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Lanthanide Perchlorate Complexes of 4-Chloroquinoline-1-oxide and 5-Chloroisoquinoline-2-oxide

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Abstract

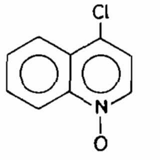
New lanthanide complexes of 4-chloroquinoline-1-oxide (CQNO) and 5-chloroisoquinoline-2-oxide (ClQNO) were synthesized. CQNO gave two sets of complexes, one set soluble in acetone with the formulae $[Ln(CQNO)_8](ClO_4)_3$, where Ln = Nd to Yb, and $[La(CQNO)_{10}](ClO_4)_3$, and the other insoluble in acetone with the formulae $[Ln(CQNO)_7](ClO_4)_3$ where Ln = La, Nd and Gd only. ClQNO gave complexes of the general composition $[Ln(ClQNO)_8](ClO_4)_3$ where Ln = La and Nd and $[Ln(ClQNO)_7](ClO_4)_3$ where Ln = Gd to Yb. The isolated complexes CQNO and ClQNO were characterized by elemental analysis, electrolytic conductance, infrared, proton NMR and electronic spectral data.

Introduction

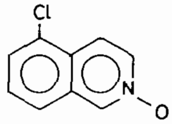
The study of lanthanide complexes of heterocyclic amine-*N*-oxides [1], reveals that the ligand-to-metal ratio (L:M) depends on the bulkiness of the amine oxide ligand. For example, complexes of lanthanide perchlorates with pyridine-1-oxide (PyO) have the L:M ratio of 8:1 but the corresponding complexes of 2,6-dimethylpyridine-1-oxide have an L:M ratio of 6:1. The work on lanthanide complexes of methyl substituted pyridine-1-oxides [1] shows that the methyl group, a group which donates electrons via mesomeric effects, at the 4-position of the ring introduces neither a steric effect nor a change in the coordination number around the metal ion. But recent studies on the complexes of lanthanide perchlorates with 4-substituted pyridine-1-oxides, with substituents other than the methyl group [2, 3], reveal that the L:M ratio is affected by these substituents at the 4-position of the heterocyclic ring. For instance, while 4-methylpyridine-1-oxide complexes of lanthanide perchlorates exhibit a L:M ratio of 8:1, the corresponding complexes of 4-dimethylaminopyridine-1-oxide show a lower L:M ratio.

Another point of interest is that the stoichiometry of the lanthanide complexes with the heterocyclic amine oxide ligands depends on the synthetic procedure adopted. For example, Pneumaticakis [4] has prepared lanthanide complexes of the type $Ln(PyO)_4(NO_3)_3$, but Ramakrishnan [5] has synthesized complexes of the formula $Ln(PyO)_3(NO_3)_3$, by changing the method of preparation.

Although lanthanide complexes of pyridine-1-oxide and its substituted analogues have been studied, lanthanide complexes of substituted quinoline-*N*-oxides and isoquinoline-*N*-oxides are not known. We report in this paper the synthesis of lanthanide perchlorate complexes of 4-chloroquinoline-1-oxide and 5-chloroisoquinoline-2-oxide. The isolated complexes have been characterized by analytical, conductance, infrared, ^1H NMR, and electronic spectral data.



CQNO



ClQNO

Experimental

Materials

Lanthanide oxides (99% pure) were obtained from Indian Rare Earths Ltd., Kerala State, India. Quinoline was obtained from S.D. Chemicals (India). Isoquinoline was purchased from Fluka Chemicals (F.R.G.). All other chemicals used were of reagent grade. The solvents were purified by standard methods.

Preparation of the Ligands

(a) 4-Chloroquinoline-1-oxide (CQNO)

Quinoline was *N*-oxidized by the method described by Ochiai [6]. 4-Nitroquinoline-1-oxide was obtained by the nitration of quinoline-1-oxide by the

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method given by Katritzky [7] for 4-nitropyridine 1-oxide. 4-Nitroquinoline-1-oxide was then converted to 4-chloroquinoline-1-oxide by the reaction of acetyl chloride on 4-nitroquinoline-1-oxide, according to the method given by Ochiai [8], for 4-chloropyridine-1-oxide and recrystallised from acetone. Melting point (m.p.) 131–132 °C (literature (lit.) 133–133.5 °C).

