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MAGNETO, SPECTRAL AND THERMAL STUDIES OF LANTHANIDE PERCHLORATO COMPLEXES OF 5,6-BENZOQUINOLINE

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ABSTRACT

A new series of complexes of 5,6-benzoquinoline (Benzqn) with lanthanide perchlorates with the general composition $Ln(ClO_4)_3 \cdot 7Benzqn$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy or Ho) were synthesised and characterised by elemental analysis, conductance, molecular weight and infrared spectra. The thermal behaviour of these complexes have also been studied.

INTRODUCTION

The complexing effect of various lanthanide ions with heterocyclic nitrogen bases has been extensively investigated [1]. Zaidi et al. [2–5] carried out work on benzoquinoline complexes with group IV metal halides. In the present work, we report the results of our studies on the complexes of benzo (*f*) quinoline (5,6-benzoquinoline) with lanthanide(III) perchlorates.

EXPERIMENTAL

5,6-Benzoquinoline was purchased from E. Merck and used without further purification. The lanthanide oxides were obtained from Rare Earth Products Ltd. (India) and were treated with 30% perchloric acid, filtered, and evaporated to dryness. All the solvents were good quality products.

Preparation of the complexes

The metal perchlorate was dissolved in acetone and treated with an acetonic solution of the ligand (molar ratio 1 : 7, with a small excess). The reaction mixture was heated with stirring over the steam bath, and a solid was formed. It was filtered, washed with acetone and ether, and preserved over phosphorus(V) oxide in a vacuum desiccator.

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Analyses

The metal content of the complexes was estimated by EDTA titrations using xylenol orange as the indicator [6]. The perchlorate was determined by the method of Kurz et al. [7]. The physical measurements were made as reported earlier [8].

RESULTS AND DISCUSSION

The interaction of Ln(III) perchlorates with 5,6-benzoquinoline results in the formation of complexes having the stoichiometry $Ln(ClO_4)_3 \cdot 7Benzqn$ (Table 1). The complexes are soluble in common organic solvents as well as in coordinating solvents such as DMSO and DMF. These oxygen-donor solvents neither substitute Benzqn in the coordination sphere nor form any adducts. The conductance values of the compounds in nitrobenzene are consistent with 1 : 3 electrolytic behaviour (Table 1). The molecular weights in freezing nitrobenzene also support the similar electrolytic behaviour of the compounds.

TABLE 1

Analytical, conductivity, molecular weight and magnetic data of lanthanide(III) perchlorate complexes

Complex	Found (calcd.) (%)			Λ_M ($ohm^{-1}\,cm^2\,mol^{-1}$)	Mol. wt. found (calcd.)	μ_{eff} (BM)
	M	N	ClO_4			
$La(ClO_4)_3 \cdot 7Benzqn$	7.32	5.10	15.46	76.9	472.3	diamag.
	(7.42)	(5.23)	(15.94)		(1872.5)	
$Ce(ClO_4)_3 \cdot 7Benzqn$	7.31	5.11	15.42	79.3	471.4	2.61
	(7.47)	(5.23)	(15.93)		(1873.5)	
$Pr(ClO_4)_3 \cdot 7Benzqn$	7.40	5.09	15.40	77.9	475.5	3.63
	(7.52)	(5.22)	(15.92)		(1874.5)	
$Nd(ClO_4)_3 \cdot 7Benzqn$	7.51	5.09	15.39	78.6	478.6	3.59
	(7.66)	(5.21)	(15.89)		(1877.5)	
$Sm(ClO_4)_3 \cdot 7Benzqn$	7.81	5.07	15.34	79.1	480.3	1.60
	(7.96)	(5.20)	(15.84)		(1883.5)	
$Gd(ClO_4)_3 \cdot 7Benzqn$	8.19	5.05	15.31	80.1	482.5	7.91
	(8.30)	(5.18)	(15.78)		(1890.5)	
$Tb(ClO_4)_3 \cdot 7Benzqn$	8.28	5.03	15.30	81.9	484.6	9.31
	(8.40)	(5.17)	(15.77)		(1892.5)	
$Dy(ClO_4)_3 \cdot 7Benzqn$	8.42	5.03	15.28	77.6	485.6	10.51
	(8.57)	(5.16)	(15.74)		(1896)	
$Ho(ClO_4)_3 \cdot 7Benzqn$	8.56	5.01	15.27	78.8	487.3	10.46
	(8.69)	(5.16)	(15.72)		(1898.5)	

TABLE 2

Partial infrared frequencies (cm^{-1}) of lanthanide(III) perchlorate complexes of 5,6-benzoquinoline

Complex	ν(C=C), ν(C=N) stretchings	ν(ring vibration)	ν(Ln–N)
Benzqn	1610m, 1585m, 1570s, 1500s	1455s, 1420m, 1390m	–
$La(ClO_4)_3 \cdot 7$Benzqn	1640m, 1620m, 1571m, 1508m	1495m, 1453m, 1390m	355m
$Ce(ClO_4)_3 \cdot 7$Benzqn	1635m, 1615m, 1575m, 1505m	1495m, 1450m, 1392m	370m
$Pr(ClO_4)_3 \cdot 7$Benzqn	1637m, 1620m 1575m, 1507m	1490m, 1450m, 1395m	375m
$Nd(ClO_4)_3 \cdot 7$Benzqn	1640m, 1620m, 1575m, 1503m	1492m, 1452m, 1395m	390m
$Sm(ClO_4)_3 \cdot 7$Benzqn	1642m, 1622m, 1575m, 1505m	1495m, 1452m, 1395m	400m
$Gd(ClO_4)_3 \cdot 7$Benzqn	1640m, 1620m, 1575m, 1510m	1488m, 1450m, 1392m	395m
$Tb(ClO_4)_3 \cdot 7$Benzqn	1637m, 1625m, 1572m, 1505m	1490m, 1450m, 1392m	360m
$Dy(ClO_4)_3 \cdot 7$Benzqn	1642m, 1623m, 1575m, 1505m	1492m, 1450m, 1392m	365m
$Ho(ClO_4)_3 \cdot 7$Benzqn	1642m, 1625m 1575m, 1503m	1495m, 1453m, 1392m	380m

m, Medium; s, strong.

