

## Quinoxaline 1,4-Dioxide Complexes with Transition Metal Chlorides [1]

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3d metal chloride complexes with quinoxaline 1,4-dioxide were prepared and characterized by means of spectral and magnetic studies. Cr(III) and Fe(III) chlorides formed monomeric complexes of the types  $[\text{CrCl}_3\text{L}(\text{OH}_2)_2] \cdot \text{H}_2\text{O}$  and  $[\text{FeCl}_3\text{L}_2(\text{OH}_2)] \cdot 6\text{H}_2\text{O}$ , involving unidentate L, aqua ligands and lattice water, while  $\text{NiCl}_2$  yielded the chloride-bridged dimer  $[(\text{OH}_2)\text{ClL}_2\text{NiCl}_2\text{NiL}_2\text{Cl}(\text{OH}_2)]$ , which also comprises unidentate L groups, coordinated through one of the N–O oxygens. The rest of the new complexes contain bridging L of two types, viz.: i)  $\text{L}_\text{O}$ , with one of the N–O oxygens acting as a bridge between adjacent metal ions; or ii)  $\text{oL}_\text{O}$ , with L functioning as a bidentate bridging ligand (i.e., each N–O oxygen is coordinated to a different metal ion). The former type of bridging leads to subnormal paramagnetism for the Co(II) and Cu(II) complexes, which appear to be of the types  $[\text{Cl}_2\text{LCo}(\text{L}_\text{O})_2\text{CoLCl}_2] \cdot 8\text{H}_2\text{O}$  and  $[\text{Cu}_4\text{Cl}_8(\text{L}_\text{O})_4(\text{oL}_\text{O})_2] \cdot 4\text{H}_2\text{O}$  (the Cu(II) compound involves bridging L of both types). Spin–spin coupling occurs in the preceding complexes by a superexchange mechanism, operating through the orbitals of the bridging oxygen atoms of the  $\text{L}_\text{O}$  bridging ligands. The new Mn(II) and Zn(II) complexes are polynuclear  $([\text{MCl}_2\text{L}_2]_n \cdot nx\text{H}_2\text{O}; x = 0 \text{ for } M = \text{Mn}; x = 1 \text{ for } M = \text{Zn})$ , with bridging chloro and bidentate,  $\text{oL}_\text{O}$ , ligands. The Cr(III), Mn(II) and Ni(II) complexes are magnetically normal high-spin compounds, but the Fe(III) complex is magnetically subnormal. This compound involves spin-state equilibria, as suggested by the variation of its magnetic susceptibility with temperature; two possible types of equilibria, i.e., high-intermediate ( $S = 5/2 - S = 3/2$ ) and high-low ( $S = 5/2 - S = 1/2$ ) spin, are discussed.

### Introduction

Several pyrazine 1-oxide (N-pyzO) [2–4], quinoxaline 1-oxide (N-qxO) [5, 6] and phenazine 5-oxide (N-phzO) [7] metal complexes have been reported in recent years. Less information is available on metal complexes of the corresponding N,N-dioxides. Schöllhorn and Weiss have prepared an intercalation compound of  $\text{TiS}_2$  with quinoxaline 1,4-dioxide (N,N-qxO<sub>2</sub>) [8], Kidani *et al.* synthesized and characterized  $\text{CuX}_2$  (X = Cl, Br) complexes with the same ligand and alkyl or aryl substituted derivatives [5], these laboratories reported recently on 3d metal chloride complexes with phenazine 5,10-dioxide (N,N-phzO<sub>2</sub>) [9], and a number of pyrazine 1,4-dioxide (N,N-pyzO<sub>2</sub>) complexes with lanthanide-(III) perchlorates and silver nitrate [10] were also prepared and characterized. In addition, a number of Cu(II) chelates with –COOH or –OH substituted N,N-qxO<sub>2</sub> or N,N-phzO<sub>2</sub> have been reported [11]. We have now extended our studies on metal complexes of diazine N-oxides, to include transition metal complexes with N,N-qxO<sub>2</sub>. The present paper deals with the syntheses and characterization of N,N-qxO<sub>2</sub> complexes with 3d metal chlorides.

### Experimental

#### Chemicals

Reagent grade chemicals were used throughout this work. N,N-qxO<sub>2</sub> was prepared by the method of McIlwain [12], and its authenticity was confirmed by elemental analysis and melting point (238–239 °C) [12], infrared [5, 13, 14] and electronic [5, 13, 15] spectra.

