3-Methylisoquinoline N-Oxide Complexes with 3d Metal Perchlorates [1]

A. N. SPECA

USI Chemicals Co., Research Division, Cincinnati, Ohio 45237, U.S.A.

L. S. GELFAND, F. J. IACONIANNI, L. L. PYTLEWSKI

Department of Chemistry, Drexel University, Philadelphia, Pa. 19104, U.S.A.

C. M. MIKULSKI

Department of Chemistry & Physics, Beaver College, Glenside, Pa. 19038, U.S.A.

and N. M. KARAYANNIS

*Amoco Chemicals Corporation, Naperville, Il. 60540, U.S.A.*

Received July 18, 1978

The methyl substituent in 3-methylisoquinoline N-oxide (L) exerts significant steric hindrance as to stabilize complexes involving L to metal ratios of less than six with 3d metal(II) perchlorates, as follows: $[ML_5(OClO_3)](ClO_4)$ *(M = Mn, Ni);* $[CoL_5(OClO_3)] \cdot (ClO_4) \cdot H_2O$; $[ML_4(OClO_3)](ClO_4)$ *(M = Fe, Cu); and* $[ZnL_3(OClO_3)](ClO_4) \cdot 3H_2O$ *(tetrahedral). In the case of* Cr^{3+} *and* Fe^{3+} *perchlorates, complexes of the* $[ML_6](ClO_4)_3$ *type have been isolated; however,* $[CrL_4(OClO_3)(OH_2)](ClO_4)_2$, $[FeL_4(OClO_3)_2](ClO_4)$ *and* $[FeL_3(OClO_3)(OH_2)_2](ClO_4)$ *complexes can be also stabilized, under the influence of the steric effects of L. Finally, during interaction of L with* $Fe(ClO_4)_3$, *a mixture of approximately 9 parts of the perchloric acid adduct of L([L_2H](ClO_4)) and 1 part of* $[FeL_6](ClO_4)_3$ *was recovered from the filtrate, after separation of the precipitate of the latter complex.*

Introduction

Pyridine N-oxide (N-pyO) and 3- or 4-substituted derivatives do not introduce any significant steric hindrance during coordination. For instance, their complexes with 3d metal perchlorates are of the types $[ML_6](ClO_4)_n$ (M^{n+} = Sc^{3+}, V^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}), $[CuL_4](ClO_4)_2$ [2–10], and, in certain cases (L = N-pyO, 4-picoline N-oxide), $[CuL_6](ClO_4)_2$ [5–8, 11]. On the other hand, *ortho*-substituted pyridine N-oxides exert significant steric hindrance during metal complex formation. Thus, 2-picoline N-oxide (2-methylpyridine N-oxide; N-picO) reportedly forms complexes of the types $[CoL_5] \cdot (ClO_4)_2$ [8, 12], $[NiL_4](ClO_4)_2$ (polymeric, probably N-oxide-bridged) [13] and $[ML_4(ONO_2)](NO_3)$ (M = Co, Ni) [14], while 2,6-lutidine N-oxide (2,6-

dimethylpyridine N-oxide; N-lutO), which introduces even more severe steric hindrance, has been found to yield $[MnL_4(OClO_3)](ClO_4)$, $[ML_4](ClO_4)_2$ (M = Fe, Co, Ni, Cu, Zn) [15], $[CoL_3(O_2ClO_2)](ClO_4)$, $[CoL_5](ClO_4)_2$ [16], $[ML_2(ONO_2)(O_2NO)]$ (M = Mn, Co, Ni, Zn) and $[CuL_2(ONO_2)_2]$ [17] complexes. Similar steric effects, leading to relatively low ligand to metal ratios, have been also reported for 2-acetyl- [18], 2-methylamino- and 2-dimethylamino- [19] pyridine N-oxides, and 2-pyridylcarbinol N-oxide [20].

Among fused ring N-pyO derivatives, the N-oxides of isoquinoline (N-iqO; I) and quinoline (N-qO; II), corresponding, respectively, to a *meta, para-* and an

I   II   III
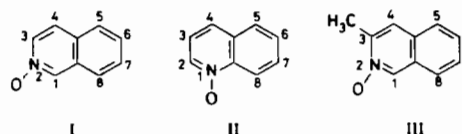
ortho, meta-disubstituted N-pyO, do not appear to exert steric hindrance during complex formation with 3d metal perchlorates. In fact, both these ligands yield 6:1 complexes with M^{3+} (M = Cr, Fe) and M^{2+} (M = Mn, Fe, Co, Ni, Zn) perchlorates and 4:1 complexes with $Cu(ClO_4)_2$ [21–23]. 4- or 6-substituted N-qO derivatives also form 3d metal perchlorate complexes, involving the preceding stoichiometries [21–23]. Moreover, both N-pyO and N-qO form 5:1 complexes with $TiO(ClO_4)_2$ [24–26]; however, whereas N-pyO yields a 8:1 complex with $Th(ClO_4)_4$ [25], the corresponding N-qO complex involves a 6:1 ligand to thorium ratio [26]. The introduction of a somewhat more pronounced steric effect by N-qO, relative to N-pyO or N-iqO, is also demonstrated by the fact that N-qO forms 1:1 adducts with Co^{2+} and Ni^{2+} acetylace-

tonates [27], while N-iqO and N-pyO yield 2:1 adducts with the same metal acetylacetonates [27, 28]. Finally, acridine N-oxide (N-acO), which corresponds to an *ortho, ortho, meta, meta*-tetra-substituted N-pyO, exerts apparently severe steric hindrance during metal complex formation: This ligand forms 4:1 complexes with Co^{2+}, Ni^{2+} and Zn^{2+} perchlorates [29], 2:1 complexes with Mn^{2+}, Co^{2+} and Zn^{2+} nitrates and thiocyanates and an 1:1 complex with $Hg(SCN)_2$ [30].

