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Lanthanide Perchlorate Complexes of 4-Nitroquinoline-1-oxide and 5-Nitroisoquinoline-2-oxide

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Novel complexes of lanthanide perchlorates with 4-nitroquinoline-1-oxide (*NQNO*) and 5-nitroisoquinoline-2-oxide (*NIQNO*) have been prepared and characterized. The complexes have the general formulae $Ln(NQNO)_8(ClO_4)_3$ (where Ln = La—Nd), $Ln(NQNO)_7(ClO_4)_3$ (where Ln = Gd—Yb), $Ln(NIQNO)_9(ClO_4)_3$ (where Ln = La—Nd), and $Ln(NIQNO)_7(ClO_4)_3$ (where Ln = Gd—Yb). The IR, proton NMR spectral data indicate the coordination of the N—O group of the ligands to he lanthanide ions.

(Keywords: 4-Nitroquinoline-1-oxide; 5-Nitroisoquinoline-2-oxide; Lanthanide perchlorates hypersensitive bands)

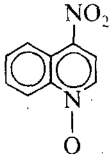
Lanthanid-Perchlorat-Komplexe von 4-Nitrochinolin-1-oxid und 5-Nitroisochinolin-2-oxid

Es wurden neue Komplexe von Lanthanidperchloraten mit 4-Nitrochinolin-1-oxid (*NQNO*) und 5-Nitroisochinolin-2-oxid (*NIQNO*) dargestellt und charakterisiert. Die Komplexe haben die allgemeinen Formeln $Ln(NQNO)_8(ClO_4)_3$ (mit Ln = La—Nd), $Ln(NQNO)_7(ClO_4)_3$ (mit Ln = Gd—Yb), $Ln(NIQNO)_9(ClO_4)_3$ (mit Ln = La—Nd) und $Ln(NIQNO)_7(ClO_4)_3$ (mit Ln = Gd—Yb). Die IR- und NMR-Daten zeigen die Koordination der N—O-Gruppe der Liganden zum Lanthanidenion an.

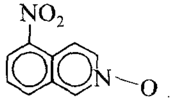
Introduction

A study of lanthanide perchlorate complexes of quinoline-1-oxide [$Ln(QNO)_8(ClO_4)_3$, Ln = La—Nd, $Ln(QNO)_7(ClO_4)_3$ Ln = Gd—Yb] and isoquinoline-2-oxide [$Ln(IQNO)_7(ClO_4)_3$, Ln = La—Yb][1], reveals that isoquinoline-2-oxide offers more steric strain at the coordination site when compared to complexes of quinoline-1-oxide with lanthanide perchlorates.

As part of our studies of lanthanide complexes of substituted quinoline-1-oxides and isoquinoline-2-oxides, to understand the effect of the substituents on the coordination number around the metal ion due to differences in their nature such as bulkiness, their position in the ring, electron donating or withdrawing tendency, we report in this paper the synthesis and characterization of lanthanide perchlorate complexes of 4-nitroquinoline-1-oxide (*NQNO*) and 5-nitroisoquinoline-2-oxide (*NIQNO*). The isolated complexes have been studied by analysis, conductance, IR, NMR and electronic spectra.



NQNO



NIQNO

Experimental

Materials

4-Nitroquinoline-1-oxide and 5-nitroisoquinoline-2-oxide were prepared by nitration of their respective N-oxides as described by *Katritzky*[2] for 4-nitropyridine-1-oxide. They were purified and recrystallized from chloroform solutions, *NQNO* m.p. 152–153° (Lit.[3] 153–154°) *NIQNO* m.p. 219–220° (Lit.[4] 220–222°).

Hysdrated lanthanide perchlorates were prepared by dissolving the corresponding oxides in 50% perchloric acid and evaporating the solution on a steam bath.

