

## Chromium(III), Manganese(II), Iron(III), and Zinc(II) Complexes of Some Substituted Aromatic Amine N-Oxides

L. C. Nathan<sup>1</sup> and R. O. Ragsdale

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Complexes of the type  $M(4\text{-Zquinoline N-oxide})_6(\text{ClO}_4)_n$  where  $Z = \text{CH}_3\text{O}$ ,  $\text{CH}_3$ ,  $\text{H}$ ,  $\text{Cl}$ , and  $\text{NO}_2$ , and  $M = \text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  with  $n=3$ ,  $M = \text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$  with  $n=2$ , have been studied. Also a series of  $\text{Zn}(4\text{-Zpyridine N-oxide})_6(\text{ClO}_4)_2$  complexes are reported ( $Z = \text{same as above}$ ). These new complexes have been characterized via elemental analyses, magnetic moments, molar conductance, conventional infrared spectra, and electronic absorption spectra. Low frequency infrared studies of the metal-oxygen vibrations have been carried out on these complexes and also on the cobalt and nickel quinoline N-oxide complexes previously reported. Comparisons with the complexes of the 4-substituted pyridine N-oxide are made.

### Introduction

Within the last few years there has been a considerable interest in the donor properties of various substituted pyridine N-oxides,<sup>2,3</sup> the most popular series being the *para*-, or 4-substituted pyridine N-oxides. Just recently the interest in pyridine N-oxides (hereafter referred to as ZPyNO) has been extended to an analogous system the substituted quinoline N-oxides (ZQNO). The hydrogen bonding interaction of ZQNO with phenol<sup>4</sup> has been studied, and coordination complexes with cobalt(II) and nickel(II) have also been reported.<sup>5-7</sup>

In our previous work on the 4-ZQNO complexes of cobalt and nickel,<sup>5</sup> we found evidence for metal-to-ligand  $\pi$ -bonding. Since nickel(II) and cobalt(II) have  $d^8$  and  $d^7$  electronic configurations, respectively, the  $t_{2g}(\pi)$  molecular orbitals are filled or nearly filled. Here we report 4-ZQNO complexes of chromium(III), manganese(II), iron(III), and zinc(II) in an attempt to study the effect of electronic configuration on the metal-to-ligand  $\pi$ -bonding. Chromium(III) (a  $d^3$  case)

and manganese(II) (a  $d^5$  case) have half filled  $t_{2g}(\pi)$  orbitals, and might show a different  $\pi$ -bonding effect. Zinc(II), a  $d^{10}$  case, is of interest since the filled d-shell might render it « inert » to  $\pi$ -bonding.

### Experimental Section

**Synthesis.** Preparation of the 4-substituted quinoline N-oxides and 4-substituted pyridine N-oxides have been previously described.<sup>4</sup> All of the coordination complexes were prepared by the following method: The appropriate metal perchlorate salt was stirred in either an ethanol-triethyl orthoformate solution or an ethanol-2,2-dimethoxypropane solution for about 15 minutes, and then an ethanolic solution of the ligand was added. A 7:1 ligand to metal salt mole ratio was used in each case. The complexes usually precipitated in a few minutes, if not immediately. The products were filtered, washed with anhydrous ether, and dried under vacuum over phosphorus pentoxide. Preparation of some of the chromium complexes resulted in oils which (except in the case of  $\text{Cr}(\text{QNO})_6(\text{ClO}_4)_3$ ) crystallized when triturated with anhydrous ether.

**Analyses.** Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt Laboratorium in Mulheim, Germany. Ligand analyses were obtained by titration with  $\text{TiCl}_3$ ,<sup>8</sup> and metal analyses were obtained by titration with EDTA.<sup>9</sup>

**Physical Measurements.** Magnetic moments and molar conductances were measured as previously described.<sup>5</sup> Infrared spectra were run as Nujol mulls in the 5000 to 650  $\text{cm}^{-1}$  region on a Beckman IR5A spectrophotometer, and in the 800 to 250  $\text{cm}^{-1}$  region on a Perkin Elmer 521 spectrophotometer. Electronic spectra were obtained on a Cary Model 14 spectrophotometer either as Nujol mulls or in nitromethane solution which contained a 6:1 mole ratio of excess ligand to retard dissociation of the complexes.

