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Polynuclear Complexes of Ni(II) and Zn(II) with Lanthanide(III) Schiff N-Isonicotinamidosalicylaldimine

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Polynuclear complexes of Ni(II) and Zn(II) chlorides with potassium bis(N-isonicotinamidosalicylideniminato) lanthanate(III) have been prepared and characterised by elemental analyses, magnetic susceptibility, infrared and electronic spectral measurements. Reliable information relating to metal-ligand bonding and geometries of the complexes have been inferred from the infrared and electronic spectral data.

INTRODUCTION

The behaviour of metal complexes of either d-transition metal ions[1] or 4f-metal ions[2,3] derived from Schiff bases to act as polydentate ligands through oxygen atoms prompted us to study the complexing ability of lanthanide complexes with Ni(II) and Zn(II) metal ions. In continuation of our previous work on the lanthanide metal complexes of Schiff bases[4–7], we report here the synthesis and properties of polynuclear complexes of potassium bis(N-isonicotinamidosalicylideniminato) lanthanate(III) with Ni(II) and Zn(II) chlorides.

EXPERIMENTAL

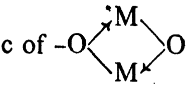
Preparation of Complexes

Potassium bis (N - isonicotinamidosalicylideniminato) lanthanate (III), *K[LnL$_2$]*, were prepared following procedures already described[4]. Polynuclear complexes of Ni(II) and Zn(II) chlorides with K[LnL$_2$] ligand were obtained by reacting hot aqueous ethanolic solution of nickel(II)/-zinc(II) chloride (0.002 mol) with acidified solution of K[LnL$_2$] (0.001 mol) in aqueous ethanol. The pH of the reaction mixture was adjusted to *ca.* 6.8 by dropwise addition of dil. KOH solution. The reddish brown/yellow complexes precipitated in case of Ni(II) and Zn(II) respectively were digested on water bath for *ca.* ½ hr. cooled to room temperature and suction-filtered. The complexes washed with water and ethanol were dried at room temperature.

RESULTS AND DISCUSSION

The reaction of N-isonicotinamidosalicylaldimine with lanthanide(III) and Ni(II)/Zn(II) cations leads to the formation of crystalline products that, on the basis of their elemental analyses and IR spectra, can be formulated as $[LnL_2(OH)(MCl)_2]_n$ where H_2L=N-isonicotinamidosalicylaldimine, Ln=La, Pr, Nd, Sm-Dy for M=Ni and Ln=La, Pr, Nd and Sm for M=Zn. All the complexes were non-melting upto 350°C and were insoluble in water and other common organic solvents. They are, however, soluble in hot glacial acetic acid. The Ni(II) complexes were scarlet-red whereas the Zn(II) complexes were yellow in colour. Because of their insolubility in DMF/DMSO, the conductance and NMR measurements were unsuccessful. Thermograms of the complexes indicate no loss of weight upto 180°C.

The magnetic moments of the present complexes deviate very slightly from the values reported for typical lanthanide ions[8]. The diamagnetic nature of I suggests dsp^2 hybridization around the Ni(II) ion. Thus, invoking a diamagnetic square-planar Ni(II) in II–VIII, one would expect the μ_{eff} values to be typical of the Ln(III) ion. The slightly lower values of the Sm(III) and Dy(III) complexes may be due to the presence of antiferromagnetic interaction and lower symmetry components. Thus, it appears that these complexes may possess a polynuclear structure with a strong metal-metal interaction giving rise to the low μ_{eff} values. The slightly higher values of Sm(III) complexes may presumably indicate low J-separation and first order Zeeman effects.

The N-isonicotinamidosalicylaldimine (H_2L) shows characteristic peaks at 1670, 1610, 1560, 1285 and 1270 cm^{-1} which may respectively be assigned to amide I, $\nu(C{=}N)$, amide II, amide (III) and $\nu(C{-}O)_{phenolic}$ modes[9]. The complexes do not show any characteristic frequencies relating to the amide groups except a sharp, strong diagnostic peak of azine group[10] ($>C{=}N{-}NC<$) suggesting destruction of the carbonyl group through amide$\rightleftharpoons$imidol tautomerism. The presumption of magnetically condensed nature of the complexes invokes a phenoxide bridging and/or enolic bridging simultaneously. The attribution of the phenolic C–O stretching mode is a debated question. It has been associated with a band at 1540 or at 1340 cm^{-1}. In the present case, however, polynucleation of the ligand with metal cations causes the composite band centered at 1340 cm^{-1} to shift drastically to lower frequencies (by 30–40 cm^{-1}) which is consistent with the drainage of electron density from the oxygen atoms due to polynucleation. Therefore, it appears that phenolic oxygen is involved in bridging the two metal atoms[11,12]. The bands appearing in the region 470–400 cm^{-1} in the spectra of the complexes may be assigned to $\nu(M{-}O)$ (phenolic/enolic) modes[13,14]. However, similar vibrations appearing at a comparatively lower region 450–380 cm^{-1} in the spectra of the present complexes may be due to the presence of phenolic as well as enolic oxygen[15,16] as bridging. All the complexes show strong bands at *ca.* 730–740 cm^{-1} characteristic of  $-O\overset{M}{\underset{M}{\langle\,\rangle}}O-$ group[17].