Recently, these laboratories initiated a series of studies of the steric effects introduced by various substituents in aromatic amine N-oxide ligands [1]. Since no systematic study of the effects of *ortho*-substituents on N-iqO or N-qO has been reported so far, the syntheses and characterization of 3d metal perchlorate complexes with 3-methylisoquinoline N-oxide (3-m-N-iqO; III) were included in the above series of studies and are reported in the present paper. It should be mentioned at this point that some coordination complexes of 2-methylquinoline N-oxide (2-m-N-qO) have been reported [13, 31, 32]. However, the stoichiometries of these complexes did not lead to any conclusions regarding the steric hindrance exerted by this ligand; in fact, both 2-methyl- and 4-methyl-N-qO were found to yield 2:1 complexes with Co^{2+} nitrite [31] and UO_2^{2+} chloride or nitrate [32]; a 2:1 complex of 2-m-N-qO with Ni^{2+} nitrate was also isolated, when ligand and salt were allowed to interact at a 2:1 molar ratio [13]. It is also worth noticing that, although several metal complexes of N-iqO have been reported [13, 21, 27, 32–34], no publications dealing with coordination compounds of any substituted derivative of this ligand have appeared in the literature.

Experimental

Chemicals

3-m-N-iqO (Ennox Chemical Co.) was utilized as received. Reagent grade hydrated metal perchlorates, triethyl orthoformate (teof) and organic solvents were used throughout this work.

Preparative Methods

During preliminary synthetic attempts it was established that interaction of ligand and M(II) perchlorate solutions leads to the precipitation of the same complex, regardless of the concentration of the solutions or the ligand to metal ratio (in the 4:1 to 6:1 region) employed. The following procedure was used for the preparation of $M(ClO_4)_2$ complexes with 3-m-N-iqO: 1 g of the ligand (6.3 mmol) was dissolved in 15 ml of a 3:2 (v/v) mixture of ethanol and teof (a dehydrating agent [35]), while the metal salt (1.5 mmol) was dissolved separately in 10–15 ml of the same solvent mixture. The ligand and salt solutions

were warmed separately at 50 °C for 30 minutes, under stirring, and, subsequently, the solution of the ligand was slowly added to the stirred metal salt solution. After completion of the addition of the ligand solution, a solid precipitate started forming; precipitation was complete after 5–15 more minutes. In the case of $Co(ClO_4)_2$, a gummy precipitate was observed while the ligand addition was in progress; this gummy product solidified when the addition of the ligand was completed. Yields of the new M^{2+} complexes: Mn^{2+} 0.50 g; Fe^{2+} 0.45 g; Co^{2+} 0.74 g; Ni^{2+} 0.69 g; Cu^{2+} 1.05 g; Zn^{2+} 0.80 g. These solid complexes were separated by filtration, washed with a small amount of the ethanol–teof mixture and stored in an evacuated desiccator over anhydrous calcium sulfate. Recrystallizations of the complexes were effected by dissolution in boiling CH_2Cl_2, filtration of the hot solution, additon (to the hot filtrate) of an amount of n-hexane sufficient to induce a light cloudiness, and overnight storage of the resulting mixture at 5 °C, for the complete precipitation of the recrystallized complexes.

Each of the M^{3+} (M = Cr, Fe) perchlorates studied produced more than one complex upon interaction with 3-m-N-iqO. Thus, by following the preceding standard synthetic procedure with $Cr(ClO_4)_3$, we obtained a gummy green solid, after complete addition of the ligand to the Cr^{3+} salt solution. The gummy product was gradually completely solidified by prolonged stirring of the reaction mixture and subsequent grinding under ethanol–teof. During attempts at the recrystallization of this product from boiling CH_2Cl_2, a red brown solid precipitated (yield 0.37 g); after separation of this solid by filtration, a dark green filtrate remained. A second solid complex (green in color; yield 0.59 g) was precipitated by mixing the filtrate with twice its volume of n-hexane, under stirring, and storing the resulting mixture at 5 °C. When our standard synthetic procedure was employed for $Fe(ClO_4)_3$, combination of ligand and salt solutions resulted in the precipitation of a yellow green solid in small quantities, which increased upon cooling to room temperature (yield 1.05 g). The yellow green solid was separated by filtration (and recrystallized as described above) from the dark brown mother liquor, which was diluted with three times its volume of petroleum ether (boiling range 30–60 °C). The resulting mixture eventually produced a grey precipitate (yield 0.2 g), upon standing at ambient temperature. During another synthetic attempt 6.3 mmol of the ligand and 1.5 mmol of $Fe(ClO_4)_3$ were dissolved separately, each in 5 ml of the ethanol–teof solvent mixture. The resulting solutions were treated separately at 50 °C for 30 minutes, under stirring, and then combined. A dark red brown gummy precipitate formed immediately; this gummy product was solidified by addition of excess petroleum ether and mixing with a spatula.

The resulting solid product was dried in an evacuated desiccator over $CaSO_4$, then ground to a powder, which was treated with boiling CH_2Cl_2, affording a yellow solid precipitate (yield 1.35 g). The yellow complex was separated by filtration (and recrystallized as above), leaving a dark red filtrate. This filtrate was mixed with three times its volume of petroleum ether, and a red brown solid (yield 0.4 g) precipitated when the resulting mixture was allowed to stand at ambient temperature overnight.

The new solid metal complexes are somewhat hygroscopic, but stable in a dry air atmosphere. They are sparingly soluble or insoluble in ethanol or acetone, but dissolve in other polar organic solvents, such as nitromethane or dimethyl sulfoxide. The Mn^{2+} complex is extremely photosensitive; its exposure to light leads to the almost immediate formation of a brown surface layer, presumably consisting of Mn^{3+}-containing products [36]. Special precautions were taken [37], in order to avoid exposure of this complex to light during storage and subsequent handling. It should be noted that many Mn^{2+} complexes with aromatic amine N-oxides are photosensitive [36, 37]. Analytical results for the new complexes (C, H, N analyses by Schwarzkopf Microanalytical Laboratory, Woodside, New York; metal analyses by atomic absorption spectroscopy) are given in Table I.