Preparation of the Complexes

NQNO Complexes: To a hot solution of *NQNO* (10 mmol) in ethylacetate (50 ml), a solution of lanthanide perchlorate (1 mmol) in ethylacetate (5 ml) was added and the mixture boiled. The solvent was removed by distillation. The pasty mass was washed with hot chloroform till washings were colorless, and dissolved in minimum amount of acetone (2 ml). The solvent was removed by evaporation under vacuum at 80–85 °C to get the dry complex, which was stored over P_2O_5 in a vacuum desiccator.

NIQNO Complexes: A solution of lanthanide perchlorate (1 mmol) in ethyl acetate (5 ml) was added to a boiling solution of *NIQNO* (10 mmol) in ethyl acetate (250 ml) with stirring. The stirring and heating was continued for 10 minutes. The precipitated complex was filtered through a sintered crucible, washed with hot chloroform and dried over phosphorus(V) oxide in a vacuum desiccator.

Analytical and Physical Methods

The metal content of the complexes was estimated by *EDTA* titrations using xylenol-orange as indicator[5]. The perchlorate was estimated by gravimetric precipitation with nitron, as described by *Welcher*[6]. The ligands *NQNO* and *NIQNO* were estimated spectrophotometrically at 248 nm and 204 nm respectively using the calibration curve method[7]. The analytical data are presented in Table 1.

The IR spectra of the complexes and the ligands in nujol mulls (in the region 600–4 000 cm^{-1}) were recorded on a Perkin-Elmer model 397 spectrophotometer. The principal IR bands and assignments are given in Table 2. Proton NMR spectra of the diamagnetic complexes and the ligands were recorded on a Bruker WH-270 spectrometer operating in the FT mode, using CD_3CN as the solvent and *TMS* as the internal standard (Table 3). Electronic spectra of Nd^{+3} and Ho^{+3} complexes in acetonitrile were recorded in the visible region on a Beckmann Model-25 spectrophotometer. The solid state spectra for the same complexes in nujol mull were recorded in the same region on a Unicam SP-700 instrument. Electrolytic conductance measurements in acetonitrile solutions of the complexes were carried out in a Siemens conductivity bridge using an immersion cell (type LTA), previously calibrated with standard KCl solution. The concentrations of the solutions used were of the order of 0.001 *M* (Table 1).

Table 1. *Analytical and molar conductance data*

	% Metal		% Ligand		% ClO_4		λm*
	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	
NQNO Complexes							
La$(NQNO)_8(ClO_4)_3$	7.15	7.10	78.72	77.66	15.47	15.24	342.8
Nd$(NQNO)_8(ClO_4)_3$	7.27	7.35	78.60	77.45	—	—	364.4
Gd$(NQNO)_7(ClO_4)_3$	8.77	8.81	75.52	74.48	—	—	342.9
Ho$(NQNO)_7(ClO_4)_3$	9.10	9.20	75.35	74.16	—	—	341.0
Yb$(NQNO)_7(ClO_4)_3$	9.68	9.61	74.93	73.83	16.68	16.56	350.4
NIQNO Complexes							
La$(NIQNO)_9(ClO_4)_3$	6.48	6.46	81.23	79.63	14.07	13.89	348.8
Nd$(NIQNO)_9(ClO_4)_3$	6.88	6.70	80.32	79.44	—	—	346.6
Gd$(NIQNO)_7(ClO_4)_3$	8.90	8.81	75.23	74.48	16.87	16.71	341.5
Ho$(NIQNO)_7(ClO_4)_3$	9.31	9.20	74.34	74.16	—	—	344.2
Yb$(NIQNO)_7(ClO_4)_3$	9.72	9.61	74.03	73.83	—	—	352.2

* Molar conductance in acetonitrile, $Ohm^{-1} cm^2 mol^{-1}$.

