

Lanthanide perchlorate complexes of quinoline-1-oxide and isoquinoline-2-oxide

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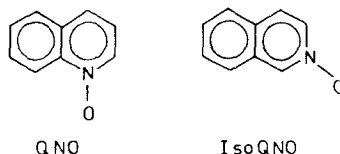
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Abstract. Complexes of lanthanide perchlorates with quinoline-1-oxide and isoquinoline-2-oxide, have been isolated for the first time and characterised by analysis, conductance, and IR, NMR and electronic spectral studies. The complexes of quinoline-1-oxide have the composition $\text{Ln}(\text{QNO})_3(\text{ClO}_4)_3$ where Ln = La, Pr or Nd and $\text{Ln}(\text{QNO})_7(\text{ClO}_4)_3$ where Ln = Gd, Dy, Ho, Er or Yb. The isoquinoline-2-oxide complexes analyse for the formula $\text{Ln}(\text{IsoQNO})_7(\text{ClO}_4)_3$ where Ln = La–Yb.

Keywords. Lanthanide perchlorates; quinoline-1-oxide; isoquinoline-2-oxide; proton NMR; electronic spectra; IR spectra; electrolytic conductance.

1. Introduction

Quinoline-1-oxide (QNO) and isoquinoline-2-oxide (isoQNO) are analogues of 2,3- and 3,4- disubstituted pyridine-1-oxide (PyNO) respectively. In general, QNO and isoQNO do not introduce severe steric hindrance during the formation of cationic complexes with transition metal ions (Karayannis *et al* 1973), and complexes of QNO and isoQNO are of the formulae similar to those obtained for the corresponding PyNO complexes. But in some of the adducts, the difference in the steric influence of QNO and isoQNO is reflected in the stoichiometry of the respective adducts. For example while QNO forms a 1:1 adduct with $\text{M}(\text{AcAc})_2$ [$\text{M} = \text{Ni}, \text{Co}$, AcAc = acetyl acetonate], isoQNO forms a 2:1 adduct with these chelates (Kluiber and Horrocks 1966). QNO complexes of lanthanide chlorides (Kingston *et al* 1969), of lanthanide iodides (Ramakrishnan and Soundararajan 1977) and of lanthanide hexathiocyanochromates(III) (Serebrinnikov *et al* 1969) and complexes of isoQNO with lanthanide iodides (Ramakrishnan 1977) have already been reported. In the complexes of QNO with lanthanide chlorides [$\text{Ln}(\text{QNO})_3\text{Cl}_3\text{H}_2\text{O}$ for Ln = Nd, Sm and



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$\text{Ln}(\text{QNO})_4\text{Cl}_3\text{H}_2\text{O}$ for $\text{Ln} = \text{Eu-Ho, Yb}$], the L:M increases with decreasing metal ion radius, violating the general trend in which L:M decreases with decreasing metal ion radius. The low L:M ratio is due to the coordination of the anions in these complexes. The stoichiometry of the $[\text{Ln}(\text{QNO})_x][\text{Cr}(\text{NCS})_6]$ (where $X = 6, 7$ and 8) indicates that the bulkiness of the QNO molecule may have little effect on the L:M ratio in these complexes, compared to the corresponding PyNO complexes $[(\text{Ln}(\text{PyNO})_8)][\text{Cr}(\text{NCS})_6]$ (Pavlenko *et al* 1971, 1973). IsoQNO yields complexes of the type $\text{Ln}(\text{isoQNO})_8\text{I}_3$ with lanthanide iodides (Ramakrishnan and Soundararajan 1977) except with Pr(III) iodide, where it appears as if the ligand does not impart severe steric hindrance to coordination at the coordination site. Thus even though both QNO and isoQNO have almost the same bulk, the position of the N-O group seems to have an influence on the stoichiometry of the complexes with these ligands. The low L:M ratio in the QNO complexes may also be due to the nature of the solvent used in the synthesis of these complexes.

In order to understand the difference in the coordinating nature of QNO and isoQNO, we have presently prepared the lanthanide perchlorate complexes of these ligands in the absence of coordinating solvents and where the perchlorate anion will be completely ionic and noncoordinate. The isolated complexes have been studied by analysis, conductance, IR, NMR and electronic spectra.

2. Experimental

2.1 Materials

Quinoline and isoquinoline were obtained from SD chemicals, India and Fluka, Germany respectively. Lanthanide oxides (99.9%) were obtained from Indian Rare Earths Ltd., Kerala. All the other chemicals were of reagent grade. The solvents were purified by standard methods.

