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MAGNETO, SPECTRAL AND THERMAL STUDIES OF LANTHANIDE(III) CHLORIDE COMPLEXES OF 5,6-BENZOQUINOLINE *N*-OXIDE *

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ABSTRACT

5,6-Benzoquinoline *N*-oxide (Benzquo) complexes of lanthanide(III) chlorides with general composition $LnCl_3$ $(Benzquo)_n$ ($n = 4$; Ln = La, Pr; $n = 5$; Ln = Nd, Sm, Gd, Tb, Dy, Ho, Yb) have been prepared and characterized by chemical analysis, electrolytic conductance, molecular weight, magnetism and infrared spectral data. Except the lanthanum complexes, all other complexes are paramagnetic in nature. Conductance data of the complexes in acetonitrile suggest that all the chloride ions are coordinated to the metal. Tentative coordination numbers of seven and eight have been assigned for the complexes. Thermogravimetric analyses of some representative complexes have also been undertaken. In all cases stable lanthanum oxide is formed at ca. 710°C.

INTRODUCTION

Recently, there has been considerable interest in metal ion complexes of aromatic amine *N*-oxides as evidenced by four review articles [1–4]. However, only a few aromatic amine *N*-oxides have been used as ligands to prepare adducts of lanthanide salts. Addition compounds containing the ligands have been studied: pyridine *N*-oxide [5–7], picoline *N*-oxide [8], 2,2′-bipyridyl *N*,*N*′-dioxide [9,10], quinoline *N*-oxide [11], pyrazine *N*-oxide [12], 2,4-lutidine *N*-oxide [13], 2,6-lutidine *N*-oxide [14], 1,10-phenanthroline *N*,*N*′-dioxide [15], 2-methylaminopyridine *N*-oxide [16], 2-thiopyridine *N*-oxide [17], 2-acetylpyridine *N*-oxide [18], 2-picolinic acid *N*-oxide [19,20], 4-dimethylaminopyridine *N*-oxide [21]. In the present communication, we describe the preparation, infrared and thermal behaviour of lanthanide(III) chloride complexes of 5,6-benzoquinoline *N*-oxide (Benzquo). The coordina-

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tion ability of Benzquo towards lanthanide(III) nitrates has already been reported [22].

EXPERIMENTAL

The ligand was prepared from 5,6-benzoquinoline by the method of Ochiai [23].

The complexes have been prepared as solids by mixing solutions containing ligand in anhydrous acetone and metal salt in methanol. The resulting mixture was stirred for ca. 1 h, the excess solvent was evaporated at room temperature and the products were recrystallized with acetone. The complexes were dried in a vacuum desiccator over P_4O_{10}.

The analyses of the complexes were done as reported in ref. 24, while the IR and TG studies were made as reported in ref. 25.

RESULTS AND DISCUSSION

The analyses of the complexes (Table 1) agree well with the formulae $LnCl_3(Benzquo)_4$ (Ln = La, Pr) and $LnCl_3(Benzquo)_5$ (Ln = Nd, Sm, Gd, Tb, Dy, Ho, Yb). Electrical conductance measurements of the complexes in acetonitrile show them to be non-electrolytes. Molecular weight determinations also agree with these results.

Magnetic properties

Paramagnetic behaviour among the tripositive lanthanides is due to the presence of unpaired 4*f* electrons. Since these electrons are well shielded from external influence, both their spin and orbital motions are significant in determining the overall observed magnetic moment for a complex compound. It follows, therefore, that the magnetic moment of a complex should indicate whether or not these 4*f* electrons are involved in bond formation. The complexes discussed herein show little deviation (Table 1) from the Van Vleck values, suggesting that bonding does not involve the 4*f* electrons, upon complexing with Benzquo [26–28].

Infrared spectra

The infrared spectra of all the complexes are similar showing no significant dependence on the central metal ion (Table 2). The N–O stretching vibration of the ligand appearing at about 1240 cm^{-1} is shifted to a lower region (1210–1230 cm^{-1}) in all the complexes indicating bonding of the ligand through the lone oxygen of the N–O group [1–4]. The N–O bending

TABLE 1

Analytical data of lanthanide(III) chloride complexes of Benzquo

Complex	Found (calc.) (%)				Mol. wt. found (calc.)	Λ_m (obm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
	Metal	C	N	Anion			
$LaCl_3(Benzquo)_4$	13.70	60.98	5.66	10.52	1005	4.1	Diamag.
	(13.55)	(60.85)	(5.46)	(10.39)	(1025.5)		
$PrCl_3(Benzquo)_4$	13.91	60.92	5.59	10.49	1010	3.2	3.60
	(13.72)	(60.73)	(5.45)	(10.36)	(1027.5)		
$NdCl_3(Benzquo)_5$	11.95	63.79	5.89	8.82	1207	5.1	3.59
	(11.75)	(63.65)	(5.71)	(8.69)	(1225.5)		
$SmCl_3(Benzquo)_5$	12.40	63.49	5.76	8.76	1210.6	4.6	1.65
	(12.18)	(63.34)	(5.68)	(8.65)	(1231.5)		
$GdCl_3(Benzquo)_5$	12.86	63.14	5.82	8.78	1220	5.3	7.86
	(12.68)	(62.99)	(5.65)	(8.60)	(1238.5)		
$TbCl_3(Benzquo)_5$	12.99	62.98	5.66	5.72	1218	4.9	9.21
	(12.82)	(62.88)	(5.64)	(5.59)	(1240.5)		
$DyCl_3(Benzquo)_5$	13.28	62.87	5.81	8.69	1230	4.8	10.50
	(13.06)	(62.70)	(5.63)	(8.56)	(1244)		
$HoCl_3(Benzquo)_5$	13.48	62.70	5.73	8.67	1228	5.2	10.46
	(13.24)	(62.58)	(5.62)	(8.54)	(1246.5)		
$YbCl_3(Benzquo)_5$	13.91	62.32	5.70	8.60	1238.7	3.7	4.50
	(13.79)	(62.18)	(5.58)	(8.49)	(1254.5)		

