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MAGNETO, SPECTRAL AND THERMAL STUDIES OF SOME LANTHANIDE NITRATE COMPLEXES OF 5,6-BENZOQUINOLINE *N*-OXIDE *

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ABSTRACT

5,6-Benzoquinoline *N*-oxide (Benzquo) complexes of lanthanide nitrates of the formulae $Ln(NO_3)_3 \cdot 4Benzquo$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Yb) have been prepared and characterized by chemical analysis, IR, magnetic susceptibility and conductance data. Conductance data of the complexes in nitrobenzene suggest that all the nitrato ions are coordinated to metal. IR data indicate that Benzquo is bonded to the metal through only the *N*-oxygen atom and bidentate nitrate groups in the complexes. Thermal properties through TG of some representative complexes have also been studied. In all cases, the stable oxide is formed at ca. 730°C.

INTRODUCTION

The last two decades have witnessed considerable interest in coordination compounds of aromatic amine *N*-oxides with various metal ions in term of donor–acceptor relationships [1–4]. Lanthanide(III) perchlorate complexes of 5,6-benzoquinoline have previously been prepared and characterized [5]. A literature survey clearly indicates that the coordination behaviour of 5,6-benzoquinoline *N*-oxide has not been studied earlier. Thus, it is worthwhile to study the lanthanide(III) nitrate complexes of 5,6-benzoquinoline *N*-oxide (Benzquo).

EXPERIMENTAL

Reagents

5,6-Benzoquinoline was obtained from Merck and its *N*-oxidation was carried out by the method of Ochiai [6]. Lanthanide nitrates were obtained

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TABLE 1

Analytical, molecular weight, conductivity and magnetic data of lanthanide(III) nitrate complexes of 5,6-benzoquinoline *N*-oxide

Compound	Colour	M.p. (°C)	Found (calc.) (%)				Ω_m (ohm^{-1} cm^2 mol^{-1})	Average mol. wt. in $PhNO_2$	Formula weight	μ_{eff} (B.M.) [a]
			M	C	H	N				
$La(NO_3)_3$ ·4Benzquo	Yellow	190	12.67 (12.58)	56.52 (56.47)	3.31 (3.26)	8.92 (8.87)	3.9	1103.5	1105	Diamag.
$Ce(NO_3)_3$ ·4Benzquo	Light brown	220	12.71 (12.66)	56.50 (56.42)	3.30 (3.25)	8.91 (8.86)	4.3	1104	1106	2.61
$Pr(NO_3)_3$ ·4Benzquo	Brown	160	12.82 (12.74)	56.47 (56.37)	3.31 (3.25)	8.91 (8.85)	5.2	1108.5	1107	3.62
$Nd(NO_3)_3$ ·4Benzquo	Light brown	130	13.08 (12.97)	56.30 (56.22)	3.28 (3.24)	8.88 (8.83)	4.9	1112	1110	3.58
$Sm(NO_3)_3$ ·4Benzquo	Light yellow	210	13.51 (13.44)	55.96 (55.91)	3.29 (3.23)	8.86 (8.78)	3.7	1115.5	1116	1.64
$Gd(NO_3)_3$ ·4Benzquo	Brown	180	14.03 (13.98)	55.65 (55.56)	3.26 (3.21)	8.81 (8.73)	3.9	1122	1123	7.88
$Tb(NO_3)_3$ ·4Benzquo	Yellow	228	14.19 (14.13)	55.52 (55.47)	3.24 (3.20)	8.79 (8.71)	4.9	1126.5	1125	9.28
$Dy(NO_3)_3$ ·4Benzquo	Brown	200	14.46 (14.40)	55.35 (55.29)	3.25 (3.19)	8.74 (8.68)	3.6	1130	1128.5	10.51
$Ho(NO_3)_3$ ·4Benzquo	Yellow	225	14.67 (14.59)	55.23 (55.17)	3.22 (3.18)	8.71 (8.66)	2.9	1130.5	1131	10.45
$Yb(NO_3)_3$ ·4Benzquo	Yellowish brown	215	15.26 (15.19)	54.86 (54.78)	3.21 (3.16)	8.66 (8.60)	3.7	1137	1139	4.51

[a] At room temperature.

from Rare Earth Products Ltd., India and were used without further purification.