2.2 Preparation of the ligands

Quinoline-1-oxide and isoquinoline-2-oxides were prepared (Ochiai 1953) by the N-oxidation of quinoline and isoquinoline respectively, purified and recrystallised from an ether-acetone mixture and an ethyl acetate solution, respectively. QNO: m.p. 57° (literature 58°); isoQNO: m.p. 104°C (literature 103°C).

2.3 Preparation of the hydrated lanthanide perchlorates

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

2.4 Preparation of lanthanide perchlorate complexes

To a hot solution of QNO or isoQNO (10 mM) in ethylacetate (30 ml), a solution of hydrated lanthanide perchlorate (1 mM) in ethyl acetate (5 ml) was added dropwise with stirring. Stirring in the hot condition was continued till the completion of the reaction. The precipitated complex was filtered, washed two to three times with hot ethyl acetate and dried in a vacuum desiccator over phosphorous (V) oxide.

2.5 Analyses

The metal contents of the complexes were estimated by EDTA titrations using xylenol orange as indicator (Lyle and Rahman 1963). The perchlorate was estimated by gravimetric precipitation with nitron as described by Welcher (1947). The ligands QNO and isoQNO were estimated spectrophotometrically at 310 nm and 295 nm respectively using the calibration curve method (Willard *et al* 1965). The analytical data are presented in table 1.

2.6 Physical methods

The IR spectra of the complexes and the ligands in nujol mulls, in the region 400–4000 cm^{-1} , were recorded on Perkin-Elmer model-397 spectrophotometer. The principal IR bands and their tentative assignments are given in table 2.

Proton NMR spectra of the diamagnetic complexes and the ligands were recorded on a

Table 1a. Analytical and molar conductance data for QNO complexes.

Complex	% Metal		% Ligand		% ClO_4^-		λ_m^* ($\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$)
	Found	Calculated	Found	Calculated	Found	Calculated	
<i>Quinoline-1-oxide complexes</i>							
[La(QNO) ₈](ClO ₄) ₃	8.64	8.69	73.90	72.63	18.47	18.68	348.2
[Pr(QNO) ₈](ClO ₄) ₃	8.96	8.81	73.81	72.53	—	—	350.8
[Nd(QNO) ₈](ClO ₄) ₃	9.06	9.00	73.78	72.30	—	—	346.4
[Gd(QNO) ₇](ClO ₄) ₃	10.80	10.69	70.12	69.02	20.18	20.29	358.7
[Dy(QNO) ₇](ClO ₄) ₃	10.85	11.01	70.01	68.77	—	—	344.2
[Ho(QNO) ₇](ClO ₄) ₃	11.11	11.15	69.91	68.65	—	—	351.1
[Er(QNO) ₇](ClO ₄) ₃	11.28	11.29	69.90	68.55	—	—	358.3
[Yb(QNO) ₇](ClO ₄) ₃	11.67	11.64	69.63	68.28	—	—	360.1

* Molar conductance in acetonitrile.

Table 1b. Analytical and molar conductance data for iso-QNO complexes.

Complex	% Metal		% Ligand		% ClO_4^-		λ_m^* ($\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$)
	Found	Calculated	Found	Calculated	Found	Calculated	
<i>Iso-quinoline-2-oxide complexes</i>							
[La(isoQNO) ₇](ClO ₄) ₃	9.43	9.56	69.50	69.91	20.42	20.55	345.9
[Pr(isoQNO) ₇](ClO ₄) ₃	9.55	9.68	69.60	69.79	—	—	341.0
[Nd(isoQNO) ₇](ClO ₄) ₃	9.73	9.89	69.83	69.63	—	—	354.1
[Gd(isoQNO) ₇](ClO ₄) ₃	10.77	10.69	69.22	69.02	—	—	358.5
[Dy(isoQNO) ₇](ClO ₄) ₃	11.11	11.01	68.57	68.77	—	—	352.8
[Ho(isoQNO) ₇](ClO ₄) ₃	11.32	11.16	68.70	68.66	—	—	348.3
[Er(isoQNO) ₇](ClO ₄) ₃	11.10	11.29	68.58	68.55	—	—	355.9
[Yb(isoQNO) ₇](ClO ₄) ₃	11.71	11.64	68.12	68.28	—	—	357.8

* Molar conductance in acetonitrile.

Bruker WH-270 spectrometer operating in the FT mode, using CD₃CN as the solvent and TMS as the internal standard (table 3).

Electronic spectra of Nd³⁺, Ho³⁺ and Er³⁺ 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 (table 4). Electrolytic conductance measurements in acetonitrile solutions of the complexes were carried out in a Siemen's 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).