Characterization Studies

Infrared spectra (Table II), magnetic susceptibility (295 °K) and molar conductivity (on $10^{-3} M$ nitromethane solutions at 25 °C) measurements (Table III), and solid-state (Nujol mull) electronic spectra (Table IV) were obtained by methods previously described [10, 15, 38].

Discussion

Stoichiometries of the New Metal Complexes

The precipitation of 3-m-N-iqO complexes with 3d metal(II) perchlorates, involving the usual, for non-sterically hindered aromatic amine N-oxides, 6:1 ligand to metal ratio is apparently not favored. The steric effects of the 3-m-N-iqO ligand lead to the stabilization of 5:1 complexes with Mn^{2+}, Co^{2+} and Ni^{2+} perchlorates, 4:1 complexes with Fe^{2+} and Cu^{2+} perchlorates, and a 3:1 complex with $Zn(ClO_4)_2$ (Table I). Some of these complexes (M = Co, Zn) are also characterized by the presence of water. In the case of M^{3+} perchlorates, 6:1 complexes can be obtained, under certain synthetic conditions; however, 4:1 or 3:1 complexes with these metal salts can also be isolated. Thus, interaction of relatively dilute ligand and $Fe(ClO_4)_3$ solutions leads to the precipitation of the yellow green $Fe(3-m-N-iqO)_6(ClO_4)_3$, but when more concentrated solutions of these two reagents are allowed to interact, a mixture of $Fe(3-m-N-iqO)_3(ClO_4)_3\cdot 2H_2O$ and $Fe(3-m-N-iqO)_4(ClO_4)_3$ is precipitated (the two components of this mixture can be separated by treatment with CH_2Cl_2, in which the 3:1 complex is insoluble and the 4:1 complex soluble). From the filtrate of the 6:1 Fe^{3+} complex, a grey product, mainly consisting of the perchloric acid adduct of the ligand [39, 40], contaminated with small amounts of the 6:1 Fe^{3+} complex is obtained. Analytical results suggest that this grey product consists of approximately nine moles of $[(3-m-N-iqO)_2H](ClO_4)$ per mol of $Fe(3-m-N-iqO)_6$-$(ClO_4)_3$ (Table I). In the case of $Cr(ClO_4)_3$, a precipitate consisting of a mixture of $Cr(3-m-N-iqO)_4$-$(ClO_4)_3\cdot H_2O$ and $Cr(3-m-N-iqO)_6(ClO_4)_3$ was initially obtained, and the components of this mixture were

TABLE I. Analytical Data for 3-m-N-iqO (L) Complexes with 3d Metal Perchlorates.[a]

Complex	Color	Analysis							
		C %		H %		N %		Metal %	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$CrL_4(ClO_4)_3\cdot H_2O$	Red brown	47.80	48.24	3.81	3.87	5.57	5.23	5.17	4.96
$CrL_6(ClO_4)_3$	Green	55.20	54.87	4.17	4.32	6.44	6.51	3.98	4.20
$MnL_5(ClO_4)_2$	Yellow orange	57.21	56.78	4.32	4.25	6.67	6.92	5.23	5.04
$FeL_4(ClO_4)_2$	Dark brown	53.89	54.18	4.07	4.31	6.28	6.46	6.26	5.97
$FeL_3(ClO_4)_3\cdot 2H_2O$	Yellow	41.52	41.43	3.60	3.49	4.84	5.05	6.44	6.75
$FeL_4(ClO_4)_3$	Red brown	48.48	48.14	3.66	3.87	5.65	5.93	5.64	5.44
$FeL_6(ClO_4)_3$	Yellow green	55.04	54.67	4.16	3.96	6.42	6.75	4.27	3.94
$CoL_5(ClO_4)_2\cdot H_2O$	Brick orange	56.03	55.69	4.42	4.27	6.53	6.34	5.50	5.55
$NiL_5(ClO_4)_2$	Light orange	56.99	57.31	4.30	4.33	6.65	6.40	5.57	5.28
$CuL_4(ClO_4)_2$	Light green	53.43	53.29	4.04	3.73	6.23	6.11	7.07	7.00
$ZnL_3(ClO_4)_2\cdot 3H_2O$	Light tan	45.27	45.25	4.18	4.32	5.28	5.34	8.21	8.21

[a]The grey product obtained during interaction of 3-m-N-iqO with $Fe(ClO_4)_3$ (*cf.* Experimental Section) analyzed as follows: C 56.21%; H 4.64%; N 6.33%; Fe 1.15%. Calculated values for a 9:1 mixture of $[L_2H](ClO_4)$ and $[FeL_6](ClO_4)_3$ (see text) are: C 56.65%; H 4.28%; N 6.61%; Fe 1.10%.

TABLE II. Pertinent Infrared Data for 3-m-N-iqO Complexes with 3d Metal Perchlorates (cm^{-1}). ^{a}