Preparation and analysis of complexes

All the lanthanide nitrate complexes were prepared as follows. Lanthanide nitrate (2 mmol) and the ligand (9 mmol) in hot methanol were mixed and the resulting solution was kept under reflux for 1 h. The viscous mass obtained on concentration of the solution was washed several times with hot methanol to remove the excess ligand. The solid complex which separated was washed thoroughly with diethyl ether and dried in vacuum over P_4O_{10}. All these complexes were analysed for metal, carbon, hydrogen and nitrogen. The physical measurements were made as reported earlier [7].

RESULTS AND DISCUSSION

Analytical data (Table 1) of the complexes show that the lanthanide(III) nitrate complexes have the general formula $Ln(Benzquo)_4(NO_3)_3$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Yb). All these complexes are non-hygroscopic solids soluble in polar solvents like acetone, acetonitrile, methanol and ethanol and insoluble in solvents of low polarity like benzene, carbon tetrachloride and chloroform.

The molar conductance values (Table 1) of the nitrato complexes in nitrobenzene show the non-electrolytic behaviour of these complexes [8]. Thus, these complexes may be formulated as $[Ln(Benzquo)_4(NO_3)_3]$. The observed magnetic moments of all these complexes agree well with the Van Vleek and Frank values [9], which suggests that the 4*f*-electrons in these complexes do not participate in bond formation.

Infrared spectra

The important infrared spectral bands of the complexes are presented in Table 2. The IR spectra of the complexes show that the N–O stretching vibration of the ligand occurs as a strong absorption at 1235 cm^{-1} with a shoulder at 1240 cm^{-1}, which is shifted to a lower frequency in the 1215–1230 cm^{-1} region. The shift to lower frequency indicates coordination of the ligand through the lone oxygen of the N–O group [1–4]. The (NO) bending vibration of the Benzquo is assigned as a strong band at ca. 840 cm^{-1} and only a slight shift of this vibration is observed on complexation [1–4]. This gives further support to oxygen–metal coordination. The positive shift of the C–H out-of-plane vibration of the ligand in all the complexes is indicative of the drainage of electron density from the pyridine ring to the metal ion. In the 350–360 cm^{-1} region, a new band appears in all the complexes which is assignable to ν(M–O) [10].

TABLE 2

Partial IR data (cm^{-1}) of $Ln(NO_3)_3 \cdot 4Benzquo$

Compound	ν(NO)	δ(NO)	ν(MO)
Benzquo	1235vs, 1240sh	840s	–
$La(NO_3)_3 \cdot 4Benzquo$	1225vs	825s	455m
$Ce(NO_3)_3 \cdot 4Benzquo$	1228vs	826s	348m
$Pr(NO_3)_3 \cdot 4Benzquo$	1230vs	822s	348m
$Mo(NO_3)_3 \cdot 4Benzquo$	1230vs	826s	350m
$Sm(NO_3)_3 \cdot 4Benzquo$	1220vs	830vs	352m
$Gd(NO_3)_3 \cdot 4Benzquo$	1231vs	828s	350m
$Tb(NO_3)_3 \cdot 4Benzquo$	1232vs	830s	360m
$Dy(NO_3)_3 \cdot 4Benzquo$	1226vs	826s	355m
$Ho(NO_3)_3 \cdot 4Benzquo$	1230vs	823s	362m
$Yb(NO_3)_3 \cdot 4Benzquo$	1230vs	830s	360m

The nature of binding of the nitrate groups to the metal can be predicted by examining the combination bands in the 1700–1800 cm^{-1} region (Table 3) [11–15]. The spectra of these complexes contain only two combinations. Bands with a separation of 45 cm^{-1} which lie in the range 29–54 cm^{-1} reported for bidentate nitrate groups [13,15] reveals bidentate bonding of nitrate groups in these complexes.