### Preparative Methods

The Cr(III) complex is very hygroscopic and its preparation and filtration necessitate dry nitrogen atmosphere (dry-box). Although the rest of the new complexes are air-stable, their preparations were also performed in the dry-box. Most of the new complexes were synthesized by the standard procedure previously described for metal chloride complexes with N-qxO, N-phzO and N,N-phzO<sub>2</sub> [6, 7, 9, 16], viz.: The hydrated or anhydrous metal chloride (1 mmol) was dissolved in the minimum required amount of acetone (20 ml for Cr(III), Fe(II), Fe(III), Co(II), Cu(II) and Zn(II) chlorides and 75 ml for MnCl<sub>2</sub>), and the resulting solution was stirred for 30 min with *ca.* 3 g molecular sieve 4A (Davison, grade 515). N,N-qxO<sub>2</sub> (3.5 mmol) was dissolved separately in 50 ml chloroform and treated with 3 g molecular sieve 4A, in the same manner as above. The ligand solution was then filtered through a medium sintered glass funnel into a filtering flask, containing a magnetic stirring bar, and the metal chloride solution was subsequently filtered through a similar funnel into the stirred ligand solution. Precipitation was immediate in most cases, with the exception of FeCl<sub>2</sub>, which failed to produce a solid precipitate by various alternative approaches examined (*e.g.*, addition of a large excess of anhydrous diethyl ether or ligroin, evaporation of the supernatant liquid, refrigeration). In the case of NiCl<sub>2</sub>, which is insufficiently soluble in acetone, a solid precipitate was obtained by interaction of a ligand solution in chloroform (3.5 mmol), pretreated with molecular sieve 4A, with a NiCl<sub>2</sub> (1 mmol) solution in a minimum amount of a 3:2 (v/v) mixture of ethanol-triethyl orthoformate (*ca.* 10 ml). The new metal complexes were filtered, quickly washed with hexane, and stored in an evacuated desiccator over P<sub>2</sub>O<sub>5</sub>. Regarding the effectiveness of the molecular sieves used during the synthetic work, it should be mentioned that they were either obtained from a fresh container, opened

shortly before use, or were regenerated by a stream of N<sub>2</sub> at 315 °C for 2 hr.

Analytical results (C, H, N analyses by Schwarzkopf Microanalytical Laboratory, Woodside, New York; metals analyses by atomic absorption spectroscopy) are given in Table I. The new metal complexes dissolve in water, dimethylsulfoxide, N,N-dimethylformamide and alcohols with apparent dissociation, suggested by dramatic color changes. A number of other solvents dissolve some of the complexes, as follows. Nitrobenzene: Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>; nitromethane: Fe<sup>3+</sup>; chloroform: Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>; acetone: Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>. Differences in the colors of the solutions of the complexes in the latter solvents from the colors of the solid complexes, indicate that the new compounds reported have the general tendency to dissociate in solution. The following melting points were determined: Fe(III) complex, 167–169 °C (decomposes); Co(II), 269–271 °C (decomposes); Cu(II), 222–225 °C; Zn(II), 225 °C. The other three complexes (Cr(III), Mn(II), Ni(II)) start shrivelling and darkening at 250–305 °C, but do not melt at temperatures up to 400 °C.

### Characterization Studies

Infrared spectra (Tables II, III), solid-state electronic spectra and magnetic susceptibility measurements (Table IV) were obtained by methods described elsewhere [3, 6]. The instability of the new complexes in solution did not allow the performance of solution electronic spectral or molar conductivity studies.

### Discussion

#### Stoichiometries of the New Metal Complexes

With the exception of the Mn(II) complex, the new compounds contain water molecules. This is apparently due to the method of preparation employ-

TABLE I. Analytical Data for N,N-qxO<sub>2</sub> Complexes With 3d Metal Chlorides.

Complex <sup>a</sup>	Color	Analyses							
		C %		H %		N %		Metal %	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
CrCl <sub>3</sub> L·3H <sub>2</sub> O	Greenish Gray	25.65	25.59	3.24	3.58	7.48	7.17	13.9	13.6
MnCl <sub>2</sub> L <sub>2</sub>	Lime Green	42.69	42.31	2.69	2.82	12.45	12.11	12.2	11.9
FeCl <sub>3</sub> L <sub>2</sub> ·7H <sub>2</sub> O	Olive Gray	31.42	31.41	4.28	4.01	9.16	9.35	9.1	8.6
CoCl <sub>2</sub> L <sub>2</sub> ·4H <sub>2</sub> O	Chartreuse	36.52	36.72	3.84	3.55	10.67	10.82	11.2	11.1
NiCl <sub>2</sub> L <sub>2</sub> ·H <sub>2</sub> O	Deep Yellow	40.71	41.18	3.00	3.08	11.89	11.69	12.4	11.9
(CuCl <sub>2</sub> ) <sub>2</sub> L <sub>3</sub> ·2H <sub>2</sub> O	Olive Green	36.42	36.21	2.81	2.54	10.62	10.75	16.1	15.7
ZnCl <sub>2</sub> L <sub>2</sub> ·H <sub>2</sub> O	Yellow	40.15	40.47	2.95	2.66	11.73	11.33	13.7	13.6

<sup>a</sup> L = N,N-qxO<sub>2</sub>.