Results and Discussion

The complexes of *NQNO* have the composition $Ln(NQNO)_8(ClO_4)_3$ where *Ln* = La, Nd and $Ln(NQNO)_7(ClO_4)_3$ where *Ln* = Gd, Ho and Yb. The complexes of *NIQNO* analyse for the formulae $Ln(NIQNO)_9(ClO_4)_3$ where *Ln* = La, Nd and $Ln(NIQNO)_7(ClO_4)_3$ where *Ln* = Gd, Ho and Yb. All complexes are soluble in polar solvents such as methanol, acetone, and acetonitrile and insoluble in chloroform and in nonpolar solvents like

Table 2. IR *spectral data for NQNO and NIQNO complexes*

NQNO	*NIQNO*	La	Nd	Gd	Ho	Yb	Assignments
1 300 s	—	1 305 s	1 305 s	1 303 s	1 302 s	1 302 s	$\nu_{N—O}$
850 w	—	851 w	852 w	851 w	852 w	852 w	$\delta_{N—O}$
770 m	—	771 m	772 m	772 m	775 m	772 m	$\gamma_{C—H}$
	—	1 100 s	1 100 s	1 100 s	1 100 s	1 100 s	$\nu_{3ClO_4^-}$
	—	620 m	620 m	620 m	620 m	620 m	$\nu_{4ClO_4^-}$
	1 340 s	1 338 s	1 338 s	1 338 s	1 339 s	1 338 s	$\nu_{N—O}$
	840 m	846 w	843 w	845 w	845 w	844 w	$\delta_{N—O}$
	739 m	745 m	742 m	742 m	742 m	743 m	$\gamma_{C—H}$
		1 100 s	1 098 s	1 100 s	1 100 s	1 100 s	$\nu_{3ClO_4^-}$
		620 m	620 m	621 m	621 m	622 m	$\nu_{4ClO_4^-}$

benzene and carbontetrachloride. Molar conductance of the complexes are in the range for 1 : 3 electrolytes[8], suggesting thereby that the perchlorate groups are ionic.

The appearance of two unsplit bands, one in the region 620–622 cm^{-1} and the other in the range 1098–1 100 cm^{-1} in the spectra of *NQNO* and *NIQNO* complexes, reveals the presence of ionic perchlorate group in the complexes. The bands are assigned to ν_4 and ν_3 modes of the T_d perchlorate group. Thus the IR spectra pertaining to the perchlorate vibrations in both *NQNO* and *NIQNO* complexes agree with the 1 : 3 electrolytic behavior of these complexes in acetonitrile solution.

The $\nu_{N—O}$ band for *NQNO* at 1 300 cm^{-1} shifts a little to higher frequencies in the *NQNO* complexes. A similar positive shift has also been found in the *NQNO* complexes of Ni and Co[9]. The $\delta_{N—O}$ and C—H out of plane vibrations of the ligand at 850 cm^{-1} and 770 cm^{-1} shift to higher frequencies indicating the coordination of N-oxide oxygen to the metal ion in the *NQNO* complexes of lanthanide perchlorates. The band at 1 340 cm^{-1} assigned to N—O stretching frequency of *NIQNO* shifts a little to lower frequencies in the spectra of *NIQNO* complexes, indicating the binding of the N-oxide oxygen to the lanthanide ion. The $\delta_{N—O}$ and C—H out of plane vibrations at 840 cm^{-1} and 739 cm^{-1} of *NIQNO* shift to higher frequencies revealing the coordination of the N—O group to the metal ion in the *NIQNO* complexes of lanthanide perchlorates.

Further evidence for the coordination of N-oxide oxygen of *NQNO* and *NIQNO* to the lanthanide ion in their complexes is found in the H^1-NMR spectra of the complexes of *NQNO* and *NIQNO* with La^{+3} (Table 3). The various assignments in PMR spectra of the *NQNO* complexes are based on the assignments reported by *Yutakakawazie*[10]. In the case of the *NIQNO* complex the assignments have been made relative to the reported

Table 3. *Proton* NMR *data for NQNO, NIQNO and their* La^{+3} *complexes in* CD$_3$CN *(chemical shifts δ in ppm with respect to TMS)*