3. Results and discussion

The analytical and conductivity data are presented in table 1. The complexes of QNO have the compositions Ln(QNO)₈(ClO₄)₃ where Ln = La, Pr, and Nd, and Ln(QNO)₇(ClO₄)₃ where Ln = Gd, Dy, Ho, Er and Yb. The complexes of isoQNO analyse for the formulae Ln(isoQNO)₇(ClO₄)₃ where Ln = La, Pr, Nd, Gd, Dy, Ho, Er and Yb. All the complexes are soluble in polar solvents such as methanol, acetone and acetonitrile. They are insoluble in chloroform and in nonpolar solvents like benzene and carbon tetrachloride. Molar conductance of the complexes are in the range for 1:3 electrolytes (Geary 1971) suggesting thereby that the perchlorate groups are ionic.

The IR spectral data are presented in tables (2a, b). The appearance of two unsplit bands, one in the region 628–630 cm⁻¹ and the other in the range 1095–1112 cm⁻¹ in the spectra of both QNO and isoQNO complexes, reveals the presence of ionic perchlorate groups in these complexes. The bands are assigned to ν₄ and ν₃ modes respectively of T_d perchlorate group. Thus the IR spectra pertaining to the perchlorate vibrations in both QNO and isoQNO complexes are in line with the 1:3 electrolytic behaviour of these complexes in acetonitrile solution.

Table 2a. Important IR frequencies (in cm⁻¹) and their assignments for QNO complexes.

Ligand	La	Pr	Nd	Gd	Dy	Ho	Er	Yb	Assignments
QNO									
1580 m	1588 m	1590 m	1588 w	1590 m	1588 m	1590 m	1590 m	1590 m	C=N stretch
1318 m	1318 w	1326 w	1320 vw	1330 vw	1320 w	1325 vw	1330 vw	1333 w	} N-O stretch*
1275 m	1275 m	1275 m	1276 w	1278 m	1275 m	1275 m	1275 m	1275 m	
1235 m	1238 m	1240 m	1238 w	1240 m	1237 m	1239 m	1240 m	1239 m	N-O stretch†
1145 m	1155 m	1156 m	1155 vw	1156 m	1155 m	1155 m	1155 m	1155 m	N-O deformation, other band character- istic of N-O mode
—	1105 s	1106 s	1103 m	1105 s	1100 s	1100 s	1100 s	1100 s	ν ₃ ClO ₄ ⁻
801	808 m	815 m	808 m	818 m	818 m	817 m	818 m	818 m	} C-H out-of-plane vibration
729	734 m	732 m	732 w	735 m	732 m	732 m	735 m	732 m	
—	629 m	629 m	629 m	629 m	629 m	630 m	628 m	630 m	ν ₄ ClO ₄ ⁻

* assigned as per data given for the ligand (Shindo 1960); † assigned as per data given for the ligand (Nelson *et al* 1968); s—strong; m—medium; w—weak; vw—very weak.

Table 2b. Important IR frequencies (in cm^{-1}) and their assignments for iso-QNO complexes.

Ligand	La	Pr	Nd	Gd	Dy	Ho	Er	Yb	Assignment
1580 <i>m</i>	1582 <i>w</i>	1582 <i>w</i>	1587 <i>w</i>	1582 <i>vw</i>	1582 <i>w</i>	1585 <i>w</i>	1582 <i>vw</i>	1587 <i>w</i>	C=N stretch
1502 <i>w</i>	1510 <i>w</i>	1510 <i>w</i>	1510 <i>w</i>	1512 <i>w</i>	1508 <i>w</i>	1507 <i>m</i>	1509 <i>w</i>	1567 <i>w</i>	Ring stretch
1338 <i>s</i>	1345 <i>m</i>	1348 <i>m</i>	1356 <i>m</i>	1345 <i>m</i>	1345 <i>m</i>	1345 <i>m</i>	1346 <i>m</i>	1347 <i>s</i>	N-O deformation (other band characteristic of N-O mode)
1260 <i>m</i>	1260 <i>m</i>	1260 <i>m</i>	1263 <i>m</i>	1260 <i>m</i>	1260 <i>m</i>	1260 <i>m</i>	1263 <i>m</i>	1262 <i>m</i>	C-H in-plane vibration*
1218 <i>s</i>	1220 <i>m</i>	1220 <i>m</i>	1220 <i>m</i>	1223 <i>m</i>	1220 <i>m</i>	1220 <i>m</i>	1221 <i>m</i>	1222 <i>m</i>	
1192 <i>s</i>	1180 <i>s</i>	1181 <i>s</i>	1183 <i>s</i>	1181 <i>s</i>	1181 <i>s</i>	1183 <i>s</i>	1184 <i>s</i>	1185 <i>s</i>	N-O stretch† (ν NO)
—	1100 <i>s</i>	1110 <i>s</i>	1108 <i>s</i>	1110 <i>s</i>	1110 <i>s</i>	1110 <i>s</i>	1110 <i>s</i>	1110 <i>s</i>	ν_3 perchlorate
827 <i>s</i>	820 <i>s</i>	820 <i>s</i>	825 <i>s</i>	820 <i>s</i>	820 <i>s</i>	820 <i>s</i>	820 <i>s</i>	822 <i>s</i>	δ N-O†
740 <i>m</i>	742 <i>s</i>	742 <i>s</i>	746 <i>s</i>	742 <i>s</i>	742 <i>s</i>	745 <i>s</i>	746 <i>s</i>	747 <i>s</i>	C-H out-of-plane vibration
—	630 <i>m</i>	630 <i>m</i>	628 <i>m</i>	630 <i>m</i>	628 <i>m</i>	625 <i>m</i>	626 <i>m</i>	627 <i>m</i>	ν_4 perchlorate

