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Metal Halide Complexes of Quinoline N-Oxide: A Study of Halide Interaction in the Coordination of Neutral Monodentate Ligand

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The coordination of different halide ions, viz. chloride, bromide and iodide in the presence of quinoline N-oxide (QNO) to di- and trivalent manganese, iron and cobalt has been studied. The complexes formed have been characterized by elemental analyses, magnetic moments, electronic and infrared spectra. In di- and trivalent metal (M^{2+} and M^{3+}) complexes, chloride is found to be coordinated, while iodide is generally coordinated in M^{2+} and non-coordinated in M^{3+} complexes. Bromide produces 1 : 1 electrolyte of the type $[M(QNO)_6][MBr_4]$ where M = Mn^{2+} and Fe^{2+} but not so in the case of Co^{2+}, which forms pseudotetrahedral complex $[Co(QNO)_2Br_2]$. Fe^{3+} produces 1 : 1 electrolyte $[Fe(QNO)_4Br_2][FeBr_4]$.

ALTHOUGH the coordination behaviour of halides in the presence of monodentate neutral ligands has been investigated by several workers, the literature is scattered and no attempt is made for a systematic study and rationalize the behaviour. In this investigation, an attempt is made to study the coordination behaviour of chloride, bromide and iodide in the presence of a neutral monodentate ligand, quinoline N-oxide. The metal ions studied are Mn(II and III), Fe(II and III) and Co(II and III).

Only a few of the di- and trivalent manganese, iron and cobalt perchlorate complexes of quinoline N-oxide (QNO) have been reported[1,2]. QNO complexes of metal (II and III) halides are even less investigated[3,4]. Coordination behaviour of QNO to di- and trivalent metal perchlorates is also studied for the sake of comparison.

Materials and Methods

QNO[5] and Mn(III) acetate[6] were prepared by the literature methods. Metal perchlorates were prepared by treating metal carbonates with perchloric acid and recrystallizing from water. Metal halides used were BDH reagents. Nitrobenzene and acetonitrile were dried over P_2O_5 and distilled before use.

In general, the complexes were prepared by mixing a solution of metal perchlorate or metal halide (0·01 mol) in ethanol, 2-propanol or 1-butanol with a slight excess of the ligand (0·06 mol) in the same solvent. Some complexes could be crystallized only after partially evaporating the solution on a water-bath under reduced pressure and cooling it. Addition of about 2 ml of triethyl orthoformate to the solution and rapid stirring induced crystallization in the case of bromo and iodo complexes. Mn(III) complexes were prepared from Mn(III) acetate in the presence of ammonium halide or perchlorate in *n*-butanol. Co(III) complexes were prepared by the oxidation of respective Co(II) salts with 6% H_2O_2 in the presence of an excess of the ligand in ice-cold *n*-butanol and glacial acetic acid. An inert atmosphere of nitrogen was maintained during the preparation of ferrous complexes.

Results and Discussion

All the complexes are coloured solids. The complexes are, in general, soluble in water but dissociate, showing that QNO is a weaker ligand than water. They are also soluble in methanol, ethanol, acetonitrile, chloroform and nitrobenzene. The bromo and iodo complexes are relatively less stable than the chloro complexes in solution as well as in the solid state.

The metal and anionic contents of the complexes were analysed by standard methods[7,8]. The analytical results are given in Table 1.

The molar conductances of the perchlorate complexes of di- and trivalent metal ions with QNO (Table 2) correspond to those of 1:2 and 1:3 electrolytes respectively[9], indicating that the perchlorate groups are not coordinated. The molar conductances of the divalent metal chloride complexes in nitrobenzene and acetonitrile are relatively low showing that chloride is coordinated to the metal ions. The chloro complexes of Mn(III) and Co(III) behave as non-electrolytes while that of Fe(III) behaves as a 1:1 electrolyte without answering the test for free chloride ions. Mn(II), Fe(II) and Fe(III) bromo complexes are 1:1 electrolytes but Co(II) bromo-complex is a non-electrolyte. The divalent metal iodo complexes are non-electrolytes in nitrobenzene showing coordinated