Compound	1 H	2 H	3 H	4 H	5 H	6 H	7 H	8 H
NQNO	—	8.50	8.20	—	8.64	7.90	(6, 7 H)	8.73
La^{+3}(*NQNO*)$_8$(ClO$_4$)$_3$	—	8.56	8.22	—	8.66	7.95	(6, 7 H)	8.70
NIQNO	8.85	—	8.49	7.95	—	8.38	7.74	8.17
La^{+3}(*NIQNO*)$_9$(ClO$_4$)$_3$	9.76	—	8.49	8.09	—	8.46	7.81	8.25

assignments for 5-nitroisoquinoline[11]. The 2-H, 3-H, 5-H and 6,7-H signals in the *NQNO* complex and all proton signals in the *NIQNO* complex show downfield shifts, confirming the coordination of the N-oxide moiety to the lanthanide ion. The observed deshielding is a consequence of the drainage of electron density towards the metal ion in the lanthanide complex. Electronic spectral data are presented in Table 4. The f-f electronic transitions of the lanthanides are found to be sharp and line-like. On complexation the spectra tend to show band energy shifts, compared to that of aquo ion complexes. In the complexes of *NQNO* and *NIQNO* small shifts to lower frequencies are found for all the bands. The red shift is called the nephelauxetic shift and has been related to the covalency in the metal ligand bond. *Sinha*[12,13] has defined a parameter δ, as a measure of the covalent character of the metal-ligand bond. This value is given by the relation

$$\delta = |(1-\beta)/\beta| \cdot 100$$

where β is the average value of the ratio $\nu_{\text{complex}}/\nu_{\text{aquo}}$. The β and δ values calculated for *NQNO* and *NIQNO* complexes are presented in Table 4. The δ values of the *NIQNO* complexes are above the values of the *NQNO* complexes, indicating a greater covalency in the metal ligand bond in the *NIQNO* complexes. *Karraker*[14] has found that the shapes of hypersensitive bands are related to the coordination number around the lanthanide ion. We find that the solid state spectral shapes (taken in nujol mulls) of Nd^{+3} and Ho^{+3} complexes closely resemble those in solution (in acetonitrile). This indicates a similarity in coordination number in the solid state and in solution. The shape of the hypersensitive band of the Nd^{+3} complex of *NIQNO* did not resemble any of those reported by *Karraker,* but it resembles those of nine coordinate *DPA* complexes of lanthanides studied by *Jagannathan*[15], thereby suggesting a nine coordinate geometry in the complexes of *NIQNO* with La^{+3}—Nd^{+3}. The spectral shapes of Nd^{+3} complex of *NQNO* and Ho^{+3} complexes of

Table 4. *Electronical spectral data in the visible region for NQNO and NIQNO complexes of* Nd^{+3} *and* Ho^{+3}

	Nd^{+3}			Ho^{+3}	
J-level	Energy (kcal)		*J*-level	Energy (kcal)	
	NQNO	*NIQNO*		*NQNO*	*NIQNO*
$^4G_{9/2}$	19.61	19.51	$^3K_6$	23.07	22.4
$^{*4}G_{7/2}$	19.14	19.05	$^{*5}F_1$, $^5G_6$	22.12	21.70
					21.45
$^{*4}G_{5/2}$, $^2G_{7/2}$	17.21	17.17	$^{*5}S_2$, $^5F_4$	18.60	18.59
$\beta =$	0.9958	0.9924	$\beta =$	0.9964	0.9718
$\delta =$	0.4220	0.7660	$\delta =$	0.3617	2.9018

* β and δ for peaks corresponding to these *J*-states have been calculated, for which the corresponding aquo values are available.

NQNO and *NIQNO* resemble the shapes of eight and seven coordinate β-diketonate complexes of lanthanide studied by *Karraker*.

Thus, the analytical conductance and infrared data together with the H^1 NMR data for lanthanide complexes of *NQNO* and *NIQNO* indicate the bonding of the N-oxide group of the ligands to the lanthanide ion in the complexes. Conductance data coupled with electronic spectral shapes of the complexes reveal that while *NQNO* and *NIQNO* complexes of La^{+3} to Nd^{+3} point to a eight and nine coordinate geometry respectively, the Gd^{+3}, Ho^{+3} and Yb^{+3} complexes of both *NQNO* and *NIQNO* have a seven coordinate geometry around the lanthanide ion.

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