

CCA-1702

YU ISSN 0011-1643

UDC 546.654

Original Scientific Paper

The Lanthanide Perchlorate Complexes with 5,6-Benzoquinoline *N*-Oxide*

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Received May 5, 1985

Adducts of lanthanide perchlorates with 5,6-benzoquinoline *N*-oxide (Benzquo) have been synthesized for the first time and characterized by analysis, electrolytic conductance, molecular weight, magnetic and IR spectral data. A tentative coordination number of six has been assigned to the complexes.

INTRODUCTION

In recent years a large number of complexes of various aromatic amine *N*-oxides with a wide variety of metal salts have been isolated and characterized¹⁻³. The donor properties of 5,6-benzoquinoline *N*-oxide (Benzquo), a new potential ligand, have been investigated for the first time towards lanthanide perchlorate in this laboratory.

EXPERIMENTAL

Material

5,6-Benzoquinoline was obtained from E. Merck and its oxide was prepared by the method described for quinoline *N*-oxide.⁴ The lanthanide oxides were obtained from Rare Earth Products Ltd., India and were treated with 30 percent perchloric acid, filtered and evaporated to dryness.

Preparation of Complexes

In a typical experiment 1 mmol of metal perchlorate was dissolved in 10 ml absolute ethanol, 5 ml of 2,2'-dimethoxy propane was added and refluxed at 65 °C for 30 min. 6 mmol of benzquo was dissolved in 20 ml of absolute ethanol. The two solutions were mixed and refluxed for 1 hr. The complexes were generally isolated as fine crystalline powders, filtered, washed with absolute ethanol and ether and dried in vacuo over P₂O₅.

Analytical Procedures

The metal content of the complexes was determined as oxides. The perchlorate was determined by the method of Kurz. The electrical conductance of the complexes was measured with a Toshniwal Conductivity Bridge at 25 °C in nitromethane and

* Presented at the fourth annual session of Indian Council of Chemists, Gorakhpur University, Gorakhpur, Dec. 30, 31, 1984 Jan. 1, 1985.

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their molecular weights were determined cryoscopically in freezing PhNO_2 . Magnetic susceptibility measurements in powder form of the complexes were made at room temperature using Gouy's balance at ca. 11000 gauss. The IR spectra of the complexes were recorded on a Perkin Elmer Infrared Spectrophotometer model 521.

RESULTS AND DISCUSSION

The lanthanide(III) perchlorates react with 5,6-benzoquinoline *N*-oxide giving crystalline compounds and their analytical data (Table I) are in good agreement with the general composition $\text{Ln}(\text{Benzquo})_6 \cdot (\text{ClO}_4)_3$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The molar conductances of the complexes in nitromethane determined at room temperature are given in Table I. The complexes dissociate in this solvent and behave as 1 : 3 electrolytes. The molecular weight data (Table I) also point to similar electrolytic behaviour of the complexes.

The values of magnetic moments (Table I) indicate that La(III) complexes are diamagnetic, as may be expected from their closed shell electronic configurations and absence of unpaired electrons. All other tripositive lanthanide ions are paramagnetic due to the presence of 4f electrons which are effectively shielded by $5s^2p^6$ electrons. The magnetic moments of the complexes remain unchanged upon coordination with Benzquo, indicating thereby that 4f electrons do not participate in bond formation. The magnetic moments of isolated complexes are within the range of paramagnetic rare earth ions^{5,6}.

IR Spectra

The IR assignments are largely based on the IR spectra of benzoquinoline⁷ and quinoline *N*-oxide⁸. In the IR spectra of the free ligand the strong absorption at 1235 cm^{-1} is present due to $\nu(\text{N—O})$, which has been observed to shift to lower frequencies upon complex formation. The decrease in the frequency of the $\nu(\text{N—O})$ stretching vibration is attributed to a change in the nature of nitrogen oxygen bond as a result of oxygen-metal coordination¹⁻³.

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 complexation¹⁻³. This is a further support of oxygen-metal coordination. Absorption associated with C—H out-of-plane deformation modes is supposed to undergo a positive shift due to tightening of the aromatic ring upon complexation. A positive shift has been observed in this mode of vibration which is in conformity with the observations of earlier workers¹⁻³.

We have assigned a band in the $370\text{—}390 \text{ cm}^{-1}$ region to $\nu(\text{M—O})$ and assume it to be indicative of *N*-oxide bonding to the lanthanide ions. The spectrum of the ligand is relatively transparent in the region and these frequencies are in good agreement with M—O stretching modes observed for several lanthanide complexes⁹⁻¹².