Compound	ν_{OH}	ν_{N-O} Region	$\nu(ClO_4)$ Regions		$\nu_{M-O}(X)$			ν_{Ligand} (500–250 cm^{-1})
			ν_3	ν_4	X = OH$_2$	X = L	X = OClO$_3$	
3-m-N-iqO = L		1276mw, 1259mw, 1215ms, 1190ms, 1169m	1141mw, 1110m, 1088w, b, 1039w 1019w	638m*				482m, 474m, 462mw, 439m, 391w, 352w, 333w, 304w, b, 296w, b, 277vw, 254vw, b
CrL$_4$(ClO$_4$)$_3$·H$_2$O	3250ms, b	1281w, 1261ms 1221ms, 1162s, 1151s	1118vs, sh, 1098vvs, 1035vs	640w, sh, 629m, 621m*, 616m*, 611w, sh	492m	420m	322w	479mw, 460w, sh, 440w, 390w, sh, 352w, 302vvw, sh, 260vvw, b
CrL$_6$(ClO$_4$)$_3$		1281w, 1262m, 1221m, 1180mw, 1162m, 1151m	1098vvs, b, 1040m, b, 1020w, b	641w, b, 626m*		419m		478ms, b, 462mw, sh, 440mw, 396w, sh, 350vw, b, 315vw, b, 300vw, sh, 280vw, 255vvw, b
MnL$_5$(ClO$_4$)$_2$		1280m, 1258mw, 1218m, 1182w, 1179m, 1163ms, 1146m	1114s, sh, 1110vs, sh, 1088vs, b, 1045s, b	639w, sh, 628m, sh, 621m*, 614m, sh		336m	284m	476m, sh, 470m, 454m, 440m, 392m, 361mw, 353w, 307w, 292m, sh, 270m, 260m
FeL$_4$(ClO$_4$)$_2$		1280m, 1260m, 1218ms, 1185ms, 1166s, 1150s	1120vs, 1110vs, sh, 1086vvs, b, 1043s, sh	640w, sh, 629m*, 621m*, 614m*		392m	326mw, sh	475m, 460m, 448m, 388m, sh, 360mw, 330mw, 307w, 280vw, 250vvw
FeL$_3$(ClO$_4$)$_3$·2H$_2$O	3440ms	1281mw, 1261m, 1220m, 1186m, 1167s, 1150s	1118vs, sh, 1103vvs, 1062vs, sh, 1020mw	638m, sh, 629m*, 623m*, 617m, sh	488m, sh	407m	340mw, 330mw	479m, 455m, b, 398m, sh, 385mw, 360mw, 303m, 293m, 288m, 270m, 260mw, 250mw
FeL$_4$(ClO$_4$)$_3$		1285w, 1260mw, 1220w, b, 1186m, 1167s, 1150s	1117vs, 1095vs, b, 1047ms, 1020mw	637w, sh, 629m*, 621m*, 612m*, sh		421m, 393ms	340m, 330ms, 320m	472s, 450m, b, 398s, sh, 379m, 355w, 307ms, 291ms, 282s, 270m, 258m
FeL$_6$(ClO$_4$)$_3$		1285m, 1260m, 1219m, 1186mw, 1163ms, 1152m	1092vs, vb, 1015vs, b	640w, sh, 627m*		405m, b		480m, sh, 474ms, 453m, 440m, 380m, b, 355mw, b, 308m, 294m, 286m, 270m, 258m
Grey Fe^{3+} product		1300m, b, 1288m, 1277m, 1241m, 1209m, 1180m, 1145ms, b	1087vs, b, 1035m, b	638w, 626m*		410vw, b		480s, 449m, 438m, 423m, 393m, b, 318mw, 282vw, b
CoL$_5$(ClO$_4$)$_2$·H$_2$O	3560–3200w, vvb	1279m, 1260m, 1218m, 1180m, 1161s, 1148ms	1120s, sh, 1100vs, b, 1039ms, 1008w	636m, sh, 630m*, 622m*, 613mw*		373m, 340m	290m, b	480m, 470m, 459m, 440m, 393mw, sh, 283m, sh, 252vw

TABLE II. *(Continued)*

NiL₅(ClO₄)₂		*1280m, 1262m,* *1217m, 1181m,* 1167s, 1149ms	*1107vs, 1095vs, sh,* *1050m, b,* 1009w	*635w, 628m, sh,* *622m*,* *618mw, sh*	378m 340m	293m, b	479s, 471ms, 460m, 439m, 330m, sh, 281mw, sh, 256vw
CuL₄(ClO₄)₂		*1280m, 1260m,* 1219m, 1184m, 1163s, 1150ms	*1112vs, sh,* *1101vs, 1078vs,* 1040mw, 1010w	*640w, 629ms*,* *620ms*, 614ms, sh*	412m*	310mb	479s, 471ms, 462m, sh, 441m, 393mw, sh 350mw, 286m, 270m, 260m
ZnL₃(ClO₄)₂·3H₂O	3560–3200w, vvb	*1281m, 1260m,* 1218ms, 1188m, 1167s, 1150s	*1110vs, 1090vs, b,* *1053s, sh,* 1015m	*641w, 626m, sh,* *619m*,* *612m, sh*	417ms, b 328m		474s, 455ms, 440ms, 355m, sh, 308vw, 280mw, b

aAbbreviations s, strong, m, medium, w, weak, v, very, b, broad, sh, shoulder Note The ν₃ and ν₄(ClO₄) band assignments are shown in italics, asterisks (*) indicate very sharp maxima

subsequently separated by treatment with CH_2Cl_2 In connection with the fact that the isolation of 6 1 complexes of 3-m-N-iqO with Cr^{3+} and Fe^{3+} perchlorates is possible, it should be mentioned that other sterically hindered ligands, which do not produce 6 1 complexes with M^{2+} perchlorates, have been found to form $[ML_6]^{3+}$ cationic complexes (M = Cr, Fe) (e g , N-lutO [15, 17] , hexamethylphosphoramide [41])

Infrared and Conductance Data

The ν_{N-O} vibrational mode of pyridine N-oxides is shifted to lower wavenumbers upon metal complex formation (coordination through the N–O oxygen) [42, 43] Nevertheless, in the cases of N-qO and N-iqO metal complexes, similar negative ν_{N-O} frequency shifts are not always observed, owing to significant overlap of the N–O stretching mode with aromatic ring vibrations of the ligand [21, 23, 44] This overlap creates also difficulties in assigning the ν_{N-O} mode For example, for N-iqO this mode has been assigned at 1180 [21, 23, 27, 34] , at 1256 [44] and as a doublet at 1260, 1206 cm^{-1} [32] by different groups 3-m-N-iqO exhibits five main absorption maxima in the ν_{N-O} region (1280–1160 cm^{-1}) (Table II) The new metal complexes show small positive frequency shifts of the free ligand bands at 1276 and 1215 cm^{-1}, and small negative frequency shifts of the ligand bands at 1190 and 1169 cm^{-1}, while the absorption at 1259 cm^{-1} remains practically unaffected In addition, the spectra of the new complexes show a new band at 1151–1145 cm^{-1} Although no unambiguous ν_{N-O} assignment for the free ligand seems possible, it is considered as likely that this mode is associated with either or both of the absorptions at 1190 and 1169 cm^{-1}, and that the appearance of two to four bands at 1186–1145 cm^{-1} in the IR spectra of the metal complexes is, at least partially, due to the anticipated negative ν_{N-O} frequency shifts In the δ_{N-O} region, the ligand shows a band at 830 cm^{-1}, this absorption is intensified and shifted to 835–840 cm^{-1} in the spectra of the metal complexes