(b) 5-Chloroisoquinoline-2-oxide (ClQNO)

Isoquinoline-2-oxide was obtained by the *N*-oxidation of isoquinoline by the method given by Ochiai [6] for quinoline-1-oxide. Isoquinoline-2-oxide was converted to 5-nitroisoquinoline-2-oxide by nitrating the isoquinoline-2-oxide by the method described for 4-nitropyridine-1-oxide by Katritzky [7]. This was recrystallized from chloroform solution, m.p. 219–220 °C (lit. 220–222 °C). ClQNO was prepared for the first time by the action of acetyl chloride on 5-nitroisoquinoline-2-oxide, adopting the method described by Ochiai for the preparation of 4-chloropyridine-1-oxide [8]. 75 ml of acetyl chloride was added to 5-nitroisoquinoline-2-oxide (20 g) with cooling at 0 °C. The reaction mixture was then heated to 50 °C under reflux on a water bath for one hour. After cooling, it was treated with ice water, made alkaline with solid sodium carbonate and extracted with chloroform. The chloroform solution was dried over potassium carbonate and concentrated. The solid formed was recrystallised from chloroform, m.p. found as 183–184 °C. The synthesis of ClQNO by this method and characterisation of ClQNO has not been reported so far. The ^{13}C NMR spectral data, however, has been reported by Ja-An Su *et al.* [9]. The purity of ClQNO prepared above was checked by taking the ^{13}C NMR for the compound. The spectrum corresponded to the reported one. The sodium fusion and extraction gave a positive test for chlorine.

Hydrated Lanthanide Perchlorates

Hydrated lanthanide perchlorates were prepared by dissolving the corresponding oxides in less than the stoichiometric amount of dilute perchloric acid, filtering off the excess of oxide and evaporating the clear solution to dryness on a water bath.

Preparation of the Complexes

(a) CQNO complexes

To a boiling solution of CQNO (12 mM) in ethyl acetate (50 ml), a solution of hydrated lanthanide perchlorate (1 mM) in ethyl acetate (10 ml), was added dropwise with stirring. The mixture was stirred hot for 15 min. The clear liquid which formed above the sticky mass, was decanted. The sticky mass was washed 3–4 times with hot ethyl acetate to remove excess of the ligand. Acetone (10 ml) was added to this sticky mass and the mixture was stirred with heating. The solution turned brown and a solid complex, insoluble in acetone, separated, only in the cases of La, Nd and Gd perchlorates. The solid complex was filtered through a sintered crucible and the brown coloured filtrate was carefully collected. The complex was washed with hot acetone 3–4 times and dried over P_2O_5 in a vacuum desiccator.

Analyses

Metal contents in all the complexes were estimated by EDTA titrations using xylenol orange as indicator [10]. The perchlorate was estimated by gravimetric precipitation with nitron, as described by Welcher [11]. CQNO and ClQNO in their complexes were estimated spectrophotometrically at 242 nm and 218 nm, respectively, using a calibration curve method.

Physical Methods

The infrared spectra of the ligands and the complexes in Nujol mull in the region 600–4000 cm^{-1} were recorded on a Perkin-Elmer model-397 spectrophotometer. Electronic spectra of Nd, Ho and Er complexes in the region 350–750 nm were obtained on a Beckmann Model-25 spectrophotometer and also on a Unicam SP-700 spectrometer. The spectra in solution were run in acetonitrile. Spectra in the solid state were obtained in Nujol mulls smeared on Whatman filter paper.

Proton NMR spectra of the ligands and their complexes with La^{3+} in CD_3CN as solvent were recorded, using TMS as the internal standard. The spectra of CQNO and its complex were recorded on a Bruker WH-270 spectrometer and spectra of ClQNO and its complex, on a Varian 80 MHz instrument, both operating in the FT mode.

Electrolytic conductance measurements were carried out in acetonitrile solutions using the Siemens conductivity bridge with an immersion type (LTA) cell, calibrated with standard KCl solution. The concentrations of the solutions used were of the order of 10^{-3} M.

Results and Discussion

The complexes of both CQNO and ClQNO are hygroscopic. They are soluble in polar organic solvents such as acetonitrile and dimethyl sulphoxide, but insoluble in carbon tetrachloride, chloroform and benzene. Complexes of CQNO with La, Nd and Gd are of two types, one soluble in acetone and the other insoluble in acetone. The complexes of CQNO with Tb to Yb and all ClQNO complexes are soluble in acetone.