vibration occurring at 840 cm^{-1} in the free ligand suffers only a small shift in these complexes. The C–H out-of-plane vibration is shifted to higher frequencies due to the decrease in electron density in the aromatic ring consequent upon the formation of the metal–ligand bond. In the far-IR region a band in the 380–360 cm^{-1} region has been attributed to the M–O stretching frequency [16]. In conclusion, the non-electrolytic behaviour of the

TABLE 2

Partial IR spectral data (cm^{-1}) of lanthanide(III) chloride complexes of Benzquo

Complex	ν(NO)	δ(NO)	ν(MO)
Benzquo	1240vs, 1215sh	840s	–
$LaCl_3(Benzquo)_4$	1225s	834s	380m
$PrCl_3(Benzquo)_4$	1230vs, 1210sh	830s	355w
$NdCl_3(Benzquo)_5$	1230s	828s	370m
$SmCl_3(Benzquo)_5$	1235vs, 1218sh	831s	360w
$GdCl_3(Benzquo)_5$	1232s, 1215sh	829s	358w
$TbCl_3(Benzquo)_5$	1228vs	825s	376m
$DyCl_3(Benzquo)_5$	1226s	830s	372m
$HoCl_3(Benzquo)_5$	1235vs	825s	364m
$YbCl_3(Benzquo)_5$	1230vs, 1212sh	827s	362m,br

TABLE 3

Thermoanalytical results of some lanthanide(III) chloride complexes of 5,6-benzoquinoline *N*-oxide

Complex	Sample weight (mg)	Residual mass (mg)	Ligand mass loss (%)						Residual (%) ca. 710°C	
			210–290°C		330–390°C		430–510°C		Theor. [d]	Exp.
			Theor. [a]	Exp.	Theor. [b]	Exp.	Theor. [c]	Exp.		
$LaCl_3 \cdot 4$Benzquo	18.2	2.60	52.29	53.61	76.06	78.16	–	–	15.89	14.32
$PrCl_3 \cdot 4$Benzquo	20.4	3.11	52.18	52.49	75.91	77.19	–	–	16.57	15.29
$NdCl_3 \cdot 5$Benzquo	16.9	2.11	43.75	45.16	63.64	64.92	79.55	80.92	13.70	12.52
$TbCl_3 \cdot 5$Benzquo	19.8	2.74	43.22	44.52	62.87	63.98	78.59	79.82	15.07	13.86
$HoCl_3 \cdot 5$Benzquo	18.9	2.63	43.02	44.19	62.57	63.82	78.21	80.12	15.16	13.95

[a] Calculated for 2.75 moles of ligand.

[b] Calculated for 4.00 moles of ligand.

[c] Calculated for remaining moles of ligand.

[d] Calculated as lanthanide oxide, Ln_2O_3 (Ln = La, Nd, Ho), Pr_6O_{11}, Tb_4O_7.

complexes suggests that all the chloride ions are coordinated to the metal. Hence a coordination number of seven for La and Pr, while eight for Nd–Yb can be postulated [29]. This may be explained as follows: (i) on going from La to Lu, the size of the trivalent lanthanide ion decreases and hence the steric effect will influence the coordination number of the lanthanides leading to a lower coordination number for the heavier lanthanide; (ii) at the same time the ionic potential of the trivalent lanthanides increases on going from La to Lu. The heavier lanthanides attract a greater number of ligands.

In the present case the influence of the second factor is dominant.

Thermal studies

We have recently reported the thermal behaviour of 5,6-benzoquinoline *N*-oxide complexes of lanthanide(III) nitrates [22]. In the present work, the thermal properties of La, Pr, Nd, Tb and Ho chlorides complexes of 5,6-benzoquinoline *N*-oxide are reported. Thermoanalytical results are summarised in Table 3. As is clear from the results, the complexes do not contain water of crystallisation. The TG curves indicate that above 200°C the compounds start to lose mass, with partial evaporation of the ligand. Up to a temperature of 290°C the mass loss corresponds to 2.75 moles of ligand and in the temperature range 330–390°C only 1.25 moles of ligand are lost. However, for Nd, Tb and Ho the remaining fifth mole of ligand is lost at 510°C. The residues obtained after heating at 710°C, to constant weight, are very close to that expected for the oxides.

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