The hydrated metal complexes exhibit ν_{OH} absorptions of two different types in the region above 3200 cm^{-1} The 4 1 Cr^{3+} and 3 1 Fe^{3+} complexes show a relatively sharp medium to strong ν_{OH} band, attributable to the presence of aqua ligands [45] , while the spectra of the Co^{2+} and Zn^{2+} compounds are characterized by a much weaker and extremely broad absorption, covering the whole 3560–3200 cm^{-1} region (Table II), and most probably due to the exclusive presence of lattice water [46] The ν_3 and ν_4 fundamental vibrational modes of ionic ClO_4^- appear as single bands only in the spectra of the 6 1 M^{3+} complexes, which were expected to contain exclusively ionic perchlorate, and that of the grey Fe^{3+} product [47] In the spectra of the rest of the

TABLE III. Magnetic Susceptibilities (295 °K) and Molar Conductivities ($10^{-3} M$ Nitromethane Solutions at 25 °C) of 3-m-N-iqO (L)–Metal Perchlorate Complexes.[a]

Complex	$10^6 \chi_M^{cor}$, cgsu	μ_{eff}, μB	Λ_M, Ω^{-1} cm^2 mol^{-1}
$CrL_4(ClO_4)_3 \cdot H_2O$	6614	3.97	209
$CrL_6(ClO_4)_3$	6158	3.83	246
$MnL_5(ClO_4)_2$	15,327	6.04	176
$FeL_4(ClO_4)_2$	12,398	5.43	178
$FeL_3(ClO_4)_3 \cdot 2H_2O$	15,166	6.00	206
$FeL_4(ClO_4)_3$	15,855	6.14	198
$FeL_6(ClO_4)_3$	15,712	6.11	254
$CoL_5(ClO_4)_2 \cdot H_2O$	8916	4.61	167
$NiL_5(ClO_4)_2$	4632	3.32	175
$CuL_4(ClO_4)_2$	2007	2.18	178
$ZnL_3(ClO_4)_2 \cdot 3H_2O$	Diamagnetic		176

[a]The grey Fe^{3+} product shows a χ_g value of 2.66×10^{-6} cgs units. If we assume that it is a 9:1 mixture of $[L_2H](ClO_4)$ and $[FeL_6](ClO_4)_3$ (combined molecular weight per Fe atom: 5087.938), the following values are calculated: $10^6 \chi_M^{cor}$, cgs units: 16,226; μ_{eff}: 6.21 μB. On the other hand, a $10^{-3} M$ solution of this product in nitromethane (on the basis of the above M.W.) shows a Λ_M value of 112 Ω^{-1} cm^2 mol^{-1}.

TABLE IV. Solid-state (Nujol mull) Electronic Spectra of 3-m-N-iqO (L) Complexes with 3d Metal Perchlorates.[a]

Complex	λ_{max}, nm
$CrL_4(ClO_4)_3 \cdot H_2O$	335vs, vb, 438s, sh, 475s, b, 612ms, sh, 643ms, b, 680ms, b
$CrL_6(ClO_4)_3$	350vs, b, 415s, b, 443s, sh, 467ms, sh, 602ms, b, 624ms, 644ms, sh, 662ms, sh
$MnL_5(ClO_4)_2$	338vs, vb, 371s, b, 440vw, b
$FeL_4(ClO_4)_2$	308vs, b, 322vs, sh, 363s, sh, 456m, sh, 697m, 734m, sh, 818m, sh, 940mw, b, 1055w, b, 1330w, vb
$FeL_3(ClO_4)_3 \cdot 2H_2O$	303vs, sh, 327vs, b, 385s, b, sh, 455m, sh, 514mw, sh
$FeL_4(ClO_4)_3$	330vs, vb, 358vs, sh, 425m, vb, 563w, sh
$FeL_6(ClO_4)_3$	307vs, sh, 323vs, sh, 332vs, vb, 363vs, sh, 407ms, sh, 433m, sh, 475m, b, 511mw, sh
Grey Fe^{3+} product	335vs, vb, 360vs, sh, 460m, sh, 565m, vb
$CoL_5(ClO_4)_2 \cdot H_2O$	321vs, sh, 340vs, b, 367s, sh, 386s, sh, 482m, b, 513m, b, 1215w, vvb
$NiL_5(ClO_4)_2$	324vs, sh, 345vs, b, 363s, sh, 400ms, vb, 683mw, 757mw, b, 833w, b, 1245w, vb
$CuL_4(ClO_4)_2$	333vs, sh, 375svs, vb, 395s, sh, 427ms, sh, 700ms. b, 770ms, b, 846m, sh, 970w, b, 1260vw, sh
$ZnL_3(ClO_4)_2 \cdot 3H_2O$	305vs, b, 314vs, sh, 339vs, b, 358m, sh, 376w, sh

[a]Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. All the spectra are characterized by extremely strong ligand absorptions in the region below 300 nm.

new complexes each of the ν_3 and ν_4 bands is triply split, obviously owing to the simultaneous presence of both ionic (T_d symmetry) ClO_4^- and unidentate coordinated $-OClO_3$ (C_{3v} symmetry) ligands [47, 48] (Table II). The observation of IR-active ν_1 and $\nu_2 (ClO_4)$ bands in the spectra of the latter complexes was not possible, as the ligand shows medium intensity absorption in both these regions (at ca. 920 and at 482–462 cm^{-1}, respectively).

