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Infrared, thermal and fluorescence investigations of 1,10-phenanthroline-*N*-oxide chelates with lanthanide chlorides

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Abstract

IR, TG, DSC, fluorescence and molar conductance studies have been carried out on complexes of 1,10-phenanthroline-*N*-oxide with lanthanide chlorides. The new complexes have the general formula $[Ln(PhenNO)_2Cl_2(H_2O)_2]Cl \cdot H_2O$ (Ln = La, Pr, Nd, Sm–Tb), of which the europium(III) complex shows strong metal-ion fluorescence.

INTRODUCTION

Considerable attention has recently been focused on the coordination behaviour of aromatic amine-*N*-oxides [1–6], the complexes of which with some rare earth ions exhibit strong metal-ion fluorescence [3,4]. 1,10-Phenanthroline-*N*-oxide (PhenNO) contains a relatively large conjuction π-bond and usually behaves as an unsymmetric N,O-bidentate ligand [7]. In order to investigate the fluorescence property and thermal behaviour of complexes of this ligand with rare earths, we report on the chelate complexes formed from the interaction of PhenNO with some lanthanide chlorides.

EXPERIMENTAL

Lanthanide chlorides were obtained by dissolving the corresponding oxides (AnalaR) in 1:1 chloric acid. The ligand was prepared from 1,10-phenanthroline by the method of Corey et al. [8]. All other chemicals were AnalaR grade.

The following general procedure was applied for the preparation of the complexes: 0.5 mmol of lanthanide chloride was dissolved in 20 cm^3 anhydrous ethanol; 1 mmol of the ligand was dissolved in 15 cm^3 anhydrous ethanol and this was added dropwise to the lanthanide solution with stirring. After 4 h of stirring, the mixture was concentrated to 8–10 cm^3. A precipitate gradually appeared. The remaining mixture was then set aside overnight at room temperature and the precipitate was filtered off, washed with 2:1 (v/v) ethanol–ether, and dried in vacuo over P_4O_{10}: yield 70–80%.

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TABLE 1

Analytical and molar conductance data of the complexes

Compound	Theory (%)				Experimental (%)				Λ_m (S cm^2 mol^{-1})
	M	C	H	N	M	C	H	N	
$\mathrm{La(PhenNO)_2Cl_3\cdot 3H_2O}$	20.08	41.67	3.21	8.10	20.10	41.90	3.11	7.93	85
$\mathrm{Pr(PhenNO)_2Cl_3\cdot 3H_2O}$	20.31	41.55	3.20	8.08	20.24	41.70	3.31	8.14	83
$\mathrm{Nd(PhenNO)_2Cl_3\cdot 3H_2O}$	20.69	41.35	3.18	8.04	20.55	41.55	3.10	8.01	84
$\mathrm{Sm(PhenNO)_2Cl_3\cdot 3H_2O}$	21.38	40.99	3.15	7.97	21.10	40.99	3.09	7.96	83
$\mathrm{Eu(PhenNO)_2Cl_3\cdot 3H_2O}$	21.56	40.90	3.14	7.95	21.31	41.10	3.06	7.83	85
$\mathrm{Gd(PhenNO)_2Cl_3\cdot 3H_2O}$	22.15	40.59	3.12	7.89	22.05	40.34	3.29	7.60	92
$\mathrm{Tb(PhenNO)_2Cl_3\cdot 3H_2O}$	22.33	40.50	3.12	7.87	22.50	39.98	3.02	7.97	83

The carbon, hydrogen and nitrogen were determined using a Carlo Erba 1106 elemental analyser; the metal ions were determined by EDTA titration using xylenolorange as indicator. Conductivity measurements were carried out with a DDS-11A conductivity bridge in nitromethane solution ($(0.89$–$1.17) \times 10^{-3}$ mol dm^{-3}) at 25 °C. The IR spectra were obtained on a 170 FT-IR spectrometer using KBr discs (4000–1000 cm^{-1}) and Nujol mulls (1000–250 cm^{-1}). Thermal runs (TG and DSC) were performed in dynamic air atmosphere at a heating rate of 10 °C min^{-1}, using sample sizes of about 10 mg, in a Du Pont 1090 thermoanalyser. The fluorescence spectra were obtained on a Hitachi 850 fluorescence spectrophotometer from the solid compounds.

