION

The infrared spectra in the region 4000–200 cm^{-1} provide some information regarding mode of coordination in the complexes and were analysed in comparison with that of the free ligand. The most relevant bands and proposed assignments for the free ligand and the complexes are listed in Table-1.

All the spectra are very similar to one another except some, but the most significant variations between the ligands and complexes concern the ν(C=N), ν(O—H), ν(>C=N—OH) δ (N—O—H) and pyridine ring bands.

The ligand L_1 as well as complexes exhibited a broad band in the region 3300 cm^{-1} which shows the presence of hydrogen bonding of —O—H group. The medium band at 1600 cm^{-1} in the free ligand attributed to ν(C=N) stretching vibrations is shifted to 45–60 cm^{-1} upon complexation to lower frequency as expected from reducing the electron density on the nitrogen atom because of coordination with lanthanide(III) cations.[15,16] A band that appeared at 1455 cm^{-1} is due to ν(C—N) of oxime group which is shifted to 5 to 15 cm^{-1} to

TABLE-1
PHYSICO-CHEMICAL PARAMETERS OF Ln(III) COMPLEXES WITH LIGANDS
L_1 AND L_2; Ln(III) = La(III), Pr(III), Nd(III), Sm(III), Eu(III) OR Gd(III)

Compounds	Colour	m.p. (°C)	% Analysis found (calcd.)					μ_{eff} (B.M.)	λ_{max} rhm^{-1} cm^2 mol^{-1}
			C	H	N	Cl	M		
$[LaL_1Cl_2]Cl$	Cream	182–187	44.95 (45.14)	3.50 (3.76)	13.05 (13.16)	10.50 (11.13)	21.50 (21.77)	–	58.8
$[PrL_1Cl_2]Cl$	Greenish	215–220	44.85 (45.00)	3.70 (3.75)	13.05 (13.12)	10.90 (11.09)	21.95 (22.02)	3.1	71.5
$[NdL_1Cl_2]Cl$	Green brown	190–195	44.55 (44.77)	3.62 (3.73)	12.90 (13.05)	10.85 (11.03)	22.12 (22.42)	3.6	75.5
$[SmL_1Cl_2]Cl$	Dirty yellow	198–203	44.10 (44.35)	3.45 (3.69)	12.23 (12.93)	10.43 (10.93)	22.95 (23.15)	2.9	72.3
$[EuL_1Cl_2]Cl$	Yellow	220–225	44.10 (44.24)	3.55 (3.68)	12.70 (12.90)	1050 (10.90)	23.10 (23.34)	4.8	74.5
$[GdL_1Cl_2]Cl$	Brown	195–200	43.55 (43.88)	3.50 (3.65)	12.60 (12.80)	10.75 (10.81)	23.75 (23.96)	6.8	78.5

Compounds	Colour	m.p. (°C)	% Analysis found (calcd.)					μ_{eff} (B.M.)	λ_{max} rhm^{-1} cm^2 mol^{-1}
			C	H	N	Cl	M		
$[LaL_2Cl_2]_2Cl_2$	Cream	280–285	44.95 (45.14)	3.55 (3.76)	13.10 (13.16)	10.90 (11.13)	21.65	–	60.1
$[PrL_2Cl_2]_2Cl_2$	Greenish	290–295	44.75 (45.00)	3.65 (3.75)	13.15 (13.12)	11.05 (11.09)	21.90	3.5	72.6
$[NdL_2Cl_2]_2Cl_2$	Greenish brown	285–290	44.50 (44.77)	3.60 (3.73)	12.85 (13.05)	10.85 (11.03)	22.10	3.6	75.8
$[SmL_2Cl_2]_2Cl_2$	Dirty yellow	280–285	44.15 (44.35)	3.55 (3.69)	12.25 (12.93)	10.67 (10.93)	22.80	2.9	72.5
$[EuL_2Cl_2]_2Cl_2$	Yellow	285–290	44.15 (44.24)	3.60 (3.68)	12.85 (12.90)	10.65 (10.90)	23.10	4.9	80.5
$[GdL_2Cl_2]_2Cl_2$	Brownish	288–293	44.38 (43.88)	3.50 (3.65)	12.50 (12.80)	10.60 (10.81)	23.25	6.9	78.6

L_1 = Bis-(2,6-diacetylpyridine monoxime) 1,2-diamino benzene; L_2 = Bis (2,6-diacetylpyridine monoxime) 1,3-diamino benzene.

high frequency side. It has indicated that the >C=N—O—H group is present in neutral form and N atom is coordinated with the metal atom.