The molar conductivities of $10^{-3} M$ nitromethane solutions of the new complexes at 25 °C are, in most cases, typical of 1:3 electrolytes for the M^{3+} com-

plexes and of 1:2 electrolytes for the M^{2+} complexes [49] (Table III). Only in the cases of the red brown Cr^{3+} and Fe^{3+} complexes and the yellow Fe^{3+} complex were the Λ_M values intermediate between those corresponding to 1:2 and 1:3 electrolytes. Since (with the exception of the 6:1 Cr^{3+} and Fe^{3+} compounds) the majority of the new metal complexes contain coordinated perchlorate in the solid state, it seems that in nitromethane solution the $-OClO_3$ ligands are displaced by CH_3NO_2 groups. This is not uncommon for nitromethane solutions of metal perchlorate complexes with aromatic amine

N-oxides [15, 50], despite the fact that $-OClO_3$ is a somewhat stronger ligand than CH_3NO_2 [51]. As far as the grey Fe^{3+} product is concerned, the observed Λ_M value of $112\,\Omega^{-1}\,cm^2\,mol^{-1}$ is not inconsistent with the postulated presence of a mixture of *ca.* 9 mol of $[(3\text{-m-N-iqO})_2H](ClO_4)$ per mol of $Fe(3\text{-m-N-iqO})_6(ClO_4)_3$ (10:12 electrolyte).

Tentative metal–ligand band assignments in the lower frequency infrared region (Table II) were based on previously reported far-IR studies of 3d metal complexes with aromatic amine N-oxide [15, 52, 53], aqua [45, 54] and perchlorato [55] ligands. On the basis of these assignments, all of the M^{3+} (M = Cr, Fe) complexes and the Mn^{2+}, Co^{2+} and Ni^{2+} compounds seem to be hexacoordinated [15, 45, 52–55]. On the other hand, the Fe^{2+}, Cu^{2+} and Zn^{2+} complexes clearly involve coordination numbers lower than six. The ν_{M-O} frequencies for the Fe^{2+} and Cu^{2+} compounds are consistent with coordination number five [15]; in the case of the Zn^{2+} complex, which exhibits the ν_{M-O} (3-m-N-iqO and $-OClO_3$) modes at higher wavenumbers, relative to the rest of the M^{2+} complexes, coordination number four is considered as most likely [15], especially in view of the fact that, for a given coordination number, the ν_{M-O} (N-oxide) frequency increases along the series $Mn^{2+} \sim Zn^{2+} < Fe^{2+} < Co^{2+} < Cu^{2+} \sim Ni^{2+}$ (Irving–Williams series) [15, 52, 53].

Magnetic Susceptibilities and Electronic Spectra

The magnetic moments of the new metal complexes (Table III) are generally normal for high-spin d^3 and d^5–d^8 transition metal complexes or the d^9 configuration [56]. The moment of the Co^{2+} complex (4.61 μB) is somewhat low for octahedral Co(II) and suggestive of some loss in orbital degeneracy of the $^4T_{1g}(F)$ ground state, caused by lower-symmetry components in the ligand field [8]. Likewise, the μ_{eff} of the Ni^{2+} complex (3.32 μB) is slightly higher than the upper limit of the "octahedral" region for Ni(II), owing to some distortion from a purely octahedral environment [8].

The solid-state electronic spectra of the new paramagnetic metal ion complexes (Table IV) are characterized by strong metal-to-ligand charge-transfer bands, originating in the UV (where they overlap with the very strong ligand absorptions) and trailing off well into the visible region (400–570 nm). Charge-transfer absorption of this type is common in 3d metal complexes with aromatic amine N-oxides [57]. As a result of this type of spectra, several d–d transition bands ($^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ for Cr^{3+}, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ for Ni^{2+}, and all of the d–d bands of the Mn^{2+} and Fe^{3+} complexes) are partially or completely masked by the charge-transfer bands. The d–d transition spectra of the Cr^{3+}, Co^{2+} and Ni^{2+} complexes are generally consistent with hexacoordinated configurations, involving the presence of lower-symmetry com-

ponents (suggested by splittings or the broad character of the d–d bands) [8]. Band assignments, nm: Cr^{3+}: Red brown complex: $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 438, 475; $\rightarrow {}^4T_{2g}(F)$ 612, 643, 680; green complex: $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 415, 443, 467; $\rightarrow {}^4T_{2g}(F)$ 602, 624, 644, 662. Co^{2+}: $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 482; $\rightarrow {}^4A_{2g}(F)$ 513; $\rightarrow {}^4T_{2g}(F)$ 1215. Ni^{2+}: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 400; $\rightarrow {}^3T_{1g}(F)$ 683, 757; $\rightarrow {}^1E_g(D)$ 833; $\rightarrow {}^3T_{2g}(F)$ 1245. On the basis of these assignments, the following approximate Dq calculations for the Cr^{3+} and Ni^{2+} complexes were made: Red brown Cr^{3+} complex: $1550\,cm^{-1}$; green Cr^{3+} complex: $1580\,cm^{-1}$; Ni^{2+} complex: $803\,cm^{-1}$. The Dq value for the 6:1 (green) Cr^{3+} complex is within the range of values reported for $[CrL_6]^{3+}$ cationic complexes with N-pyO, N-qO, N-acO and derivatives (1558–$1686\,cm^{-1}$) [2, 3, 6–8, 15, 23, 29]; the red brown Cr^{3+} complex, which involves 3-m-N-iqO, aqua and the considerably weaker perchlorato ligand, shows a somewhat lower Dq value, as would be expected. Finally, the Dq of $803\,cm^{-1}$ calculated for the Ni^{2+} complex is also within the range of values reported for hexacoordinated Ni^{2+} cationic complexes with aromatic amine N-oxides (780–$875\,cm^{-1}$) [2, 3, 6–8, 13, 21, 22]; for $[Ni(N\text{-iqO})_6](ClO_4)_2$ a Dq value of $805\,cm^{-1}$ has been calculated [21].