For the perchlorate ions, out-of-the four normal modes, only ν_3 and ν_4 are IR active. The former occurring a broad single intense band in the 1090 cm^{-1} region and the latter as a single sharp intense band at 625 cm^{-1} are indicative of T_d symmetry for the perchlorate group^{13,14}. Therefore, the ionic nature of the perchlorate ions found in the molar conductivity measurements is supported by the IR results.

TABLE I
Analytical Data of Lanthanide(III) Perchlorates Complexes

Complex	Found (Calc.)/%				Anion	Ω_m ohm ⁻¹ cm ² mol ⁻¹	M. wt. Found (Calc.)	μ_{eff} B. M.	Diamag.
	M	C	H	N					
La(Benzquo) ₆ (ClO ₄) ₃	8.92 (9.04)	56.36 (56.29)	3.60 (3.51)	5.61 (5.47)	19.56 (19.42)	220	388 (1536)		
Ce(Benzquo) ₆ (ClO ₄) ₃	9.21 (9.11)	56.42 (56.25)	3.59 (3.51)	5.60 (5.46)	19.52 (19.40)	223	388 (1537)	2.56	
Pr(Benzquo) ₆ (ClO ₄) ₃	9.22 (9.16)	56.39 (56.22)	3.61 (3.51)	5.59 (5.46)	19.50 (19.39)	221	389 (1538)	3.60	
Nd(Benzquo) ₆ (ClO ₄) ₃	9.51 (9.35)	56.21 (56.10)	3.60 (3.50)	5.59 (5.45)	19.49 (19.35)	225	392 (1541)	3.58	
Sm(Benzquo) ₆ (ClO ₄) ₃	9.82 (9.71)	55.78 (55.88)	3.59 (3.48)	5.57 (5.42)	19.46 (19.28)	232	396 (1547)	1.62	
Gd(Benzquo) ₆ (ClO ₄) ₃	10.21 (10.11)	55.72 (55.63)	3.58 (3.47)	5.57 (5.40)	19.42 (19.19)	228	398 (1554)	7.89	
Tb(Benzquo) ₆ (ClO ₄) ₃	10.30 (10.21)	55.69 (55.57)	3.48 (3.47)	5.56 (5.39)	19.41 (19.17)	225	398 (1556)	9.15	
Dy(Benzquo) ₆ (ClO ₄) ₃	10.52 (10.41)	55.56 (55.44)	3.48 (3.46)	5.54 (5.38)	19.38 (19.13)	228	399 (1559.5)	10.50	
Ho(Benzquo) ₆ (ClO ₄) ₃	10.62 (10.56)	55.49 (55.36)	3.46 (3.45)	5.52 (5.37)	19.35 (19.10)	225	400 (1562)	10.45	

TABLE II
 IR Spectral Data (cm^{-1}) of the Complexes

Complexes	ν (NO)	δ (NO)	ν_3 (ClO_4)	ν_4 (ClO_4)	ν (M—O)
Benzquo	1240sh 1235vs	840vs	—	—	—
La(Benzquo) $_6$ (ClO_4) $_3$	1220s	835s	1085s, br	620s	380m
Ce(Benzquo) $_6$ (ClO_4) $_3$	1215s	830s	1082s, br	622s	375m
Pr(Benzquo) $_6$ (ClO_4) $_3$	1210s	828s	1088s, br	625s	385m
Nd(Benzquo) $_6$ (ClO_4) $_3$	1215s	830s	1080s, br	620s	370m
Sm(Benzquo) $_6$ (ClO_4) $_3$	1210s	830s	1090s, br	620s	380m
Gd(Benzquo) $_6$ (ClO_4) $_3$	1215s	830s 825m	1088s, br	625s	385m
Tb(Benzquo) $_6$ (ClO_4) $_3$	1212s	825m	1087s, br	625s	382m
Dy(Benzquo) $_6$ (ClO_4) $_3$	1210s	830s	1085s, br	625s	372m
Ho(Benzquo) $_6$ (ClO_4) $_3$	1215s	832s	1085s, br	620s	385m

The IR spectra of all the complexes definitely indicate the absence of water or ethanol and tentatively assign the coordination number 6 to the lanthanide ions in all these complexes.

Acknowledgements. — The authors are grateful to C.S.I.R., New Delhi, for financial support.

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SAŽETAK**Kompleksi lantanid-perklorata s 5,6-benzokinolin N-oksidom***R. K. Agarwal i S. K. Gupta*

Sintetizirani su kompleksi lantanid-perklorata (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy i Ho) s 5,6-benzokinolin N-oksidom. Navedeni kompleksi karakterizirani su elementnom analizom i određivanjem molarne mase, te IR spektrometrijom, određivanjem magnetskih svojstava i molarne provodnosti. Na temelju dobivenih eksperimentalnih podataka pretpostavljen je koordinacijski broj šest kod svih sintetiziranih kompleksa.