TABLE 1 — CHARACTERIZATION DATA OF THE COMPLEXES

Sl No.	Complex	Colour	M (%)		N (%)		Anion (%)	
			Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1	$[Mn(QNO)_6][ClO_4]_2$	Red	4·80	4·89	7·23	7·47	17·35	17·7
2	$[Fe(QNO)_6][ClO_4]_2$	Red brown	5·25	4·97	7·29	7·46	18·02	17·69
3	$[Co(QNO)_6][ClO_4]_2$	Pink	5·16	5·22	7·98	7·44	17·19	17·63
4	$[Mn(QNO)_6][ClO_4]_3$	Dark red	5·50	4·48	6·15	6·86	25·70	24·49
5	$[Fe(QNO)_6][ClO_4]_3$	Brown	5·51	4·56	5·99	6·86	25·42	24·38
6	$[Co(QNO)_6][ClO_4]_3$	Red brown	5·21	4·99	7·25	6·84	23·85	24·32
7	$[Mn(QNO)_2Cl_2]$	do	13·85	13·21	6·96	6·73	16·68	17·05
8	$[Fe(QNO)_2Cl_2]$	Yellow	12·85	13·4	7·02	6·71	17·56	17·02
9	$[Co(QNO)_2Cl_2]$	Blue	14·84	14·04	6·93	6·66	16·21	16·89
10	$[Mn(QNO)_3Cl_3]$	Dark red	8·85	9·22	7·19	7·04	16·45	17·82
11	$[Fe(QNO)_4Cl_2][FeCl_4]$	Brown	12·5	12·30	6·85	6·19	23·12	23·50
12	$[Co(QNO)_3Cl_3]$	Dark red	10·40	9·80	7·88	6·99	18·25	17·73
13	$[Mn(QNO)_6][MnBr_4]$	Brown	8·96	8·44	6·95	6·46	23·9	24·59
14	$[Fe(QNO)_6][FeBr_4]$	do	8·95	8·58	6·63	6·45	24·95	24·56
15	$[Co(QNO)_2Br_2]$	Green	11·20	11·57	6·21	5·50	30·39	31·45
16	$[Mn(QNO)_3Br_3]$	Red brown	7·88	7·53	5·21	5·76	32·45	32·87
17	$[Fe(QNO)_4Br_2][FeBr_4]$	Brown	9·85	9·54	5·11	4·78	40·35	40·94
18	$[Mn(QNO)_2I_2]$	do	9·53	9·18	4·93	4·67	42·85	42·39
19	$[Fe(QNO)_2I_2]$	do	8·72	9·31	4·84	4·66	42·87	42·32
20	$[Co(QNO)_2I_2]$	Green	10·11	9·78	5·15	4·64	42·63	42·10
21	$[Mn(QNO)_6]I_3$	Dark green	4·80	4·20	6·86	6·43	29·56	29·16
22	$[Fe(QNO)_6]I_3$	Black	4·53	4·27	6·49	6·42	29·95	29·14

iodide but exhibit varying electrolytic nature in acetonitrile. This shows that the iodo complexes are solvolysed in acetonitrile involving the equilibrium (1) $[M(QNO)_2I_2]+\text{solvent} \rightarrow [M(QNO)_2I(\text{solv})]^{+}+I^{-}$

or

$$[M(QNO)_2(\text{solv})]^{2+}+2I^{-} \quad \ldots(1)$$

Trivalent metal iodo complexes behave as 1:3 electroles both in acetonitrile and nitrobenzene. This shows that iodide has no tendency for coordination to Mn(III) and Fe(III) unlike the respective divalent metal ions. There is, however, poor tendency for coordination with the corresponding divalent metal ions in acetonitrile but not so in trivalent metal ion complexes. This may be due to the softer character of divalent metal ions. Iodide, being soft, shows greater tendency for overlap of its orbitals with the orbitals of the soft metal ions.

The magnetic moments, μ_{eff}, of the complexes given in Table 2 show that they are all high-spin type except those of Co^{3+} which are spin-paired diamagnetic. QNO complexes of metal (II and III) perchlorates have magnetic moments which suggest octahedral configuration around the metal ions[10]. Mn(III) complexes of QNO reported here possess magnetic moments which indicate distortion in their octahedral symmetry.

Similarly, Fe(III) and Co(III) halide complexes are assigned distorted octahedral configurations. The magnetic moments (4·7-4·8 B.M.) of Co(II) halide complexes indicate a pseudo-tetrahedral configuration for the metal ion while Co(III) complexes with chloride show near octahedral stereochemistry.

Coordination of aromatic amine N-oxides through the oxygen of N-O is manifested by the characteristic shifts of various ligand bands in their vibrational spectra[11,12]. However, in 3*d*-transition metal complexes of QNO, νNO is found either at the same frequency as in the free ligand (1235 cm^{-1}) or it is slightly lowered. This may be due to the coupling of νN-O with the vibrations of the quinoline ring system in these compounds[13]. Extensive metal ligand π bonding may also be contributing to the effect[1]. The substitution of the different halide ions in the coordination sphere does not seem to affect appreciably the νN-O of the complexes. In all the perchlorate complexes ν_3 and ν_4 of ClO_4 appear around 1100 and 624 cm^{-1}, respectively, showing T_d symmetry for ClO_4^-.