The d–d transition spectrum of the Fe^{2+} complex is characterized by the presence of six absorption maxima at 697–1330 nm, and is compatible with a pentacoordinated configuration [58], which is also suggested by the location of the ν_{Fe-O} bands (*vide supra*). As far as the spectrum of the Cu^{2+} complex is concerned, coordination number five is also favored by the multiple d–d maxima observed [58], as well as the fact that the two strongest of these absorptions (700, 770 nm) occur at significantly lower energies [8, 59] than the corresponding bands in the tetracoordinated $[Cu(N\text{-pyO})_4](ClO_4)_2$ (680, 729 nm) [6].

Conclusion

During the present study it was established that the methyl substituent in 3-m-N-iqO exerts significant steric hindrance as to restrict the ligand to metal ratios in the complexes of this N-oxide with M^{2+} perchlorates to 3–5:1. Furthermore, in addition to the 6:1 3-m-N-iqO complexes with Cr^{3+} and Fe^{3+} perchlorates, the 4:1 and (in the case of Fe^{3+}) the 3:1 analogs can be also stabilized, as a result of the steric hindrance introduced by the ligand.

With respect to the most likely structural types of the new metal complexes, the following formulations are proposed, on the basis of the overall evidence. Hexacoordinated complexes: $[M(3\text{-m-N-iqO})_6](ClO_4)_3$ (M = Cr, Fe); $[Cr(3\text{-m-N-iqO})_4(OClO_3)(OH_2)](ClO_4)_2$; $[Fe(3\text{-m-N-iqO})_4(OClO_3)_2](ClO_4)$ (similar

to the tri-n-butylphosphine oxide analog [60]); $[Fe(3-m-N-iqO)_3(OClO_3)(OH_2)_2](ClO_4)_2$; $[M(3-m-N-iqO)_5(OClO_3)](ClO_4)$ (M = Mn, Ni); $[Co(3-m-N-iqO)_5(OClO_3)](ClO_4) \cdot H_2O$. Pentacoordinated complexes: $[M(3-m-N-iqO)_4(OClO_3)](ClO_4)$ (M = Fe, Cu); regarding the Cu^{2+} complex, it should be remarked that the formation of a $[CuL_4(OClO_3)]^+$ complex cation is rather unusual for cationic complexes of this metal ion with aromatic amine N-oxides, which are almost invariably square-planar of the $[CuL_4]^{2+}$ type [2, 3, 6–8]. Tetracoordinated complex: $[Zn(3-m-N-iqO)_3(OClO_3)](ClO_4) \cdot 3H_2O$; this compound is most probably pseudotetrahedral, in view of the tendency of Zn^{2+} to assume a tetrahedral rather than square-planar configuration in its tetracoordinated compounds.

Finally, the isolation of a mixture, mainly consisting of $[(3-m-N-iqO)_2H](ClO_4)$, contaminated with small amounts of $[Fe(3-m-N-iqO)_6](ClO_4)_3$ (grey Fe^{3+} product) is not unprecedented. In fact, adduct formation between aromatic amine N-oxides and mineral [39, 61] or organic [62] acids occurs quite readily, and several attempts at the synthesis of metal perchlorate complexes with N- or P-oxide ligands have reportedly resulted in the precipitation of either the perchloric acid adduct of the ligand [63] or a mixture of this adduct with authentic metal complex [40].