* assigned as per data given for the ligand (Shindo 1960); † assigned as per data given for the ligand (Nelson *et al.* 1968); *s*—strong; *m*—medium; *w*—weak; *vw*—very weak.

Table 3. Important proton NMR spectral data for QNO, iso-QNO and their La³⁺ complexes in acetonitrile.

Compound	Chemical shifts in ppm with respect to tetramethyl silane							
	1H	2H	3H	4H	5H	6H	7H	8H
QNO	—	8.4857	7.4557	7.8220	7.8190	7.6823	7.7766	8.5853
La ³⁺ QNO complex	—	9.0391	7.2607	7.5798	7.9374	7.4505	7.5911	8.4421
Iso-QNO	8.7341	—	8.0490	7.6010	7.8102	(5, 6,	7, 8 H)	
La ³⁺ iso-QNO complex	9.0048	—	8.3167	7.6497	7.7730	(5, 6,	7, 8 H)	

Table 4. Electronic spectral data in the visible region for Nd³⁺, Ho³⁺ and Er³⁺ complexes of QNO and iso-QNO.

J level	Nd ³⁺		J level	Ho ³⁺		J level	Er ³⁺	
	Energy (KK)			Energy (KK)			(Energy KK)	
	QNO	Iso-QNO		QNO	Iso-QNO		QNO	iso-QNO
⁴ G _{9/2}	19.53	19.60	³ K ₆	24.01	23.98	⁴ F _{5/2}	22.32	22.17
⁴ G _{7/2}	19.04	19.12	[*] ⁵ F ₁ , ⁵ G ₆	22.11	22.13	⁴ F _{7/2}	20.53	20.45
⁴ G _{5/2} , ² G _{7/2}	17.10	17.19	⁵ S ₂ , ⁵ F ₄	18.62	18.60	[*] ² H _{11/2}	19.14	19.18
			⁵ F ₅	15.60	15.66	⁴ F _{9/2}	15.33	15.20
	$\beta = 0.9899$	0.9958		$\beta = 0.9959$	0.9968		$\beta = 0.9969$	0.9989
	$\delta = 1.0203$	0.5328		$\delta = 0.4117$	0.3210		$\delta = 0.3109$	0.1101

* β and δ have been calculated for the starred J levels, for which comparable aquo values are available; KK—kilokaiser.

The $\nu_{\text{N-O}}$ for QNO and its complexes splits into two bands at 1318 cm⁻¹ and 1275 cm⁻¹. The splitting is attributed to a strong coupling of $\nu_{\text{N-O}}$ with other vibrations of QNO (Shindo 1960). According to Nelson *et al* (1968) however the 1235 cm⁻¹ band is probably due to $\nu_{\text{N-O}}$. The IR spectra of QNO complexes, show little shift of $\nu_{\text{N-O}}$. In fact, there is a little shift to higher frequencies of $\nu_{\text{N-O}}$ in many of the complexes, probably due to the impure nature of the $\nu_{\text{N-O}}$. However the N–O deformation band at 1145 cm⁻¹, the C–H out-of-plane vibration at 729 and 801 cm⁻¹ and the $\nu_{\text{C=N}}$ band at 1580 cm⁻¹ all shift to higher wave numbers in the IR spectra of the QNO complexes indicating thereby the coordination of N-oxide oxygen to the metal ion.