The perchlorate complexes of di- and trivalent metals have been assigned octahedral configurations on the basis of their magnetic moments and electronic spectra (Table 2). The presence of three bands instead of a band expected for spin-allowed transition $^5E_g \rightarrow {}^5T_{2g}$ for Mn(III) complexes indicates lowering of symmetry from O_h to D_{4h} due to Jahn-Teller distortion. The di- and trivalent metal, chloride complexes possess either pseudo-tetrahedral or distorted octahedral structure. Because of favourable crystal field stabilization energy, Co(II) shows a distinct tendency to acquire near tetrahedral geometry in the presence of chloride, bromide and iodide. This tendency probably prevents the formation of 1:1 electrolyte in the case of Co^{2+} similar to those of its congeners Mn^{2+} and Fe^{2+}, which produce $[M(QNO)_6][MBr_4]$.

The bromo complexes of Fe(II) and Mn(II) may be formulated as $[M(QNO)_6]^{2+}[MBr_4]^{2-}$, where M $= Fe^{2+}$ and Mn^{2+}, on the basis of their chemical analysis, molar conductance and molecular weight determination in nitrobenzene. Similarly, the chloro and bromo complexes of Fe(III) are assigned the structure $[Fe(QNO)_4X_2][FeX_4]$, where $X = Cl^-$ or Br^-. The iodide complexes of trivalent metals are octahedral, in which the iodide behaves like perchlorate. However, the behaviour of iodide

TABLE 2 — ELECTRICAL CONDUCTANCE IN NON-AQUEOUS SOLVENTS, MAGNETIC MOMENTS AND ELECTRONIC SPECTRA OF THE COMPLEXES

*Sl No.	Λ_M (ohm^{-1} cm^2 mole^{-1}) at 30°		μ_{eff} (B.M.)	λ_{max}, nm (ϵ_{max})	Assignment	Probable symmetry
	Nitrobenzene	Acetonitride				
1	59·6	296·7	5·86	550 w, 500, 405, 360 and 340 (all w) 405 w	$^6A_{1g}\rightarrow {}^4T_{1g}$(G), $^4T_{2g}$, ($^4E_g + {}^4A_{1g}$), $^4T_{2g}$ (D) and ^4E_g(D) respectively	Octahedral (O_h)
2	—	204·5	5·42	1025 w	$^5T_{2g}\rightarrow {}^5E_g$	Octahedral (O_h)
3	—	293·1	4·92	1150 sh 690 w 550 m 465	$^4T_{1g}$ (F)$\rightarrow {}^4T_{2g}$ (F) $\rightarrow {}^4A_{2g}$ (F) $\rightarrow {}^4T_{2g}$ (P) (Charge transfer band)	Octahedral (O_h)
4	—	365·4	4·95	700 w 620 w 510 sh	$^5A_{1g}\rightarrow {}^5B_{1g}$ $^5B_{2g}\rightarrow {}^5B_{1g}$ $^5E_{1g}\rightarrow {}^5B_{1g}$	Distorted octahedral ($D_{4}h$)
5	85·8	342·6	5·95	835 w 540 m 505 w 440 sh 345 sh	$^6A_{1g}\rightarrow {}_4T_{1g}$ (G) $\rightarrow {}^4T_{2g}$ (G) $\rightarrow {}^4E_g + {}^4A_{1g}$ (G) $\rightarrow {}^4E_g$ (D)	Octahedral (O_h)
6	—	398·2	Dia-magnetic	625 s 395 s	$^1A_{1g}\rightarrow {}^1T_{1g}$ $^1A_{1g}\rightarrow {}^1T_{2g}$	Octahedral (O_h)
7	0·4	—	5·85	630 br 540 sh 490 sh 470 w 360 sh	$^6A_{1g}\rightarrow {}^4T_{1g}$ (G) $\rightarrow {}^4T_2$ (G) $\rightarrow {}^4E +{}^4 A_1$ (G) $\rightarrow {}^4T_{2g}$(D) $\rightarrow {}^4E$ (D)	Pseudo-tetrahedral
8	9·43	—	5·38	940 w	$^5E\rightarrow {}^5T_2$	Tetrahedral (T_d)
9	4·1	61·15	4·71	640 sh (30·6) 620 s (34·3) 578 s (26·2)	$^4A_2\rightarrow {}^4T_2$ (F) $\rightarrow {}^4T_1$ (F) $\rightarrow {}^4T_1$ (P)	Pseudo-tetrahedral
10	—	14·39	4·88	1210 s 1030 w 950 w	$^5A_1\rightarrow {}^5B_1$ $^5B_2\rightarrow {}^5B_1$ $^5E_2\rightarrow {}^5B_1$	Distorted octahedral (C_{3v})
11	28·7	162·6	5·85	675 w 560 w 520 w 325 w	$^5A_1\rightarrow {}^4T_1$ (^4G) $\rightarrow {}^4T_2$ (^4G) $\rightarrow {}^4E+{}^4A_1$($^4G$) $\rightarrow {}^4E$ (D)	Trans-distorted octahedral cation with tetrahedral anion
12	—	29·85	Dia-magnetic	720 s 430 s	$^1A_1\rightarrow {}^1E$ $^1A_1\rightarrow {}^1B_2$	Distorted octahedral (C_{3v})
13	27·64	117·7	5·92	515 sh 450 w 316 s	$^6A_1\rightarrow {}^4T_1$ (^4G) $\rightarrow {}^4T_2$ (^4G) $\rightarrow {}^5E_g+{}^4A_1$ (^4G)	Octahedral cation with tetrahedral anion
14	—	112·7	5·34	890 w	$^5E_g\rightarrow {}^5T_{2g}$	Octahedral cation with tetrahedral anion
15	5·83	67·25	4·75	630 s (83·9) 585 s (86·6)	$^4A_2\rightarrow {}^4T_2$ (F) $^5A_2\rightarrow {}^4T_1$ (F)	Pseudo-tetrahedral
16	—	65·8	4·79	570 w 465 w 420 w	$^5A_{2g}\rightarrow {}^5B_{1g}$ $^5B_2\rightarrow {}^5B_{1g}$ $^5E_g\rightarrow {}^5B_{1g}$	Distorted octahedral ($D_{4}h$)
17	—	155·6	5·79	654 w 545 w 490 sh, 420 sh 314 w	$^6A_1\rightarrow {}^4T_1$ (^4G) $\rightarrow {}^4T_2$(^4G) $\rightarrow {}^4E + {}^4A_1$ (^4G) $\rightarrow {}^4E$ (D)	Trans-distorted octahedral cation with tetrahedral anion