TABLE II. The  $\nu_{N-O}$  Spectral Region for N,N-qxO<sub>2</sub>-Metal Chloride Complexes (cm<sup>-1</sup>).<sup>a</sup>

N,N-qxO <sub>2</sub>	1373s	1346m	1320m	1311m	1287s	1230s	1174w		
M									
Cr <sup>3+</sup>	1388s		1323m		1284m	1240m, sh	1223m	1180m	
Mn <sup>2+</sup>	1386s	1352w	1331m		1290s	1240m	1225m	1187w	1164m
Fe <sup>3+</sup>	1385s		1330m		1285m	1240m, sh	1221m	1180m	1161m
Co <sup>2+</sup>	1387s		1325m		1282m	1240m, sh	1220m	1179m	1161m
Ni <sup>2+</sup>	1376s		1329m		1283s	1238m	1221m	1188m	1161m
Cu <sup>2+</sup>	1380s		1326m	1295w	1280m	1245m	1218m	1170m	1160m
Zn <sup>2+</sup>	1378s, 1370s		1331m		1278s	1243m	1214m	1196m, sh	1174s

<sup>a</sup>Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

TABLE III. Far Infrared Spectra (525–33 cm<sup>-1</sup>) of N,N-qxO<sub>2</sub> Complexes with Metal Chlorides (cm<sup>-1</sup>).<sup>a</sup>

Compound	Main Far-ir Maxima
N,N-qxO <sub>2</sub> = L	491w, 475w, 419m, 384m, 295m, 218w, 164m, 146m, 129w, sh, 124w, sh, 114w, sh, 94w
CrCl <sub>3</sub> L·3H <sub>2</sub> O	525m, 493w, b, 448w, 419w, 385w, 343m, 337m, 311w, 188w, b
MnCl <sub>2</sub> L <sub>2</sub>	504m, 493w, 411m, 382w, 320m, 270w, 259w, 223m, 204m, 173s, 148w, 137w, 124w, 114w
FeCl <sub>3</sub> L <sub>2</sub> ·7H <sub>2</sub> O	511w, 500w, sh, 430w, 417w, 385m, 373w, 365m, 320m, 311m, sh, 290w, sh, 194w, b
CoCl <sub>2</sub> L <sub>2</sub> ·4H <sub>2</sub> O	508w, sh, 499m, 429m, sh, 417m, 383m, 375m, sh, 317w, sh, 307m, 281w, 258w, 249w, b, 198m, b, 180m, 163w, 146w, 137w, 129w, 123w, 116w, 102w, 97w
NiCl <sub>2</sub> L <sub>2</sub> ·H <sub>2</sub> O	507m, 495m, 467w, 435m, 415m, 381m, 328m, 254m, sh, 228m, 208m, 191s, 152w, 126w, 112w
(CuCl <sub>2</sub> ) <sub>2</sub> L <sub>3</sub> ·2H <sub>2</sub> O	515w, 499w, 470w, 445w, b, 421w, 416w, 379m, sh, 376m, 326m, 307w, 284w, 264w, 211w, 178w, 168w, sh, 121w, 90w
ZnCl <sub>2</sub> L <sub>2</sub> ·H <sub>2</sub> O	503m, 494w, 432w, 420m, 383m, 331s, 321m, sh, 296m, 258w, 246w, 209w, 185w, 166w, b, 149m, 128m, 115m

<sup>a</sup>Abbreviations: s, strong; m, medium; w, weak; b, broad; v, very; sh, shoulder.

TABLE IV. Electronic Spectra (Nujol mull) and Magnetic Properties (297 °K) of N,N-qxO<sub>2</sub> Complexes with Metal Chlorides.

Compound	$\lambda_{max}$ , nm	$10^6 \chi_A^{cor}$ , cgsu	$\mu_{eff}$ , $\mu_B$
N,N-qxO <sub>2</sub> = L	260s, sh, 385m, 438m		
CrCl <sub>3</sub> L·3H <sub>2</sub> O	267vs, 399vs, 458s, sh, 649m, sh, 659m, sh, 695m-w, sh	6745	4.04
MnCl <sub>2</sub> L <sub>2</sub>	265s, 390s, 413s, 525m, sh, 550m, vb, sh	14,465	5.92
FeCl <sub>3</sub> L <sub>2</sub> ·7H <sub>2</sub> O	228vs, 250sh, 405vs	11,553	5.26
CoCl <sub>2</sub> L <sub>2</sub> ·4H <sub>2</sub> O	227m, 262m, b, 409m, b, 465m, sh, 512m-w, 543w-m, 559w-m, 612w, 670w, 739w, sh, 840w, b, 1175vw, b	7015	4.12 <sup>a</sup>
NiCl <sub>2</sub> L <sub>2</sub> ·H <sub>2</sub> O	267s, 410s, b, 623m, sh, 815m-w, b, 1140w, b, 1330w, b	4829	3.40
(CuCl <sub>2</sub> ) <sub>2</sub> L <sub>3</sub> ·2H <sub>2</sub> O	226vs, 259sh, 398s, 480s, sh, 499s, 559m-s, 685w, b, 880m-w, vb	454	1.04 <sup>a</sup>
ZnCl <sub>2</sub> L <sub>2</sub> ·H <sub>2</sub> O	253vs, sh, 394s, b	diamagnetic	