The band appearing at 1192 cm⁻¹ assigned to the N–O stretching frequency of isoQNO (Clemo and Dagtish 1950; Kluiber and Horrocks 1966; Nelson *et al* 1968) shift to the lower frequency by ≈ 12 cm⁻¹ in the spectra of isoQNO complexes indicating the binding of the N-oxide oxygen to the lanthanide metal ion. The N–O deformation band at 1339 cm⁻¹, the C–H out-of-plane vibrations at 740, 822 cm⁻¹ and the $\nu_{\text{C=N}}$ band at 1580 cm⁻¹ all shift to higher frequencies revealing the coordination of the N–O group to the metal ion.

Further evidence for the coordination of N-oxide oxygen of QNO and isoQNO to the lanthanide metal ion, in their complexes is found in the proton NMR spectra of QNO

and isoQNO complexes with La^{3+} (table 3). The various assignments in the PMR spectra of the complexes have been made as per the assignments reported by Hamm and Philipsborn (1971). The 2H and 5H signals in the QNO complex and the 1H, 3H, and 4H signals in the isoQNO complex have 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.

The electronic spectra taken in acetonitrile solution in the visible region for Nd^{3+} , Ho^{3+} and Er^{3+} complexes of QNO and isoQNO are given in figure 1. The 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 those of aquo ion complexes. In the complexes of QNO and isoQNO 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 (1966, 1971) has defined a parameter δ , as a measure of the covalent character of the metal ligand bond, which is given by the relation,

$$\delta(\%) = [(1 - \beta)/\beta] \times 100,$$

where β is the average value of the ratio $\nu_{\text{complex}}/\nu_{\text{aquo}}$. The β and δ values calculated for QNO and isoQNO complexes are presented in table 4. The values of QNO complexes being greater than those for the isoQNO complexes point to a greater covalency in the metal ligand bond in QNO complexes than in isoQNO complexes. Karraker (1968) has

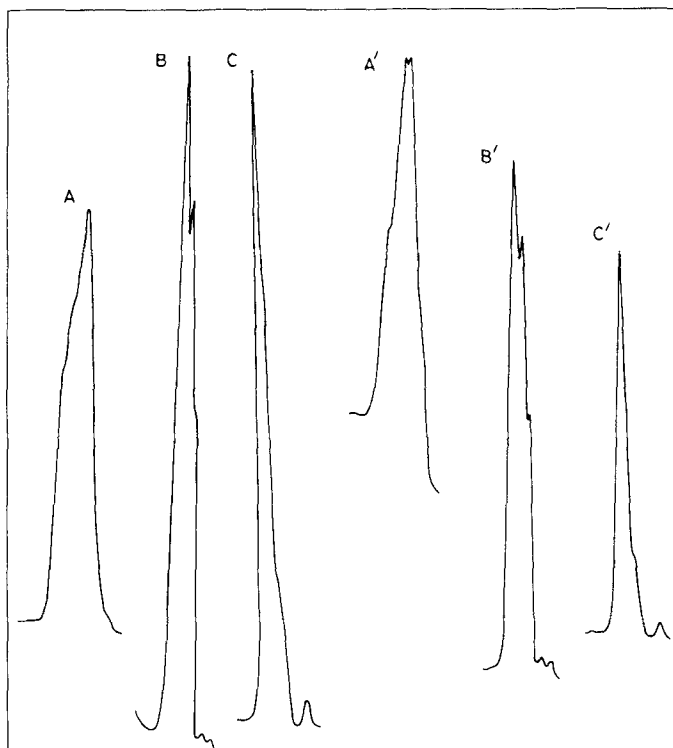


Figure 1.

found that the shapes of the 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+} , Ho^{3+} and Er^{3+} complexes closely resemble those in solution (in acetonitrile). This indicates a similarity in coordination number in the solid state and in solution. The shapes of the hypersensitive bands of Nd^{3+} , Ho^{3+} and Er^{3+} complexes of isoQNO and Ho^{3+} and Er^{3+} complexes of QNO markedly resemble the shapes of the seven coordinate diketonate complexes of lanthanides studied by Karraker. The spectral shape of the Nd^{3+} complex of QNO however resembles those of the eight coordinate complexes reported by Karraker.

4. Conclusions

The analytical, conductance and IR data coupled with ^1H NMR data for the lanthanide complexes of QNO and isoQNO 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 QNO complexes of La^{3+} , Pr^{3+} , Nd^{3+} have eight coordinate geometry, the QNO complexes of lanthanides, where $\text{Ln} = \text{Gd, Dy, Ho, Er and Yb}$, and all the lanthanide complexes of isoQNO are of seven coordinate geometry around the lanthanide ion.

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