Analytical data for the complexes are presented in Tables I and II. The complexes of CQNO soluble in acetone analyse for the formulae $[Ln(CQNO)_8](ClO_4)_3$, where Ln = Nd to Yb and $[La(CQNO)_{10}]$-

TABLE I. Analytical and Molar Conductance Data for CQNO Complexes

Complex	Metal (%)		Ligand (%)		Anion (%)		Λ_m [a]
	Found	Calculated	Found	Calculated	Found	Calculated	
(a) Soluble in acetone							
$La(CQNO)_{10}(ClO_4)_3$	6.05	6.22	80.26	80.41	13.56	13.37	356.3
$Nd(CQNO)_8(ClO_4)_3$	7.55	7.68	76.26	76.44	16.07	15.88	359.0
$Gd(CQNO)_8(ClO_4)_3$	8.16	8.31	76.10	75.91	15.94	15.77	339.0
$Tb(CQNO)_8(ClO_4)_3$	8.52	8.39	76.05	75.85	15.98	15.76	344.5
$Dy(CQNO)_8(ClO_4)_3$	8.58	8.57	75.52	75.70	15.95	15.73	345.3
$Ho(CQNO)_8(ClO_4)_3$	8.56	8.68	75.84	75.61	15.94	15.71	366.7
$Er(CQNO)_8(ClO_4)_3$	8.90	8.79	75.73	75.51	15.84	15.69	351.6
$Yb(CQNO)_8(ClO_4)_3$	9.22	9.07	75.48	75.29	15.82	15.64	362.2
(b) Insoluble in acetone							
$La(CQNO)_7(ClO_4)_3$	8.21	8.20	74.23	74.18	17.43	17.62	345.5
$Nd(CQNO)_7(ClO_4)_3$	8.58	8.50	73.79	73.95	17.71	17.56	340.3
$Gd(CQNO)_7(ClO_4)_3$	9.43	9.19	73.55	73.39	17.60	17.43	341.5

[a]Molar conductance in acetonitrile ohm^{-1} cm^2 mol^{-1} at 25 °C.

TABLE II. Analytical and Molar Conductance Data for ClQNO Complexes

Complex	Metal (%)		Ligand (%)		Anion (%)		Λ_m [a]
	Found	Calculated	Found	Calculated	Found	Calculated	
$La(ClQNO)_8(ClO_4)_3$	7.36	7.42	76.42	76.66	15.81	15.93	393.7
$Nd(ClQNO)_8(ClO_4)_3$	7.58	7.68	76.29	76.44			343.8
$Gd(ClQNO)_7(ClO_4)_3$	9.10	9.18	73.22	73.39	17.33	17.43	363.9
$Ho(ClQNO)_7(ClO)_4)_3$	9.48	9.59	72.91	73.06			380.8
$Er(ClQNO)_7(ClO)_4)_3$	9.59	9.71	72.82	72.96			373.4
$Yb(ClQNO)_7(ClO_4)_3$	10.08	10.01	72.22	72.72			357.7

[a]Molar conductance in acetonitrile in ohm^{-1} cm^2 mol^{-1} at 25 °C.

$(ClO_4)_3$, and those insoluble in acetone analyse for $[Ln(CQNO)_7](ClO_4)_3$, where Ln = La, Nd and Gd. The analytical data for ClQNO complexes point to the formulae $[Ln(ClQNO)_8](ClO_4)_3$, where Ln = La and Nd, and $[Ln(ClQNO)_7](ClO_4)_3$, where Ln = Gd, Ho, Er and Yb.

Molar conductance data (Tables I and II) for both CQNO and ClQNO complexes in acetonitrile solutions indicate that the complexes of both the ligands behave as 1:3 electrolytes in this solvent [12].

Important infrared frequencies for the ligands and their complexes along with their assignments are given in Tables IIIa, IIIb and IV. The characteristic vibrations pertaining to the ionic perchlorate group are retained in the complexes of both CQNO and ClQNO. The ν_3 mode of the ClO_4^- group occurring in the range 1095–1100 cm^{-1} and the ν_4 mode in the region 620–622 cm^{-1} remain unsplit, showing that the perchlorate groups in the complexes have T_d symmetry. This is in line with the conductivity evidence for ionic perchlorate groups.

Coordination of the *N*-oxide group of CQNO and ClQNO to the lanthanide ion is shown by the shifts of the ν_{N-O}, δ_{N-O} and ν_{C-H} bands. The ν_{N-O} vibrations shift to lower frequencies by about 5 to 10 cm^{-1} in the complexes from those of the ligands. The N–O bending and C–H out-of-plane bending vibrations of the ligands exhibit a positive shift in their respective complexes, indicating thereby the binding of the *N*-oxide oxygen to the lanthanide ion, and a decrease in the π-electron density of the heterocyclic ring as a result of coordination of the ligand to the metal ion.