<sup>a</sup> $\mu_{eff}$  values at lower temperatures: Co<sup>2+</sup> complex: 203 °K, 4.08  $\mu_B$ ; 177 °K, 4.06  $\mu_B$ ; 159 °K, 4.05  $\mu_B$ ; 143 °K, 4.04  $\mu_B$ . Cu<sup>2+</sup> complex: 203 °K, 0.98  $\mu_B$ ; 177 °K, 0.95  $\mu_B$ ; 159 °K, 0.91  $\mu_B$ ; 143 °K, 0.88  $\mu_B$ .

Abbreviations: s, strong; m, medium; w, weak; b, broad; v, very; sh, shoulder.

ed. Molecular sieve 4A is not as effective a dehydrating agent as triethyl orthoformate or 2,2-dimethoxypropane [17], which are usually utilized for the syntheses of anhydrous coordination compounds. However, as pointed out previously [6, 16], the latter dehydrating agents, which produce alcohols during their hydrolyses [17], do not facilitate the precipitation of 3d metal complexes with quinoxaline and

phenazine N-oxides and N,N-dioxides. This is obviously due to the dissociation of these complexes in the presence of the alcohol liberated. The Ni(II) and Cu(II) chloride complexes with N,N-qxO<sub>2</sub> are somewhat more resistant to the presence of ethanol, as demonstrated by the fact that the new Ni(II) complex was precipitated in the presence of ethanol-triethyl orthoformate (this precipitate, nevertheless,

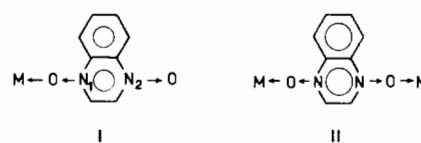
decomposes if allowed to remain suspended in the supernatant liquid for more than 1–2 min), whereas Kidani *et al.* reportedly obtained  $\text{CuCl}_2$  and  $\text{CuBr}_2$  complexes with  $\text{N,N-qxO}_2$  from ethanolic solutions, at moderately elevated temperatures [5]. In all other cases investigated, no solid 3d metal chloride complexes with  $\text{N,N-qxO}_2$  could be obtained by using triethyl orthoformate or 2,2-dimethoxypropane as the reaction medium. Under our synthetic conditions,  $\text{CrCl}_3$  produced a 1:1 complex,  $\text{Mn(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$  and  $\text{Zn(II)}$  chlorides 1:2 complexes, and  $\text{CuCl}_2$  a 2:3 complex with  $\text{N,N-qxO}_2$  (Table I). It is worth mentioning here that one referee suggested that exposure of ligand and salt to molecular sieve 4A for only 30 min is probably too short to effect complete dehydration. In view of this comment, we intend to explore the possibility of preparing anhydrous  $\text{N,N-qxO}_2$  complexes, by substantially increasing the contact time (1–2 days) of our reagents with the molecular sieve, in the near future.

### Infrared Spectra

As Kidani *et al.* pointed out [5], previous assignments for the  $\nu_{\text{N-O}}$  mode at 1370 [14] and 1342 [13]  $\text{cm}^{-1}$  are probably at too high frequencies for free  $\text{N,N-qxO}_2$ , in view of the fact that  $\nu_{\text{N-O}}$  occurs at 1258  $\text{cm}^{-1}$  in  $\text{N,N-pyzO}_2$  [18] and 1270, 1257  $\text{cm}^{-1}$  in  $\text{N,N-phzO}_2$  [9, 19]. Kidani proposed that both bands at 1373 and 1287  $\text{cm}^{-1}$  in  $\text{N,N-qxO}_2$  may have  $\nu_{\text{N-O}}$  character [5]. Comparison of the ir spectra of quinoxaline (qx) [20],  $\text{N-qxO}$  ( $\nu_{\text{N-O}}$  at 1325–1319  $\text{cm}^{-1}$ ) [5, 6] and  $\text{N,N-qxO}_2$ , shows that each of these compounds exhibits a band at ca. 1370  $\text{cm}^{-1}$ , which is shifted to higher frequencies upon 3d metal complex formation. The parent base shows also a band at 1356  $\text{cm}^{-1}$ , undergoing small positive frequency shifts in its metal complexes [20]. Both qx and  $\text{N-qxO}$  do not have ir absorptions at 1300–1270 and 1240–1210  $\text{cm}^{-1}$  [5, 6, 20]. Hence, it is considered as likely that the strong  $\text{N,N-qxO}_2$  absorptions at 1287 and 1230  $\text{cm}^{-1}$  (Table II) have predominantly  $\nu_{\text{N-O}}$  character. It should be noted at this point, that difficulties in assigning  $\nu_{\text{N-O}}$  with certainty have been encountered in infrared studies of several other aromatic amine N-oxides (*e.g.*, quinoline and acridine N-oxides) [21].