RESULTS AND DISCUSSION

The analytical data for the newly synthesised complexes listed in Table 1 indicate that all of these complexes conform to the single general formula $\mathrm{Ln(PhenNO)_2Cl_3 \cdot 3H_2O}$ (where Ln = La, Pr, Nd, Sm–Tb).

The molar conductance values of the complexes measured in nitromethane lie in the range 83–92 S cm^2 mol^{-1} (Table 1), which indicates that all the complexes are 1:1 electrolytes [9] implying that two $\mathrm{Cl^-}$ ions are coordinated to the metal ions.

IR spectra

Table 2 gives the relevant IR spectral data for PhenNO and its complexes. The free ligand exhibits a rich spectrum in the 1600–250 cm^{-1} region [10] which undergoes characteristic frequency shifts upon coordination. The ν(N–O) observed at 1270 and 1250 cm^{-1} in the free ligand are shifted towards lower frequencies in the complexes due to coordination of the oxygen atom of the ligand to the metal ion [1,2,10]. The δ(N–O) in the free

TABLE 2

Infrared spectra (4000–250 cm^{-1}) of the complexes [a]

Compound	ν (N–O)		δ (N–O)	ν (M–O)	ν (M–N)	ν (O–H)	ρ_r (H_2O)
PhenNO	1270(s)	1250(s)	810(s)				
La(PhenNO)$_2$Cl$_3$·3H$_2$O	1260(s)	1238(s)	814(s)	367(w)	277(w)	3206(br,s)	609(m)
Pr(PhenNO)$_2$Cl$_3$·3H$_2$O	1260(s)	1239(s)	814(s)	367(w)	278(w)	3211(br,s)	610(w)
Nd(PhenNO)$_2$Cl$_3$·3H$_2$O	1259(s)	1239(s)	815(s)	368(w)	279(vw)	3225(br,s)	610(w)
Sm(PhenNO)$_2$Cl$_3$·3H$_2$O	1258(s)	1237(s)	817(s)	365(w)	279(w)	3326(br,s)	608(m)
Eu(PhenNO)$_2$Cl$_3$·3H$_2$O	1259(s)	1235(s)	817(s)	366(w)	280(w)	3245(br,s)	611(w)
Gd(PhenNO)$_2$Cl$_3$·3H$_2$O	1258(s)	1234(s)	818(s)	368(w)	280(w)	3267(br, s)	613(w)
Tb(PhenNO)$_2$Cl$_3$·3H$_2$O	1256(s)	1235(s)	820(s)	369(w)	282(w)	3216(br, s)	612(m)

[a] br, broad; s, strong; w, weak; vw, very weak; m, medium.

ligand, observed at 810 cm^{-1}, exhibits a small shift in the spectra of the complexes as expected [1,2,10]. Coordination through the nitrogen atom of the pyridine fragment of the ligand is demonstrated by frequency shifts and splittings of the several IR bands associated with the vibration of this fragment [7,10–13]. In the far-infrared region, metal–ligand vibrations are tentatively assigned to ν(Ln–O) and ν(Ln–N) modes [14]. The IR spectral evidence above suggests that the ligand acts as a bidentate O,N-chelating agent forming a six-membered ring with the metal ions.

In all the IR spectra of the complexes, the broad, strong bands that appear in the region 3400–3150 cm^{-1} are due to ν(OH) of the lattice and/or coordinated water molecules. In addition, weak bands assigned to $\rho_r(H_2O)$ are found near 610 cm^{-1}, providing evidence for the presence of coordinated water molecules [14]. The ν(Ln–Cl) [15] could not be observed because they absorb below the frequency limit of the spectrometer used in the present studies.

Thermal studies

The results of the thermal analyses are summarized in Figs. 1 and 2 and Tables 3 and 4.

The TG and DSC curves for PhenNO, given in Fig. 1, show that its pyrolytic decomposition begins at 185 °C and finishes at 610 °C, with total elimination of the sample. The DSC curve of PhenNO shows an endothermic peak at 171°C due to melting. The ligand then decomposes immediately, producing exothermic peaks at 201 and 539 °C.