The electronic spectra of I, III and XI were recorded in nujol mull. The spectrum of I exhibits bands at 22980 cm^{-1}, a weak shoulder at 24390 cm^{-1} and a strong absorption at 26315 cm^{-1}. The presence of the above shoulder indicates the complex to be diamagnetic[18,19] which was however,

TABLE 1
ELEMENTAL ANALYSIS AND GENERAL BEHAVIOUR OF THE COMPLEXES

Com-plex	Empirical formula	Analysis found (calcd.) %					μ_{eff} (B.M.)
		Ln	Ni/Zn	Cl	N_2H_4	N	
I	$[LaL_2(OH)(NiCl)_2]$	15.35	12.83	7.83	6.98	8.98	diamagnetic
		(15.06)	(12.73)	(7.70)	(6.94)	(9.11)	
II	$[PrL_2(OH)(NiCl)_2]$	15.42	12.96	7.65	6.85	9.00	1.97
		(15.24)	(12.70)	(7.68)	(6.92)	(9.09)	
III	$[NdL_2(OH)(NiCl)_2]$	15.98	12.85	7.60	6.88	9.00	
		(15.55)	(12.66)	(7.65)	(6.90)	(9.06)	2.24
IV	$[SmL_2(OH)(NiCl)_2]$	16.21	12.50	7.32	6.74	8.98	2.32
		(16.10)	(12.57)	(7.60)	(6.85)	(8.96)	
V	$[EuL_2(OH)(NiCl)_2]$	16.72	12.60	7.58	6.78	8.76	3.83
		(16.24)	(12.55)	(7.59)	(6.84)	(8.98)	
VI	$[GdL_2(OH)(NiCl)_2]$	16.78	12.72	6.98	6.68	8.90	8.04
		(16.71)	(12.48)	(7.55)	(6.80)	(8.93)	
VII	$[TbL_2(OH)(NiCl)_2]$	17.14	12.33	6.98	6.48	8.88	7.82
		(16.82)	(12.47)	(7.54)	(6.79)	(8.92)	
VIII	$[DyL_2(OH)(NiCl)_2]$	17.28	12.18	6.89	6.59	8.82	8.85
		(17.22)	(12.41)	(7.50)	(6.76)	(8.88)	
IX	$[LaL_2(OH)(ZnCl)_2]$	14.82	14.20	7.62	6.59	8.76	diamagnetic
		(14.84)	(13.97)	(7.59)	(6.84)	(8.98)	
X	$[PrL_2(OH)(ZnCl)_2]$	14.98	13.99	7.60	6.84	8.92	2.01
		(15.02)	(13.94)	(7.57)	(6.82)	(8.96)	
XI	$[NdL_2(OH)(ZnCl)_2]$	15.50	13.90	7.61	6.84	8.84	2.25
		(15.32)	(13.89)	(7.55)	(6.80)	(8.93)	
XII	$[SmL_2(OH)(ZnCl)_2]$	15.88	13.84	7.55	6.97	8.92	2.38
		(15.87)	(13.80)	(7.50)	(6.76)	(8.87)	

established by room temperature magnetic susceptibility measurements. This suggests a square planar geometry around the Ni(II) metal ions. The spectrum of III shows bands at 11445, 12460 and 13330 cm^{-1} corresponding to the transitions $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4F_{5/2}$ and $^4F_{9/2}$ respectively. The characteristic band due to the hypersensitive transition ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) and other spectral bands of Nd(III) are not discernible in the spectrum because of their overlapping with the medium intensity absorption band (16660–22220 cm^{-1}; $\epsilon \simeq 60$) characteristic of the square planar Ni(II)[20]. However, in the spectrum of XI which is a Zn(II) analogue of III, the hypersensitive band of Nd(III) was observed apart from some other bands obviously due to the absence of the d–d transition in Zn(II) ion. The various bands observed show bathochromic shifts in comparison to the metal aquo-ion[21], which may be due to the decrease in interelectronic repulsion parameter ($\bar{\beta}$)[22]. The shape of the hypersensitive band (17094 cm^{-1}) resembles the seven coordinated [Nd(thd)$_3$hfaa] (thd= $Me_3CCOCHOCMe_3$; hfaa=$CF_3COCHCOCF_3$) reported by Karraker[23]. The following bonding parameters were calculated from the hypersensitive band using the literature procedures[24,25].

$$\text{nephelauxetic ratio } (\bar{\beta}) = 0.9893$$

$$\text{bonding parameter } (b^{1/2}) = 0.0732$$

$$\text{angular overlap parameter } (\eta) = 0.0054$$

$$\text{Sinha's parameter } (\delta\%) = 0.0816$$

All these parameters suggest a weak covalent nature of metal-ligand interaction.

Based on the elemental analyses and the various physico-chemical studies, the empirical formula $[LnL_2(OH)(MCl)_2]_n$ has been proposed with the tentative structure (Fig. 1) showing the bridging chlorines as polymeric

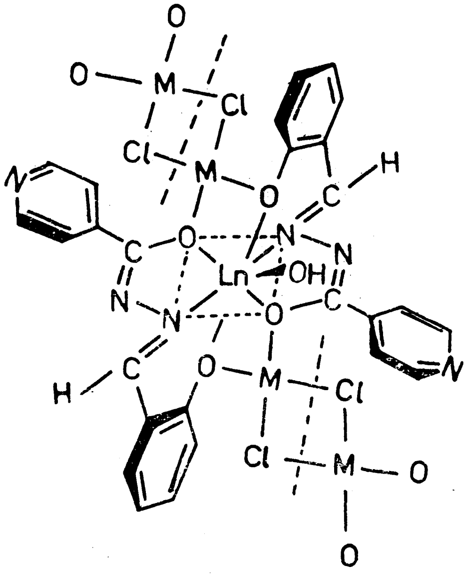


Fig. 1. Structure of $[LnL_2(OH)(MCl)_2]$

linking units. The structure, however, tends to assume significant distortion around Ln(III) due to the non-planarity of the ligand and the steric and electrostatic effects.

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