The variations of the ligand bands in the  $\nu_{\text{N-O}}$  region, upon complex formation with the various metal ions studied, are shown in detail in Table II. The ligand bands at 1373 and 1320  $\text{cm}^{-1}$  show small positive shifts, and those at 1346 and 1311  $\text{cm}^{-1}$  disappear, in most cases. Whereas the absorptions at 1287 and 1230  $\text{cm}^{-1}$  appear to produce invariably four bands in the 1290–1170  $\text{cm}^{-1}$  region, upon metal complex formation. Coordination of  $\text{N,N-qxO}_2$  through one of the oxygens, as in (I), would obviously result in dissimilar N–O bonds. Considering pure  $\sigma$ -bonding, one would expect the drain of elec-

trons towards the metal ion to decrease the bond order of  $\text{N}_1\text{--O}$ , while increasing the bond order of  $\text{N}_2\text{--O}$  [22, 23]. However, 3d metal ions (including  $\text{Zn(II)}$ ) have a definite tendency for  $d_\pi\text{--}p_\pi$  back-bonding in their complexes with aromatic amine N-oxides [23];  $\pi$ -bonding would tend to minimize the above effects of  $\sigma$ -bonding. In general, the effects of  $\sigma$ -bonding predominate over those of  $\pi$ -bonding, as indicated by negative  $\nu_{\text{N-O}}$  frequency shifts in 3d metal complexes with N-oxides of aromatic monoamines (pyridine and derivatives) [23, 24]. On the other hand, coordination of  $\text{N,N-qxO}_2$  through both oxygens, as in (II), would tend to leave the  $\nu_{\text{N-O}}$  relatively unchanged [25]. In light of the preceding discussion, each of the ligand bands at 1287 and 1230  $\text{cm}^{-1}$  is split into two components, one located relatively close to the above frequencies and another exhibiting a substantial negative frequency shift (42–



60  $\text{cm}^{-1}$ ), in the spectra of the complexes; the former of these components presumably corresponds to uncomplexed N–O and the latter to coordinated N–O. Hence, it appears that in all the new complexes, at least part of the  $\text{N,N-qxO}_2$  ligands are coordinated through only one of the N–O oxygens.

The  $\delta_{\text{N-O}}$  mode in  $\text{N,N-qxO}_2$  is probably associated with a band at 814  $\text{cm}^{-1}$ ; this band exhibits small shifts and splittings in the spectra of the metal complexes, as expected [24]. In the  $\nu_{\text{OH}}$  (water) region, the  $\text{Co(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$  complexes show a weak very broad absorption, covering the 3600–3200  $\text{cm}^{-1}$  region, and attributable to the presence of lattice water [26], while the  $\text{Ni(II)}$  complex shows, in contrast, a more intense and relatively sharp band with its maximum at 3300  $\text{cm}^{-1}$ , suggestive of the exclusive presence of aqua ligands [27]. The  $\text{Cr(III)}$  and  $\text{Fe(III)}$  compounds exhibit both the above types of  $\nu_{\text{OH}}$  bands and seem, therefore, to contain both aqua ligands and lattice water. Finally, the spectrum of the water-free  $\text{Mn(II)}$  complex is devoid of  $\nu_{\text{OH}}$  absorptions.

Tentative metal–ligand band assignments in the lower frequency ir-region (Table III) were based on analogous studies with  $\text{N,N-qxO}_2$  [5] and related ligands [2, 3, 6, 7, 28–31], as well as 3d metal chloride [31–34] and aqua [35] complexes. The ligand bands at 419 and 384  $\text{cm}^{-1}$  seem to be relatively insensitive to metal complex formation. The spectrum of the new  $\text{Cu(II)}$  complex is different from that of  $\text{Cu(N,N-qxO}_2)_2\text{Cl}_2$  (reported by Kidani *et al.*), which exhibits the  $\nu_{\text{Cu-O}}$  mode at 397 and  $\nu_{\text{Cu-Cl}}$  at 323 and 276  $\text{cm}^{-1}$  [5]. Our band assignments for  $(\text{CuCl}_2)_2(\text{N,N-qxO}_2)_3 \cdot 2\text{H}_2\text{O}$  ( $\nu_{\text{Cu-O}}$  445, 376;