The TG and DSC curves for the complexes show similar patterns of decomposition in four steps; a typical pattern, the TG and DSC curves of the samarium(III) complex, is given in Fig. 2. Two dehydration steps are observed. The weight losses determined for these processes compare

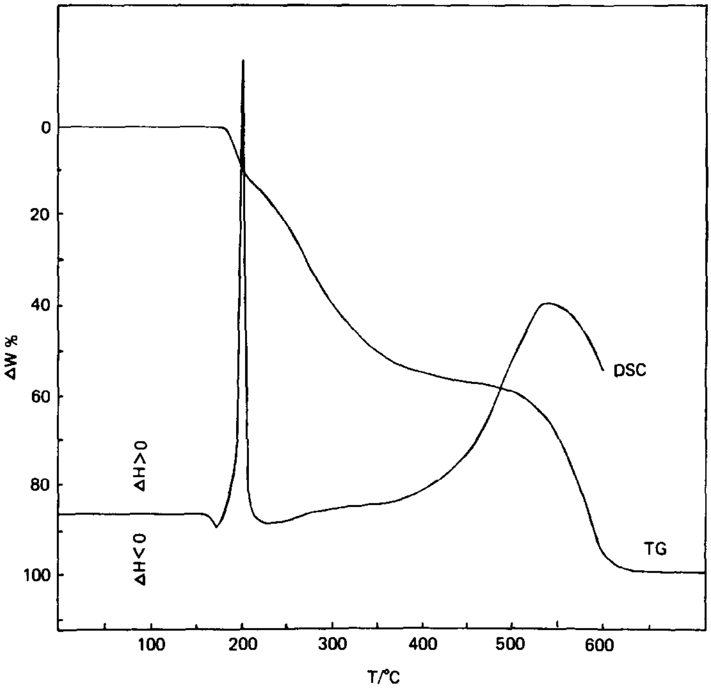

Fig. 1. TG and DSC curves of PhenNO.

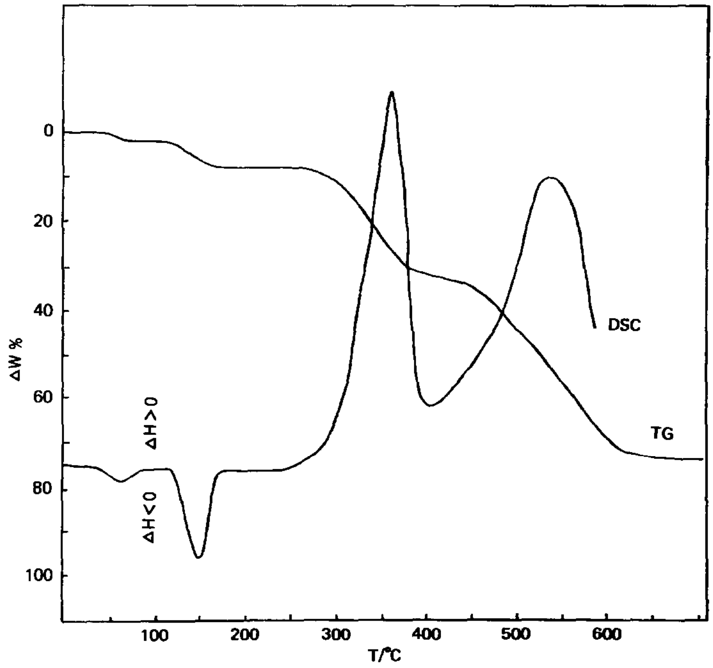

Fig. 2. TG and DSC curves of $Sm(PhenNO)_2Cl_3 \cdot 3H_2O$.

TABLE 3

Dehydration processes for the complexes

Ln	$Ln(PhenNO)_2Cl_3 \cdot 3H_2O \rightarrow Ln(PhenNO)_2Cl_3 \cdot 2H_2O$					$Ln(PhenNO)_2Cl_3 \cdot 2H_2O \rightarrow Ln(PhenNO)_2Cl_3$				
	Temp. up to (°C)	DSC peak	Weight loss (%)		Enthalpy (kJ mol^{-1})	Temp. range (°C)	DSC peak	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found				Calc.	Found	
La	84	56	2.60	3.08	16.1	116–155	137	5.21	6.01	74.7
Pr	87	58	2.62	3.71	14.8	120–161	140	5.19	5.34	76.0
Nd	89	63	2.58	2.83	15.2	121–170	143	5.17	4.41	77.7
Sm	83	61	2.56	1.96	15.0	113–173	146	5.12	5.91	80.1
Eu	84	77	2.56	3.13	14.9	108–190	150	5.11	5.86	83.0
Gd	89	80	2.54	2.88	16.3	100–201	147	5.07	4.39	79.3
Tb	86	79	2.53	3.26	16.9	110–231	149	5.06	5.49	82.0