Additional evidence for the coordination of CQNO and ClQNO to the lanthanide ion in their complexes has been obtained from the proton NMR spectra of the diamagnetic La^{3+} complexes. The proton NMR spectral data are given in Table V. For CQNO and its lanthanum complex the assignments were made relative to those reported for 4-Br, 8-methylquinoline and 4-methoxyquinoline-1-oxide [13]. For ClQNO, the proton NMR spectrum has not been reported so

TABLE IIIa. Important Infrared Frequencies (in cm^{-1}) and their Assignments for CQNO Complexes Soluble in Acetone[a]

Ligand CQNO	La	Nd	Gd	Tb	Dy	Ho	Er	Yb	Assignments
1565	1570	1570	1568	1568	1565	1570	1570	1570	$\nu_{C=N}$
1510	1510	1515	1515	1515	1513	1515	1518	1515	ring stretch
1310	1305	1305	1300	1302	1300	1300	1305	1302	ν_{NO}
	1100	1100	1095	1095	1100	1095	1095	1100	ν_3 perchlorate
829	835	840	835	839	840	838	838	835	δ_{NO}
760	770	770	765	768	765	765	768	762	C–H out-of-plane
	620	620	620	620	620	620	620	620	ν_4 perchlorate

[a] Assigned as per data given for the ligand [20].

TABLE IIIb. Important Infrared Frequencies (cm^{-1}) and their Assignments for CQNO Complexes Insoluble in Acetone[a]

Ligand CQNO	La	Nd	Gd	Assignments
	1690	1690	1690	$\nu_{C=C} + \nu_{C=N}$
1565	1570	1570	1572	$\nu_{C=N}$
1510	1515	1515	1518	ring stretch
1310	1307	1310	1310	ν_{NO}
	1095	1095	1095	ν_3 perchlorate
829	837	835	838	δ_{NO}
760	775	773	775	C–H out-of-plane
	620	620	622	ν_4 perchlorate

[a] Assigned as per data given for the ligand [20].

far. Hence the assignments for the ClQNO NMR signals have been made tentatively, by comparing the spectrum of ClQNO with those of IQNO and NIQNO, reported previously [14, 15]. The 2H and 3H signals of CQNO and all proton signals of ClQNO shift downfield in the spectra of their respective La^{3+} complexes, confirming the coordination of the *N*-oxide moiety of the ligands to the lanthanide ion. The observed deshielding of the heterocyclic ring protons is a consequence of the drainage of the electron density from the ring to the lanthanide ion in the complexes.

The electronic spectral data for Nd^{3+}, Ho^{3+} and Er^{3+} complexes of CQNO and ClQNO are presented in Table VI. The sharp f–f bands exhibit red shifts with respect to the aquo ions. This is a consequence of complex formation and has been found in many lanthanide complexes [16]. These red shifts have been ascribed to the nephelauxetic effect [17] and result from changes in the inter-electronic repulsion parameters (F_k) in the complexes. The nephelauxetic red shift could well be used as a measure for covalency in the metal–ligand bond [17]. Sinha [18] has proposed a δ-scale to express qualitatively the covalent character of the Ln^{3+}-ligand bond in the complexes. It is expressed by the percentage relation

$$\delta\,(\%) = \left[\frac{1-\beta}{\beta}\right] \times 100$$

where β is the average value of the ratio

$$\frac{\nu_{\text{complex}}}{\nu_{\text{aquo}}}$$

where ν_{complex} and ν_{aquo} are the energies of absorption expressed in kilo Kaisers. The δ values for the complexes are given in Table VI. It is found that the δ values for the present complexes are positive, suggesting thereby a certain amount of covalency in the Ln^{3+}-ligand bond.