The magnetic moments of the lanthanide(III) complexes (Table 1) show a slight deviation from the Van Vleek values [9,10], thereby indicating that 4*f*-electrons do not participate in bond formation in these compounds. Thus, the magnetic moments of these complexes are within the range predicted and that observed in the compounds with lanthanide ions [11–13].

Infrared spectra

The spectra of 5,6-benzoquinoline and its complexes have been studied by various workers [5,14]. Singh [15] has attempted to correlate the vibrational frequencies of quinoline with the equivalent vibrations of pyridine and has used a similar system of numbering the vibrational modes. The authors have made assignments (Table 2) to the absorptions of 5,6-benzoquinoline and its complexes on the basis of the work reported by Singh [15] and others [5,14].

Seven bands attributed to C–C and C=N stretchings and ring vibrations occur in the range 1610–1390 cm^{-1} in the spectra of the free ligand. Four absorptions in the same region (8a, 8b, 19a, 19b) have also been identified in the spectrum of the pyridine part. The additional bands due to the ligand

TABLE 3

Infrared frequencies (cm^{-1}) of the ClO_4 ion

Complex	ν_3	ν_1	ν_4
$La(ClO_4)_3 \cdot 7$Benzqn	1105s	930w	620s
$Ce(ClO_4)_3 \cdot 7$Benzqn	1110s	928sh	622s
$Pr(ClO_4)_3 \cdot 7$Benzqn	1108s	930w	621s
$Nd(ClO_4)_3 \cdot 7$Benzqn	1105s	928w	620s
$Sm(ClO_4)_3 \cdot 7$Benzqn	1110s	930w	625s
$Gd(ClO_4)_3 \cdot 7$Benzqn	1100s	929sh	622s
$Tb(ClO_4)_3 \cdot 7$Benzqn	1105s	930sh	620s
$Dy(ClO_4)_3 \cdot 7$Benzqn	1108s	929w	622s
$Ho(ClO_4)_3 \cdot 7$Benzqn	1105s	928w	620s

s, Strong; w, weak; sh, shoulder.

may thus be associated with a carbocyclic ring as suggested by Shindo and Tamura [16]. On complexation, these frequencies shifted to a higher wavenumber, which clearly indicates that the ligand is bound through the hetero nitrogen atom (Table 2).

Other important absorptions, i.e., C–H in-plane deformation, ring breathing and C–H out-of-plane deformations, also show positive shifts on complexation which further confirm the N-bonding. Upon complexation, new bands appear in the region 400–350 cm^{-1} which are tentatively assigned to ν(Ln–N) modes [1].

The bands assigned in Table 3 to the perchlorate ion in each of the complexes suggest an exclusively ionic character for the perchlorate ion. The splittings observed for ν_4, ν_1 and ν_2 are attributed to a solid-state effect. The bands due to perchlorate ions indicate that they are not coordinated to the tripositive lanthanides [17,18]; the forbidden ν_1 stretching mode is observed either as weak band or shoulder at ca. 930 cm^{-1}.

In conclusion, the trivalent lanthanide ions are bound by the seven nitrogens of the seven ligands.

Thermal studies

West et al. [19–21] have reported thermal results on various lanthanide(III) perchlorate complexes of various aromatic amine *N*-oxides. However, the thermal investigations of lanthanide(III) perchlorate complexes of aromatic amines have been carried out only to a limited extent. The thermoanalytical results of these complexes are summarised in Table 4.

The thermogravimetric curves indicate that above 100°C the complexes start to lose mass with partial evaporation of the ligand. Ligand molecules are lost in the temperature range 290–350°C. At temperatures close to 510°C, all the ligand is lost. These changes are clearly shown in DTG curves

TABLE 4

Thermoanalytical results obtained for the complexes of formula $Ln(ClO_4)_3 \cdot 7Benzqn$

Ln	Sample weight (mg)	Residual mass (mg)	Ligand's mass loss (%)				Residue (%) ca.760°C	
			290–350°C		ca. 510°C			
			Theor. [a]	Exp.	Theor. [b]	Exp.	Theor. [c]	Exp.
La	27.93	2.63	60.21	62.31	76.63	78.16	8.70	9.41
Ce	26.82	2.92	60.18	62.16	76.59	78.07	9.18	10.88
Pr	27.21	2.56	60.14	62.08	76.55	78.11	9.08	9.40
Nd	25.92	2.58	60.05	61.92	76.43	77.92	8.94	9.95
Sm	21.62	2.21	59.86	61.81	76.18	77.81	9.23	10.22
Gd	23.92	2.41	59.64	61.62	75.90	77.61	9.57	10.07
Tb	23.69	2.37	59.57	61.46	75.82	77.41	9.88	10.00
Dy	24.24	2.47	59.46	61.34	75.68	77.31	9.83	10.18
Ho	25.39	2.63	59.38	61.21	75.58	77.12	9.95	10.35

[a] Calculated for 5.5 ligand.

[b] Calculated for 7 ligand.

[c] Calculated as lanthanide oxide Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7.

by exothermic peaks. The residues obtained after heating at ca. 760°C to constant weight are very close to that expected for the oxides.

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