$\nu_{\text{Cu-Cl}}$  326, 307, 264  $\text{cm}^{-1}$ ) favor a lower than hexacoordinated configuration [29–31, 34], probably involving two different types of N,N-qxO<sub>2</sub> ligands [31]. For the Co(II) complex, the following band assignments are made:  $\nu_{\text{Co-O}}$  at 375, 307 and  $\nu_{\text{Co-Cl}}$  at 281, 258, 249  $\text{cm}^{-1}$ . These assignments favor coordination number five [30, 34] and the presence of both terminal and bridging N,N-qxO<sub>2</sub> [31]. The rest of the new metal complexes appear to be hexacoordinated, on the basis of the following metal-ligand band assignments (in  $\text{cm}^{-1}$ ) [28–30, 32–35], and electronic spectral evidence (*vide infra*):  $\nu_{\text{M-O}}$  (aqua): Cr 493; Fe 500; Ni 435;  $\nu_{\text{M-O}}$  (N,N-qxO<sub>2</sub>): Cr 448; Mn 320, 270; Fe 430; Ni 328; Zn 331, 321, 296;  $\nu_{\text{M-Cl}}$ : Cr 343, 337, 311; Mn 259, 223, 204; Fe 365, 320, 311; Ni 254, 228, 208, 191; Zn 258, 246, 209. From these data, it seems that the Mn(II) and Zn(II) complexes comprise both terminal and bridging N,N-qxO<sub>2</sub> and chloro ligands, while the Ni(II) compound is characterized by the presence of terminal N,N-qxO<sub>2</sub> and both terminal and bridging chloro groups [31].

Certain far-ir ligand bands, that may be due to N–O vibrations, are those at 295 and 164  $\text{cm}^{-1}$ . In fact, both these bands are absent from the spectrum of the parent base [36], and are obviously metal-sensitive (Table III). These absorptions are, thus, assigned as the  $\beta_{\text{N-O}}$  (295) and  $\gamma_{\text{N-O}}$  (164) modes of the ligand [37]. No assignments of these modes in the spectra of the metal complexes are attempted, since there is undoubtedly considerable overlap between these N–O bands and various metal–ligand stretching and bending modes [29, 36].

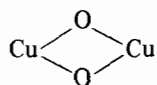
#### Electronic Spectra and Magnetic Properties

The new Cr(III), Mn(II) and Ni(II) complexes exhibit normal magnetic moments (Table IV) for high-spin compounds of these metal ions [38]. The  $\mu_{\text{eff}}$  of the Fe(III) complex (5.26  $\mu\text{B}$ ) is somewhat low for spin-free Fe<sup>3+</sup>. The corresponding N-qxO complex ((FeCl<sub>3</sub>)<sub>2</sub>(N-qxO)<sub>3</sub>·2H<sub>2</sub>O), has a  $\mu_{\text{eff}}$  of 3.71  $\mu\text{B}$ , and was characterized as involving spin-free ( $S = 5/2$ )–spin-paired ( $S = 1/2$ ) equilibria [6], by analogy to several aromatic amine N-oxide ferric complexes, which show equilibria of this type [39]. Studies of the temperature dependence of the magnetic susceptibility of the new Fe(III) complex, conducted by Professor A.B.P. Lever's laboratory (York University, Toronto, Ont., Canada; the fully automated Faraday magnetic balance system used has been described in the literature [40]), gave the following results (each set of three numbers shows the temperature (°K),  $10^6 \chi_{\text{M}}$  (cgs units) and (in italics) the  $\mu_{\text{eff}}$  ( $\mu\text{B}$ ) values): 315.1, 10,883, 5.26; 296.8, 11,553, 5.26; 278.8, 12,222, 5.24; 260.0, 13,018, 5.22; 241.7, 13,896, 5.21; 223.5, 14,942, 5.19; 205.1, 16,114, 5.16; 187.6, 17,539, 5.15; 169.5, 19,258, 5.13; 152.1, 21,184, 5.10; 134.4, 23,828,