TABLE 4

Decomposition processes of the dehydrated complexes

Process	Temp. range (°C)	DSC peaks	Thermal nature of transformation	Residue (%)	
				Calc.	Found
PhenNO → pyrolytic process	185–610	201, 539	Exo	–	–
La(PhenNO)$_2$Cl$_3$ → La$_2$O$_3$	243–650	344, 538	Exo	23.55	24.40
Pr(PhenNO)$_2$Cl$_3$ → Pr$_6$O$_{11}$	240–682	349, 533	Exo	24.54	24.97
Nd(PhenNO)$_2$Cl$_3$ → Nd$_2$O$_3$	249–676	355, 543	Exo	24.13	25.01
Sm(PhenNO)$_2$Cl$_3$ → Sm$_2$O$_3$	258–687	358, 546	Exo	24.80	25.13
Eu(PhenNO)$_2$Cl$_3$ → Eu$_2$O$_3$	236–696	358, 550	Exo	24.97	24.80
Gd(PhenNO)$_2$Cl$_3$ → Gd$_2$O$_3$	220–720	360, 551	Exo	25.52	24.83
Tb(PhenNO)$_2$Cl$_3$ → Tb$_4$O$_7$	239–729	363, 548	Exo	26.26	27.11

favourably with the theoretical values (see Table 3). The dehydration enthalpies have been calculated and are given in Table 3. The first dehydration step takes place below 90 °C, with the loss of one molecule of lattice water; this was shown by DSC to be endothermic (14.8–16.9 kJ mol^{-1}); the second step occurs at 137–150 °C with larger values of dehydration enthalpies

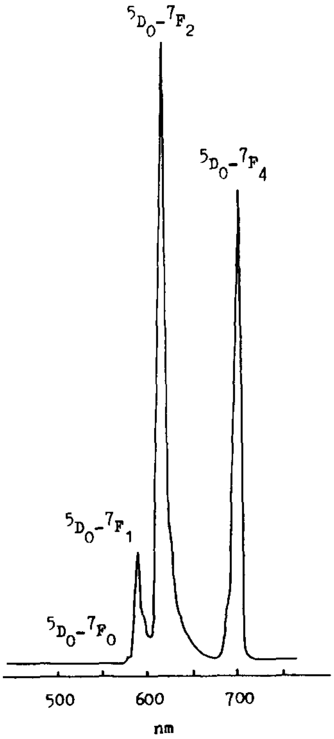

Fig. 3. Emission of Eu(PhenNO)$_2$Cl$_3$·3H$_2$O (solid); excitation with 320 nm radiation.

TABLE 5

Partial energy level scheme for solid europium(III) complex. The values refer to the barycentre of the band group (cm^{-1})

Level	$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$	$^5D_0$
(cm^{-1})	0	249	969	—[a]	2969	17256

[a] Not observed.

(74.3–83 kJ mol^{-1}), implying the presence of two water molecules in the coordination sphere. This result is consistent with the IR spectra and was confirmed by the fluorescence spectra analysis (see below).

The dehydrated complexes are stable up to ≈ 220 ° C and then (≈ 220–730 ° C) decompose producing two exothermic peaks as shown in Table 4. The residual weights are in good agreement with the values required for the metal oxides which were characterised by X-ray diffraction analyses [16].

Electronic fluorescence spectral analyses

Only the europium(III) complex shows strong emission when excited with near-ultraviolet radiation. The emission spectrum of the complex is reported in Fig. 3 and Table 5. Fluorescence arises from ligand-to-cation energy transfer, mainly from the lowest resonance level. The most intense transition is $^5D_0 \rightarrow {}^7F_2$ at 614 nm, followed by $^5D_0 \rightarrow {}^7F_4$ at 700 nm and $^5D_0 \rightarrow {}^7F_1$ at 580 nm. The $^5D_0 \rightarrow {}^7F_3$ transition is not observed. A weak line appears at 579 nm arising from the $^5D_0 \rightarrow {}^7F_0$ transition. The emission spectrum does not change on dehydrating the complex below 90 ° C, indicating the presence of lattice water molecules. The spectrum, however, changes on dehydration below 200 ° C, suggesting the presence of coordinated water molecules. This agrees with the results of the thermal analyses.

In conclusion, the lanthanide ions in the new complexes may attain a coordination number of eight, with four sites occupied by the two bidentate PhenNO molecules and the other four by the two Cl^- ions and two H_2O molecules. The molecular formula is $[Ln(PhenNO)_2Cl_2(H_2O)_2]Cl \cdot H_2O$.

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