Evidence for the coordination of the pyridine nitorgen atom comes from systematic shifts to higher frequencies of bands, characteristic of the pyridine ring vibration[17]. The energy pyridine band observed in the spectrum of the ligand at 1560 cm^{-1}, which corresponds to ν(C=N) of the heterocyclic ring, is shifted by about 25 cm^{-1} to higher frequencies in the spectra of the complexes, indicating that the double bond character of C=N increases as a consequence of coordination by nitrogen. The bonding of the pyridine ring in the complexes is also shown by an increase of about 50 cm^{-1} in the ring breathing frequency found at 955 cm^{-1} in the spectrum of the free ligand. The low energy pyridine ring in-plane and out-of-plane vibrations also shifted to higher frequencies at 625 and 420 cm^{-1} which is a good indication of coordination of the heterocyclic nitrogen[18].

The spectrum of the ligand in the region between 390 and 250 cm^{-1} contains only two weak bands at 280 and 325 cm^{-1}. This would indicate that the additional band observed in the region 390–350 cm^{-1} in the spectra of all the lanthanide complexes should be assigned to the metal nitrogen stretching vibration[19] and one to ν(Ln—Cl) vibration.

TABLE-2
INFRARED (cm^{-1}) SPECTRAL DATA FOR LIGAND AND ITS COMPLEXES

Compounds	ν(OH)	ν(C=N)	ν(Py)				ν(M—N)	ν(M—Cl)
Ligand	3360	1600	1560	955	625	400	–	–
$[LaL_1Cl_2]Cl$	3200	1555	1580	985	645	410	365	280
$[PrL_1Cl_2]Cl$	3220	1540	1585	990	640	405	360	285
$[NdL_1Cl_2]Cl$	3250	1540	1590	998	645	415	365	283
$[SmL_1Cl_2]Cl$	3190	1555	1590	1000	660	420	370	290
$[EuL_1Cl_2]Cl$	3260	1548	1590	990	650	425	325	290
$[GdL_1Cl_2]Cl$	3230	1552	1590	1005	670	420	368	285
$[LaL_2Cl_2]_2Cl_2$	3195	1550	1590	1000	650	430	370	285
$[PrL_2Cl_2]_2Cl_2$	3215	1555	1595	1005	675	440	365	287
$[NdL_2Cl_2]_2Cl_2$	3220	1548	1590	998	670	430	360	285
$[SmL_2Cl_2]_2Cl_2$	3220	1545	1590	1005	652	430	370	295
$[EuL_2Cl_2]_2Cl_2$	3195	1558	1597	1005	650	428	380	295
$[GdL_2Cl_2]_2Cl_2$	3225	1552	1598	1000	652	430	370	290

The absorption bands of metal complexes show a shift of the spectral bands towards lower energy in comparison to those of aquo ion due to nephelauxetic effect[21]. The various spectral parameters, *viz.*, bonding parameter ($b^{1/2}$), nephelauxetic ratio (β), % covalency parameter (δ) and covalency angular overlap parameter (η) are calculated and reported in Table-3. The values of $b^{1/2}$ and δ %

are indicative of a considerable amount of covalency between the metal and ligand[22].