### Results

Analytical data in Table I indicate that all the compounds are six-coordinate octahedral-type comp-

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Table I. Analytical Data

Complex	%C		%H		%N		% Metal <sup>a</sup>		% Ligand <sup>a</sup>		Dec. Pt., °C <sup>b</sup>
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
Cr(CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> · H <sub>2</sub> O	49.52	49.55	4.12	4.38	5.78	5.68					171-174
Cr(CH <sub>3</sub> C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> · H <sub>2</sub> O	54.45	54.88	4.26	4.62	6.35	6.51					169-173
Cr(ClC <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> · 5H <sub>2</sub> O	42.75	42.55	3.06	3.09	5.54	5.45					178-181
Cr(NO <sub>2</sub> C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> · 5H <sub>2</sub> O	41.01	41.04	3.57	3.28					76.51	76.99	173-186
Mn(CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> · 7H <sub>2</sub> O	50.39	50.29	4.79	4.38	5.88	5.56	4.21	4.78			200-201
Mn(CH <sub>3</sub> C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> · 2H <sub>2</sub> O	57.93	57.78	4.70	4.86	6.78	6.25	4.55	4.25			193-200
Mn(C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	57.70	58.31	3.77	3.32	7.48	6.99	4.89	4.94			174-182
Mn(ClC <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	48.73	48.23	2.73	2.82	6.32	6.24	4.13	4.20			169-170
Fe(C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> · H <sub>2</sub> O	52.22	52.12	3.57	3.78	6.77	6.66	4.50	4.32			203-205
Zn(CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>					4.97	4.74	79.90	79.49			199-200
Zn(CH <sub>3</sub> C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>					5.37	5.27	78.32	79.12			196-205
Zn(C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>					5.76	5.60	76.72	76.94			203-204
Zn(ClC <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>					4.87	4.06	80.31	79.78			141-146
Zn(CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>					6.45	6.27	73.97	73.03			169-177
Zn(CH <sub>3</sub> C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>					7.12	6.85	71.23	71.23			183-187
Zn(C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>					7.83	7.50	68.26	69.28			223-231
Zn(ClC <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>					6.27	6.27	74.59	75.63			134-136
Zn(NO <sub>2</sub> C <sub>2</sub> H <sub>4</sub> NO) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>					5.92	5.83	76.14	77.09			211-222

<sup>a</sup> Metal and ligand analyses were run immediately after drying and the calculated percentages are based on anhydrous complexes.

<sup>b</sup> Decomposition points are uncorrected.

plexes. Molar conductance values for  $2.0 \times 10^{-3} M$  nitromethane solutions (Table II) are in the range for 2:1 electrolytes for the zinc and manganese complexes and in the range for 3:1 electrolytes for the chromium and iron complexes.<sup>10,11</sup> The magnetic moments (Table II) are observed to be at the high end of the range typical for high spin octahedral complexes.

Study of the nitrogen-oxygen stretching frequency for the 4-ZQNO complexes (Table II) shows that there is no shift to lower energy upon complexation as was observed for the corresponding 4-ZPyNO complexes, where shifts from 10 to 50  $\text{cm}^{-1}$  were observed.<sup>12,13</sup> This data is consistent with that found for the cobalt and nickel 4-ZQNO complexes.<sup>5</sup>

Assignment of the metal-oxygen stretching frequencies was made by comparing spectra of the ligands and their corresponding complexes and by comparing spectra of all the metal complexes of a given ligand with one another. The assignments fall into the same range as those reported for the 4-ZPyNO complexes (Table III).<sup>12-14</sup> We find that the  $\nu_{\text{M-O}}$  band is one of the stronger peaks in the 450 to 250  $\text{cm}^{-1}$  region, usually broad and somewhat asymmetric.