TABLE IV. Important Infrared Frequencies (cm^{-1}) and their Assignments for ClQNO and its Complexes

Ligand ClQNO	La	Nd	Gd	Ho	Er	Yb	Assignments
1610m	1615m	1613m	1614m	1615w	1615m	1615m	$\nu_{C=N}$
1520s	1528s	1528s	1530s	1530m	1530s	1530s	ring stretch
1240m	1230m	1230m	1230m	1230m	1230m	1228m	ν_{N-O}
	1095s	1095s	1095s	1095m	1095s	1095s	$\nu_{3}\text{ClO}_4^-$
840m	845w	845w	848w	844w	844w	845w	δ_{N-O}
740m	742m	742m	744m	743m	743m	745m	C–H out-of-plane
	622m	621m	622m	621m	620m	620m	$\nu_{4}\text{ClO}_4^-$

TABLE V. Important ^1H NMR Spectral Data for CQNO and ClQNO and their La^{3+} Complexes[a]

Compound	1H	2H	3H	4H	5H	6H	7H	8H
CQNO		8.378	7.479		8.218	7.834	7.842	8.623
$La(CQNO)_{10}(ClO_4)_3$		8.739	7.416		8.120	7.658	7.744	8.547
$La(CQNO)_7(ClO_4)_3$		8.884	7.495		8.171	7.677	7.784	8.543
ClQNO[b]	8.750		8.440	7.900		8.400	7.650	8.080
La^{3+} ClQNO complex[b]	9.720		8.500	7.980		8.440	7.780	8.150

[a]Chemical shifts (δ) in ppm with respect to tetramethylsilane, in CD_3CN). [b]Assignments have been made tentatively in comparison with the spectra for IQNO and as the data for ClQNO have not been reported in the literature so far.

TABLE VI. Electronic Spectral Data for Nd^{3+}, Ho^{3+} and Er^{3+} Complexes of CQNO and ClQNO

Nd^{3+}				Ho^{3+}			Er^{3+}		
J level	Energy (kK)			J level	Energy (kK)		J level	Energy (kK)	
	CQNO complexes		ClQNO complexes		CQNO complexes	ClQNO complexes		CQNO complexes	ClQNO complexes
	7	8	8		8	7		8	7
$^4G_{9/2}$	10.493	19.608	19.474				$^4F_{7/2}$	20.513	20.492
$^4G_{7/2}$	19.029	19.047	19.012	$^5S_2$, $^5F_4$	18.372	18.239	$^2H_{11/2}$	19.084	19.066
$^4G_{5/2}$, $^2G_{7/2}$	17.272	17.294	17.241	$^5F_5$	15.387	15.307	$^4S_{3/2}$	18.433	18.348
							$^4I_{9/2}$	15.337	15.267
β	0.9926	0.9953	0.9914		0.9968	0.9906		0.9962	0.9934
δ	0.7458	0.4738	0.8699		0.3194	0.9471		0.3816	0.6619

The shapes, positions and intensities of the electronic spectral bands for the complexes are similar both in the solid and solution states, suggesting a similarity in the coordination environment in both states. Karraker [19], after a systematic study of the electronic spectra of various β-diketone complexes of lanthanides, found that the hypersensitive bands varied with the coordination number round the lanthanide ion. A comparison of the hypersensitive band shapes for the present complexes with the reported shapes for the corresponding β-diketonates of lanthanide reveals that the spectral shape of $^4G_{5/2}2G_{7/2} \leftarrow {}^4I_{9/2}$ band for $[Nd(CQNO)_8](ClO_4)_3$ and $[Nd(ClQNO)_8](ClO_4)_3$ correspond to those of eight coordinate lanthanide β-diketonates. The band shape for $[Nd(CQNO)_7](ClO_4)_3$ insoluble in acetone resembles those of seven coordinate complexes reported by Karraker. The hypersensitive $^5G_6 \leftarrow {}^5I_8$ and $^2H_{11/2} \leftarrow {}^4I_{15/2}$ bands for Ho^{3+} and Er^{3+} complexes, respectively, of CQNO are similar to the reported shapes of the eight coordinate complexes of the same lanthanide. For Ho^{3+} and Er^{3+} complexes of ClQNO, shapes resemble those of the corresponding seven coordinate complexes studied by Karraker.

Conclusions

The infrared spectral data for the complexes of both CQNO and ClQNO, along with the proton NMR spectral data for diamagnetic complexes, indicate the binding of the ligand molecule to the lanthanide ion through the N-oxide group.

Molar conductance data and infrared spectra for the lanthanide complexes coupled with electronic absorption spectral shapes both in the solution and solid states for Nd^{3+}, Ho^{3+} and Er^{3+} complexes suggest the following coordination numbers for the lanthanide ions:

Complex	Coordination number	Ln^{3+} metal ion
CQNO complexes	8 and 7	Nd and Gd
CQNO complexes	8 only	Tb, Dy, Ho, Er and Yb
CQNO complexes	10 and 7	La
ClQNO complexes	8 only	La and Nd
ClQNO complexes	7 only	Gd, Ho, Er and Yb

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