TABLE-3
ELECTRONIC SPECTRAL DATA AND OSCILLATOR STRENGTHS OF Nd(III) COMPLEXES

Complex	Bands (cm^{-1})	Assignments	$P \times 10^{-6}$	Spectral parameter
$[NdL_1Cl_2]Cl$	11550	$\longrightarrow {}^4F_{3/2}$	$\beta = 0.9985$	3.71
	12410	$\longrightarrow {}^4F_{5/2}$	$b^{1/2} = 0.0240$	10.10
	13420	${}^4T_{9/2} \longrightarrow {}^4F_{7/2}$	$\delta\% = 0.1196$	17.65
	17215	$\longrightarrow {}^4G_{5/2}, {}^2G_{7/2}$	$\eta = 0.0005$	12.35
	19190	$\longrightarrow {}^4G_{9/2}$		

L_1 = Bis-(2,6-diacetylpyridine monoxime) 1,2-diamino benzene,

The hypersensitive bands of metal complexes have been used for producing the coordination environment around the metal ion.

The nujol mull spectral features of Nd(III) complexes resemble that of the eight coordinated Nd(III) complexs reported by Karraker[23] sugesting the coordination number eight around the metal ion in these complexes. The nujol mull and DMF solution spectra of Pr(III), Nd(III), Sm(III) and Dy(III) complexes show almost similar spectral profiles suggesting no change in coordination due to solvation effect.

Some diagnostic information concerning the nature of chromophore and geometry of lanthanide complexes is obtained from the emission f-f spectra. Among the Ln(III) complexes, Eu(III) complexes have been extensively studied since the low J-values give rise to a smaller number of closely spaced energy levels. Transition from ${}^5D_0$ to the various ${}^7F_J$ levels are used to interpret the site symmetry around Eu(III) ion[24]. The room temperature emission spectra at 585 and 610 nm are due to transition from ${}^5D_0$ to the ${}^7F_1$ and ${}^7F_2$ levels and at liquid nitrogen temperature at 590, 665 and 700 nm are due to transition from ${}^5D_0$ to, ${}^7F_1$, ${}^7F_3$ and ${}^7F_4$ respectively.

The complex of Sm(III) at room temperature exhibits a weak transition at 560 nm along with two intense transitions at 605 and 640 nm which may be assigned to the transitions ${}^6H_{5/2} \rightarrow {}^4I_{13/2}$ and ${}^6H_{5/2} \rightarrow {}^4F_{9/2}$.

The magnetic moments of the complexes show very little deviation from Van Vleck values indicating minor participation of the 4f electrons in bonding. The slightly higher values observed in case of Sm(III) complexes may presumably include temperature dependent magnetism on account of low J-J separation[20].

The nuclear magnetic resonance spectrum of the complexes obtained in DMSO-d_6 solution with TMS as internal standard shows the pyridine protons at

δ 8.1–8.7, the methylene protons at δ 3.6 and the methyl protons at δ 2.6 ppm. Integrated intensities of the above signals are in the ratio 3 : 4 : 6 respectively. This is in consistent with the proposed formulation of the complex.

On the basis of spectral and analytical data it seems reasonably to assume that the complexes of Ln(III) ion have octa-coordinate hexagonal bipyramidal structure with the six nitrogen donor atoms of macrocyclic ligand occupying the equatorial plane and the axial positions being filled with —Cl— ions as shown in Fig. 1.

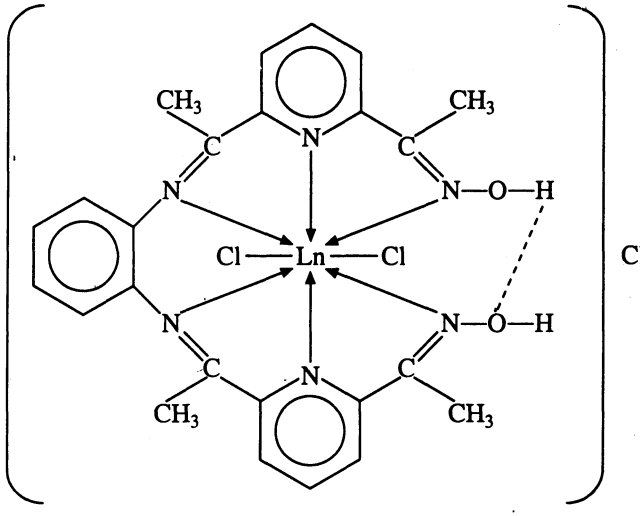

Fig. 1

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