**Chromium(III) Complexes.** The electronic spectra of the chromium complexes were examined in nitromethane solution containing a 6:1 mole ratio of excess ligand, and the ligand field parameters  $Dq$ ,  $B$ , and  $\beta$  were calculated by the method of Lever.<sup>15</sup> The electronic spectrum of the  $\text{Cr}(\text{QNO})_3(\text{ClO}_4)_3$  complex was obtained by dissolving some of the oil in nitromethane solution and adding excess ligand. For the spectra of all the chromium complexes, the first and second d-d transitions can be used to predict the position of the third band ( $\sim 34400$  to  $36500 \text{ cm}^{-1}$ ), which cannot

be observed due to the charge transfer bands extending into the visible region.

**Manganese(II) Complexes.** The bright orange to deep red color of these complexes is quite striking when compared with most manganese(II) salts which are very pale pink in color. This intensive color is attributed to the charge transfer bands which extend far into the visible region. It is this phenomenon that prevents one from getting any useful electronic absorption data from solution spectra, as the charge transfer bands mask the weak spin-forbidden d-d transitions. It was, however, possible to observe more bands in solid state Nujol mull spectra. Often spectra of manganese complexes with organic ligands do not afford sufficient information to evaluate all the parameters needed to solve the six secular equations. Thus various approximations are needed, each of which reduces the accuracy of the fit between the

Table II. Infrared Data, Molar Conductance, and Magnetic Moments

Complex	$\nu_{\text{N-O}}(\text{cm}^{-1})$	$\Lambda_m(\text{cm}^2\text{mho mole}^{-1})^a$	$\mu_{\text{eff}}(\text{B.M.})^b$
L=4-CH <sub>3</sub> OQNO	1280		
CrL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1294	210	4.06
MnL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1289	179	6.00
ZnL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1292	182	
L=4-CH <sub>3</sub> QNO	1206		
CrL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1217	214	3.99
MnL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1212	172	6.28
ZnL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1215	179	
L=QNO	1229		
MnL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1228	177	6.12
FeL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1230	247	6.02
ZnL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1230	179	
L=4-ClQNO	1302, 1251		
CrL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1304, 1263	222	4.09
MnL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1302, 1256	180	6.10
ZnL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1305, 1263	189	
L=4-NO <sub>2</sub> QNO	1300		
CrL <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub>	1302	198	3.91

<sup>a</sup> For  $2.0 \times 10^{-3} M$  solutions in nitromethane. <sup>b</sup> Gouy Method at room temperature.

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**Table III.** Metal-Oxygen Bands for Aromatic Amine Oxide Complexes, (cm<sup>-1</sup>)

	Z	CrL <sub>6</sub> X <sub>3</sub> <sup>a</sup>	MnL <sub>6</sub> X <sub>2</sub>	FeL <sub>6</sub> X <sub>3</sub>	CoL <sub>6</sub> X <sub>2</sub>	NiL <sub>6</sub> X <sub>2</sub>	ZnL <sub>6</sub> X <sub>2</sub>
4-ZPyNO	CH <sub>3</sub> O	340 <sup>b</sup>		311 <sup>b</sup>	282 <sup>b</sup>	299 <sup>d</sup>	409 280
	CH <sub>3</sub>	445 <sup>b</sup>		412 <sup>b</sup> 403	392 <sup>b</sup> 384	393 <sup>b</sup> 325 <sup>d</sup>	376
	H	428 <sup>b</sup> 431 <sup>c</sup> 405 402	311 <sup>c</sup>	385 <sup>b c</sup>	340 <sup>b</sup> 331 <sup>c</sup> 330	340 <sup>b</sup> 337 <sup>d</sup> 328	310 319 <sup>c</sup>
	Cl	481 <sup>b</sup> 460		442 <sup>b</sup>	362 <sup>b</sup> 355	367 <sup>b</sup> 347 <sup>d</sup> 365	349
	NO <sub>2</sub>			424 <sup>b</sup>	367 <sup>b</sup> 354	370 <sup>b</sup> 374 <sup>d</sup> 360	380 344
4-ZQNO	CH <sub>3</sub> O	441	414 389		416	403	418
	CH <sub>3</sub>	443	387		385	382	392
	H		338	363	349	350	357
	Cl	456	365		389	387	383
	NO <sub>2</sub>	450			375 355	368	

<sup>a</sup> X = ClO<sub>4</sub><sup>-</sup>. <sup>b</sup> Reference 12. <sup>c</sup> Reference 14. <sup>d</sup> Reference 13.