TABLE 2 — ELECTRICAL CONDUCTANCE IN NON-AQUEOUS SOLVENTS, MAGNETIC MOMENTS AND ELECTRONIC SPECTRA OF THE COMPLEXES — *contd*

*Sl No.	Λ_M (ohm^{-1} cm^2 mole^{-1}) at 30°		μ_{eff} (B.M.)	λ_{max} mn (ϵ_{max})	Assignment	Probable symmetry
	Nitro-benzene	Aceto-nitride				
18	—	165·8	5·8	570 w, br 360 w	$^6A_1 \rightarrow {}^4T_1{}^{\cdot}$ (^4G) $\rightarrow {}^4T_2$ (^4G)	Tetrahedral (Td)
19	9·23	113·4	5·17	930 w 390 s	$^5E \rightarrow {}^5T_2$ Charge transfer	Tetrahedral (T_d)
20	8·2	254·9	4·84	675 s (646·9) 660 s (642·1) 620 sh (468·7)	$^4A_2 \rightarrow {}^4T_2$ (^4F) $\rightarrow {}^4T_1$ (^1F) $\rightarrow {}^4T_1$ (^4P)	Pseudo-tetrahedral
21	71·1	377·2	4·82	690 w 605 w 500 w	$^5A_{1g} \rightarrow {}^5B_{1g}$ $^5B_{2g} \rightarrow {}^5B_{1g}$ $^5E_{1g} \rightarrow {}^5B_{1g}$	Distorted octahedral (D_{4h})
22	82·45	347·6	5·96	640 w, br 340 sh 315 s	$^5A_{1g} \rightarrow {}^4T_{1g}$ (G) $\rightarrow {}^4E_g$ (D) Charge transfer	Octahedral (O_h)

*Sl Nos. refer to the compounds listed in Table 1.

†Spectra of the complexes 1-8, 11-14, 16-19 and 21 and 22 were taken in nujol; of 9, 15 and 20 in $CHCl_3 + CH_3OH$; and of 10 in CH_3OH.

and perchlorate ions differ considerably in the case of divalent metal ions.

The investigations incorporated in the work show that the configurations of the complexes of QNO depend on the nature of the halide ions and oxidation state of the metal ion. Chloro complexes of di- and trivalent metals always possess chloride within the coordination sphere, the divalent ions forming four coordinated while the trivalent ions forming near octahedral complexes. As a consequence of comparatively softer character of divalent metal ions, iodide gets coordinated to the metal(II); while the trivalent metal ions being hard, iodide remains outside the coordination sphere and the metal ions form complexes with six coordinated QNO. Bromide shows a very peculiar behaviour forming 1:1 electrolytes in the case of Mn(II) and Fe(II) producing $[M(QNO)_6][MBr_4]$ while Fe(III) forms $[Fe(QNO)_4Br_2][FeBr_4]$. Co(II) does not form such a 1:1 electrolyte because of its greater tendency to form tetrahedral complexes.

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