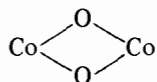
5.08; 117.1, 27,144, 5.06; 99.9, 31,554, 5.04; 81.3, 37,216, 4.93 (the sample decomposes at temperatures above 315 °K, as indicated by loss of weight). The preceding data might be interpreted in terms of either high–low ( $S = 5/2$ – $S = 1/2$ ,  ${}^6\text{A}_1$ – ${}^2\text{T}_2$  ground states) [39, 41–44] or high–intermediate ( $S = 5/2$ – $S = 3/2$ ,  ${}^6\text{A}_1$ – ${}^4\text{T}_1$  ground states) [45, 46] spin equilibria. By assuming  $\mu_{\text{eff}}$  values of 5.92, 3.80 and 2.30  $\mu\text{B}$  for the  $S = 5/2$ ,  $S = 3/2$  and  $S = 1/2$  states, respectively, the high-spin isomer content would decrease from 75% to 64% in the former, and from 64% to 48% in the latter case, as the temperature decreases from 315° to 81 °K [44]. For  ${}^6\text{A}_1$ – ${}^2\text{T}_2$  equilibria, the energy separation  $E$  between the two ground states was determined by fitting the experimental data in the calculated  $E/\zeta$  curve diagrams ( $\mu_{\text{eff}}$  vs.  $\text{KT}/\zeta$  plots; assumptions:  $\zeta = 370 \text{ cm}^{-1}$ ;  $g = 2.0$ ;  $k$  is calculated at 0.7) [41, 42], to be ca.  $-340 \text{ cm}^{-1}$  in the 314–150 °K region. This would indicate that the high-spin  ${}^6\text{A}_1$  state is the lowest lying [41–44]. However some doubt as to this type of equilibria arises from the fact that the experimental results at 150–81 °K do not follow the general trend exhibited by tris-(dialkyldithiocarbamato) [41, 42] or tris-(monothio- $\beta$ -diketonato) [43, 44] ferric chelates, which fit the  $\mu_{\text{eff}}$  vs.  $\text{KT}/\zeta$  plots fairly well. In contrast, the experimental  $E/\zeta$  curve shows severe deviation from the calculated  $E/\zeta$  curves [41], even when interaction with the  ${}^4\text{T}_1$  state and configurational mixing near the crossover point are taken into account [42]; as a result of this, an  $E/\zeta$  value of ca.  $-1.5$ , corresponding to  $E = -555 \text{ cm}^{-1}$ , is obtained for the new complex at 81.3 °K. On the other hand, the experimental results seem to be in much better agreement (at 315–81 °K) with data reported for [Fe(mcd)<sub>3</sub>]·X solvates (mcd = 4-morpholinecarbodithioato-S,S' ligand; X = CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, H<sub>2</sub>O, toluene), which involve the rather uncommon  $S = 5/2$ – $S = 3/2$  type of equilibria [45, 46]. Solvent hydrogen bonding to ligand sulfur atoms is thought to cause production of a low lying  $S = 3/2$  ground state in these solvates. The variation of  $\mu_{\text{eff}}$  with temperature for the new ferric complex at 315–81 °K is strikingly similar to that observed for [Fe(mcd)<sub>3</sub>]·H<sub>2</sub>O in the same temperature range [46]. Furthermore, the new complex is also a solvate of the probable type [FeCl<sub>3</sub>(N,N-qxO<sub>2</sub>)<sub>2</sub>(OH<sub>2</sub>)]·6H<sub>2</sub>O involving lattice water, which can conceivably form hydrogen bonds to various coordinated ligand atoms. Although the preceding discussion seems to favor high–intermediate spin equilibria for the ferric complex, for an unambiguous distinction between the two possible types of spin-state equilibria, additional magnetic susceptibility measurements at 80–4 °K would be necessary.

The room temperature magnetic moments of the Co(II) and Cu(II) complexes are also low for high-spin Co<sup>2+</sup> or a d<sup>9</sup> configuration (Table IV). Studies of the temperature dependence of the magnetic suscepti-

bilities of these compounds at 143–203 °K, performed at these laboratories by using a Cahn magnetic susceptibility system type 7600, are shown in footnote a of Table IV. In the case of Cu(II), magnetically subnormal binuclear complexes with aromatic amine N-oxides, involving N-oxide bridging, are quite common [24, 47, 48]. In these complexes, spin–spin coupling between the Cu<sup>2+</sup> ions of the dimer occurs by a superexchange mechanism, operating through the orbitals of the bridging oxygen atoms [47, 48]. The magnetic moments of such complexes undergo substantially larger decrease with decreasing temperature [47] than that observed with the new Cu(II) complex. The magnetic behavior of this complex with temperature resembles that of other polynuclear Cu(II) complexes with aromatic amine N,N-dioxides, such as CuLBr<sub>2</sub> (L = 2,2'-bipyridine N,N-dioxide) [48] and (CuCl<sub>2</sub>)<sub>2</sub>(N-phzO)<sub>3</sub>·2H<sub>2</sub>O [7], which have been formulated as involving



bridges [7, 48]; it is, thus, likely that the new Cu(II) complex has a similar structure to that proposed for the N-phzO analog [7] (*vide infra*). In the case of high-spin pentacoordinated Co(II), the region of theoretically predicted  $\mu_{\text{eff}}$  values lies between 4.20 and 4.60  $\mu\text{B}$  [49]. The overall electronegativity and nucleophilic reactivity of the O<sub>3</sub>Cl<sub>2</sub> donor set are heavily in favor of a high-spin configuration [50], so that spin-state equilibria can be ruled out for the new complex. The small decrease of  $\mu_{\text{eff}}$  with temperature in the case of this complex is presumably due to the effects of spin–spin coupling, since in magnetically normal high-spin pentacoordinated Co(II) complexes,  $\mu_{\text{eff}}$  shows small increases with decreasing temperature [51]. Hence, the magnetic evidence favors the presence of



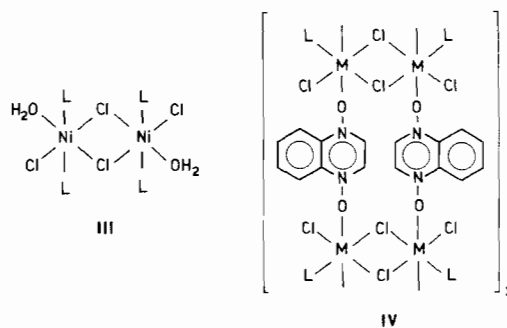
bridges in the new Co(II) compound.