References

1 A. N. Speca, L. S. Gelfand, F. J. Iaconianni, L. L. Pytlewski, C. M. Mikulski and N. M. Karayannis, *Proceedings, XIX ICCC, Prague, Czechoslovakia*, September 4–8, 1978; Vol. II, 116a.
2 R. G. Garvey, J. H. Nelson and R. O. Ragsdale, *Coord. Chem. Rev., 3*, 375 (1968).
3 N. M. Karayannis, L. L. Pytlewski and C. M. Mikulski, *Coord. Chem. Rev., 11*, 93 (1973).
4 J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree, *J. Am. Chem. Soc., 83*, 3770 (1961).
5 R. L. Carlin, *J. Am. Chem. Soc., 83*, 3773 (1961).
6 R. Whyman, W. E. Hatfield and J. S. Paschal, *Inorg. Chim. Acta, 1*, 113 (1967).
7 J. Reedijk, *Rec. Trav. Chim. Pays-Bas, 88*, 499 (1969).
8 W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem., 7*, 1835 (1968).
9 N. P. Crawford and G. A. Melson, *J. Chem. Soc. A*, 141 (1970).
10 N. M. Karayannis, M. J. Strocko, C. M. Mikulski, E. E. Bradshaw, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem., 32*, 3962 (1970).
11 D. W. Herlocker, *J. Inorg. Nucl. Chem., 34*, 389 (1972).
12 B. A. Coyle and J. A. Ibers, *Inorg. Chem., 9*, 767 (1970).
13 J. H. Nelson and R. O. Ragsdale, *Inorg. Chim. Acta, 2*, 439 (1968).
14 N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chem., 13*, 1146 (1974).
15 N. M. Karayannis, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 3*, 415 (1969); N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem., 33*, 3185 (1971).
16 N. M. Karayannis, C. M. Mikulski, L. S. Gelfand, E.S.C. Schwartz and L. L. Pytlewski, *J. Inorg. Nucl. Chem., 39*, 1555 (1977).
17 N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem., 34*, 3139 (1972).
18 V. S. Hagley, R. E. Kohrman and D. X. West, *J. Inorg. Nucl. Chem., 39*, 1959 (1977).
19 R. E. Kohrman, P. G. Phadtare and D. X. West, *J. Inorg. Nucl. Chem., 37*, 301, 1296 (1975); D. X. West, *Inorg. Nucl. Chem. Lett., 14*, 155 (1978).
20 S. A. Boyd, R. E. Kohrman and D. X. West, *J. Inorg. Nucl. Chem., 38*, 1605 (1976); C. A. Frank and D. X. West, *ibid., 39*, 793, 1452 (1977).
21 J. H. Nelson, L. C. Nathan and R. O. Ragsdale, *Inorg. Chem., 7*, 1840 (1968).
22 J. H. Nelson and R. O. Ragsdale, *Inorg. Chim. Acta, 2*, 230 (1968).
23 L. C. Nathan and R. O. Ragsdale, *Inorg. Chim. Acta, 3*, 473 (1969).
24 P. R. Murthy and C. C. Patel, *Can. J. Chem., 42*, 856 (1964).
25 V. Krishnan and C. C. Patel, *Can. J. Chem., 43*, 2685 (1965).
26 V. Krishnan and C. C. Patel, *Can. J. Chem., 44*, 972 (1966).
27 R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc., 88*, 1399 (1966).
28 R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc., 87*, 5350 (1965).
29 C. J. Popp, L. C. Nathan, T. E. McKean and R. O. Ragsdale, *J. Chem. Soc. A*, 2394 (1970).
30 G. B. Aitken and G. P. McQuillan, *Inorg. Chim. Acta, 15*, 221 (1975).
31 L. El-Sayed and R. O. Ragsdale, *Inorg. Chem., 6*, 1644 (1967).
32 B. Jezowska-Trzebiatowska and H. Wieczorek, *Bull. Acad. Pol. Sci., Ser. Sci. Chim., 25*, 407, 443 (1977).
33 Y. Muto, M. Kato, H. B. Jonassen and L. C. Cusachs, *Bull. Chem. Soc. Japan, 42*, 417 (1969).
34 J. J. MacDougall, L. C. Nathan and J. H. Nelson, *Inorg. Chim. Acta, 17*, 243 (1976).
35 P. W. N. M. van Leeuwen and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett., 3*, 145 (1967).
36 L. C. Nathan, J. Cullen and R. O. Ragsdale, *Inorg. Nucl. Chem. Lett., 12*, 137 (1976).
37 C. M. Mikulski, L. S. Gelfand, L. L. Pytlewski, J. S. Skryantz and N. M. Karayannis, *Inorg. Chim. Acta, 21*, 9 (1977).
38 N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 8*, 91 (1974).
39 J. Reedijk, H. D. K. Codee and W. L. Groeneveld, *J. Inorg. Nucl. Chem., 35*, 1014 (1973).
40 D. E. Chasan, L. L. Pytlewski, C. Owens and N. M. Karayannis, *Ann. Chim. (Paris), Ser. XV, 1*, 241 (1976).
41 J. T. Donoghue and R. S. Drago, *Inorg. Chem., 1*, 866 (1962); *2*, 1158 (1963).
42 Y. Kakiuti, S. Kida and J. V. Quagliano, *Spectrochim. Acta, 19*, 201 (1963).
43 L. C. Nathan and R. O. Ragsdale, *Inorg. Chim. Acta, 10*, 177 (1974).
44 H. Shindo, *Chem. Pharm. Bull., 8*, 845 (1960).
45 I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta, 20*, 429 (1964).
46 M. Hass and G. B. B. M. Sutherland, *Proc. Roy. Soc., 236A*, 427 (1956).
47 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961); B. J. Hathaway, D. G. Holah and M. Hudson, *ibid.*, 4586 (1963).
48 A. E. Wickenden and R. A. Krause, *Inorg. Chem., 4*, 404

(1965); S. F. Pavkovic and D. W. Meek, *ibid.*, *4*, 1091 (1965); M. E. Farago, J. M. James and V. C. G. Trew, *J. Chem. Soc. A*, 820 (1967).

49 W. J. Geary, *Coord. Chem. Rev.*, *7*, 81 (1971).

50 N. M. Karayannis, C. M. Mikulski and L. L. Pytlewski, *Chimika Chronika, New Ser.*, *3*, 121 (1974).

51 V. M. Vdovenko, L. G. Mashirov and D. N. Sugloblov, *Radiokhimiya*, *9*, 37 (1967).

52 A. D. van Ingen Schenau, W. L. Groeneveld and J. Reedijk, *Spectrochim. Acta*, *30A*, 213 (1974); A. D. van Ingen Schenau, C. Romers, D. Knetsch and W. L. Groeneveld, *ibid.*, *33A*, 859 (1977).

53 A. T. Hutton and D. A. Thornton, *J. Mol. Struct.*, *39*, 33 (1977).

54 K. Ichida, Y. Kuroda, D. Nakamura and M. Kubo, *Spectrochim. Acta*, *28A*, 2433 (1972).

55 J. R. Ferraro and A. Walker, *J. Chem. Phys.*, *42*, 1278 (1965).

56 B. N. Figgis and J. Lewis, *Progress in Inorg. Chem.*, *6*, 37 (1964).

57 W. Byers, B. Fa-Chun Chou, A. B. P. Lever and R. V. Parish, *J. Am. Chem. Soc.*, *91*, 1329 (1969).

58 M. Ciampolini and N. Nardi, *Inorg. Chem.*, *5*, 41, 1150 (1966); *6*, 445 (1967); M. Ciampolini and G. P. Speroni, *ibid.*, *5*, 45 (1966).

59 I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. A*, 1678 (1968); A. A. G. Tomlinson and B. J. Hathaway, *ibid. A*, 1685 (1968).

60 N. M. Karayannis, C. M. Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, *9*, 582 (1970).

61 M. Szafran, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, *11*, 111 (1956).

62 Z. Dega-Szafran, Z. Naskret-Barciszewska and M. Szafran, *Rocz. Chem.*, *47*, 749 (1973).

63 H. Gehrke, D. Eastland, L. Haas and G. Carlson, *Inorg. Chem.*, *10*, 2328 (1971).