In conclusion, the IR data of these complexes along with the non-electrolytic behaviour of the complexes in nitrobenzene suggest a coordination number of 10 for the lanthanide ions in these complexes.

Thermal studies

Agarwal and co-workers [16–23] have recently reported the thermal properties of metal complexes of aromatic amine *N*-oxides. Comparatively less is known about the thermal behaviour of lanthanide(III) complexes of aromatic amine *N*-oxides, although West et al. [10,24,25] have reported the thermal properties of amine *N*-oxides. In the present work, thermal properties of nitrate complexes of Benzquo have been discussed. Thermoanalytical results of these complexes are summarized in Table 4.

The TG curves of the present complexes do not show the presence of water molecules either in or out of the coordination sphere. The analysis of thermal data indicates that above 150°C the complex starts to lose mass with partial evaporation of the ligand. Ligand molecules have been lost in the temperature range 210–320°C, where a 47.51–49.31% loss is observed because of the loss of the 2.7 moles of ligand, and from 430 to 490°C a loss of 70.49–72.06% is observed because of the complete loss of the ligand molecules. The residue obtained after heating at ca. 730°C to constant weight is very close to that expected for the oxides.

TABLE 3

Infrared frequencies (cm^{-1}) of the NO_3 ion

Compound	$(\nu_2+\nu_5)$	$(\nu_2+\nu_6)$	$(\nu_2+\nu_5)-(\nu_2+\nu_6)$	ν_1	ν_2	ν_4	ν_3	ν_5	ν_6
$La(NO_3)_3 \cdot 4Benzquo$	1789vw	1735vw	54	1522s	1035s	1315s	820s	740s	715vw
$Ce(NO_3)_3 \cdot 4Benzquo$	1778vw	1730vw	48	1520s	1040s	1320s	822s	735s	718vw
$Pr(NO_3)_3 \cdot 4Benzquo$	1774vw	1732vw	42	1525s	1032s	1317s	818s	738s	705vw
$Nd(NO_3)_3 \cdot 4Benzquo$	1787vw	1742vw	45	1518s	1045s	1310s	815s	742s	710vw
$Sm(NO_3)_3 \cdot 4Benzquo$	1782vw	1732vw	50	1520s	1048s	1312s	1822s	740s	708vw
$Gd(NO_3)_3 \cdot 4Benzquo$	1790vw	1745vw	45	1515s	1036s	1315s	822s	788s	710vw
$Tb(NO_3)_3 \cdot 4Benzquo$	1787vw	1740vw	47	1522s	1040s	1310s	820s	745s	712vw
$Dy(NO_3)_3 \cdot 4Benzquo$	1788vw	1736vw	52	1518s	1050s	1318s	815s	736s	706vw
$Ho(NO_3)_3 \cdot 4Benzquo$	1782vw	1732vw	50	1520s	1040s	1320s	818s	742s	715vw
$Yb(NO_3)_3 \cdot 4Benzquo$	1790vw	1742vw	48	1518s	1042s	1322s	815s	740s	708vw

TABLE 4

Thermoanalytical results obtained for the complexes of formula $Ln(Benzquo)_4(NO_3)_3$

Ln	Sample weight (mg)	Residual mass (mg)	Ligand mass loss (%)				Residual (%) ca. 730°C	
			210–320°C		430–490°C		Theor. [c]	Exp.
			Theor. [a]	Exp.	Theor. [b]	Exp.		
Pr	26.9	3.76	47.56	49.31	70.46	72.06	15.38	13.97
Nd	28.9	3.98	47.49	48.96	70.27	71.92	15.13	13.77
Sm	27.3	3.84	47.17	48.71	69.89	71.42	15.59	14.06
Dy	26.2	3.98	46.65	47.80	69.11	70.91	16.52	15.00
Ho	25.4	3.91	46.55	47.51	68.96	70.49	16.71	15.4

[a] Calculated for 2.7 moles of ligand.

[b] Calculated for total mass of ligand.

[c] Calculated as lanthanide oxide, Ln_2O_3 (Ln = Nd, Sm, Dy, Ho) and Pr_6O_{11}.

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