The Nujol mull UV spectrum of N,N-qxO<sub>2</sub> shows bands at 260, 385 and 438 nm (Table IV). These bands undergo significant shifts and occasional splittings upon metal complex formation. The new metal complexes are also characterized by intense metal-to-ligand charge-transfer absorption, originating in the UV and trailing off into the visible region, as is commonly the case with aromatic amine N-oxide 3d metal complexes [52]. The ligand and charge-transfer absorptions overlap with some of the higher energy (d–d) bands (*e.g.*, <sup>3</sup>A<sub>2g</sub>(F)→<sup>3</sup>T<sub>1g</sub>(P) for the Ni(II) and <sup>4</sup>A<sub>2g</sub>(F)→<sup>4</sup>T<sub>1g</sub>(F) for the Cr(III) complex). The Cr(III) and Ni(II) complexes appear to be low-symmetry, hexacoordinated, as suggested by splittings of

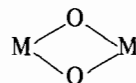
the (d–d) transition bands [53], which are assigned as follows (in nm, for pure O<sub>h</sub> symmetry): Cr(III): <sup>4</sup>A<sub>2g</sub>(F)→<sup>4</sup>T<sub>1g</sub>(F) 458; →<sup>4</sup>T<sub>2g</sub>(F) 640, 659, 695; Ni(II): <sup>3</sup>A<sub>2g</sub>(F)→<sup>3</sup>T<sub>1g</sub>(P) 410; →<sup>3</sup>T<sub>1g</sub>(F) 623, 815; →<sup>3</sup>T<sub>2g</sub>(F) 1140, 1330. The Cu(II) complex shows the most intense absorptions of the split (d–d) band at 480–560 nm; this is in favor of coordination number 4 or 5 [7, 47, 48, 54, 55]. Finally, the (d–d) spectrum of the Co(II) complex favors coordination number five, as it exhibits several maxima at 450–1200 nm [53, 55, 56], and, especially, at 739 and 840 nm [53, 56, 57].

#### Nature of the New Metal Complexes

Hexacoordinated configurations are favored by the overall evidence presented, for the Cr(III), Mn(II), Fe(III), Ni(II) and Zn(II) complexes. The M(III) complexes do not exhibit any evidence suggestive of the presence of bridging ligands, and are probably monomeric of the types [CrCl<sub>3</sub>(N,N-qxO<sub>2</sub>)(OH<sub>2</sub>)<sub>2</sub>]·H<sub>2</sub>O and [FeCl<sub>3</sub>(N,N-qxO<sub>2</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]·6H<sub>2</sub>O. The Ni(II) complex appears to be a chloro-bridged dimer of type (III), whereas structure (IV) (M = Mn, Zn), involving both terminal unidentate and bridging bidentate N,N-qxO<sub>2</sub> ligands, as well as both terminal and bridging Cl groups, is considered as most likely for the Mn(II) and Zn(II) compounds (the Zn(II) complex contains also one molecule of lattice water per Zn<sup>2+</sup> ion).

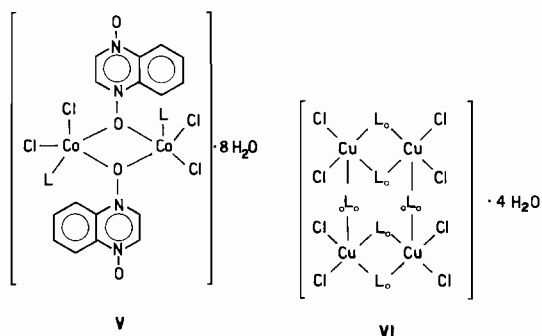


As already discussed in detail, the magnetic properties of the Co(II) and Cu(II) complexes are suggestive of spin–spin coupling, arising from the presence of



bridges. Thus, it would appear that at least part of the N,N-qxO<sub>2</sub> ligands in these compounds coordinate through one N–O oxygen, which functions as a bridging atom between neighboring metal ions. For the Co(II) complex, which is pentacoordinated and seems to comprise chemically non-equivalent N,N-qxO<sub>2</sub> ligands (large  $\nu_{\text{Co-O}}$  splitting; *vide supra*), the binuclear structure (V), involving terminal N,N-qxO<sub>2</sub>

as well as bridging of the above type (designated as  $L_O$ ) is the most compatible with the overall evidence.



Finally for the Cu(II) complex, a structural type similar to that proposed for the N-phzO analog [7], comprising both possible types of N,N-qxO<sub>2</sub> bridging groups, *i.e.*,  $L_O$  and bidentate bridging ligands (designated as  $O_L O$ ); forming bridges by coordination of each of their oxygens to a different metal ion, as was shown in structure (IV) above), is considered as most likely (structure (VI)). This structure involves pentacoordinated Cu(II).

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