**Table IV.** Electronic Absorption Spectral Data

Complex	Medium	Obs. Bands (cm <sup>-1</sup> ) ε(liter mole <sup>-1</sup> cm <sup>-1</sup> )	Assignment	Dq	β	Calc. bands
Cr(CH <sub>3</sub> OQNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub> <sup>a</sup>	16000 (140) 22600 (244)	<sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> (F)	1600	.73	
Cr(CH <sub>3</sub> QNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub> <sup>a</sup>	15600 (135) 22000 (266)	<sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> (F)	1558	.72	
Cr(QNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub> <sup>b</sup>	16200 23500	<sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> (F)	1618	.83	
Cr(ClQNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub> <sup>a</sup>	15600 (147) 22700 (308)	<sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> (F)	1562	.80	
Cr(NO <sub>2</sub> QNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub> <sup>a</sup>	15800 (104) <sup>c</sup>	<sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>2g</sub>	1575	—	
Mn(CH <sub>3</sub> OQNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	mull	18200	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G)	710	.76	18000
		20400	<sup>d</sup>			
		20800	<sup>d</sup>			
		21800	→ <sup>4</sup> T <sub>2g</sub> (G)			
		~28200 <sup>e</sup>	→ <sup>4</sup> T <sub>2g</sub> (D)			
~29400 <sup>e</sup>	→ <sup>4</sup> E <sub>g</sub> (D)					
Mn(CH <sub>3</sub> QNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	mull	18200	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G)	747	.78	18200
		19800	<sup>d</sup>			
		20900	<sup>d</sup>			
		22000	→ <sup>4</sup> T <sub>2g</sub> (G)			
		25100	→ <sup>4</sup> E <sub>g</sub> , <sup>4</sup> A <sub>1g</sub> (G)			
~28000 <sup>e</sup>	→ <sup>4</sup> T <sub>2g</sub> (D)					
~29200 <sup>e</sup>	→ <sup>4</sup> E <sub>g</sub> (D)					
Mn(QNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	mull	18200	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G)	703	.77	18200
		19700	<sup>d</sup>			
		20800	<sup>d</sup>			
		22000	→ <sup>4</sup> T <sub>2g</sub> (G)			
		24400	→ <sup>4</sup> E <sub>g</sub> , <sup>4</sup> A <sub>1g</sub> (G)			
~27600 <sup>e</sup>	→ <sup>4</sup> T <sub>2g</sub> (D)					
~29200 <sup>e</sup>	→ <sup>4</sup> E <sub>g</sub> (D)					
Mn(ClQNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	mull	17600	<sup>d</sup>	690	.78	18600
		18900	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G)			
		20200	<sup>d</sup>			
		25200	→ <sup>4</sup> E <sub>g</sub> , <sup>4</sup> A <sub>1g</sub> (G)			
		~27500 <sup>e</sup>	→ <sup>4</sup> T <sub>2g</sub> (D)			
~29200 <sup>e</sup>	→ <sup>4</sup> E <sub>g</sub> (D)					
Fe(QNO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	mull	12000	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G)	1373		12500
		18700	→ <sup>4</sup> T <sub>2g</sub> (G)			
		20000	<sup>d</sup>			
		22700	→ <sup>4</sup> E <sub>g</sub> , <sup>4</sup> A <sub>1g</sub> (G)			
		~28700 <sup>e</sup>	→ <sup>4</sup> E <sub>g</sub> (D)			

<sup>a</sup> 2.0×10<sup>-3</sup> M in complex, 1.2×10<sup>-2</sup> M in excess ligand. <sup>b</sup> Oil dissolved in CH<sub>3</sub>NO<sub>2</sub> with excess ligand added. <sup>c</sup> Other bands masked by charge transfer band. <sup>d</sup> Unassigned. <sup>e</sup> Somewhat obscured by ligand bands.

theoretical and the experimental spectrum. In this work the ligand field calculation was done by using the equations of Lever<sup>15</sup> to construct a theoretical Tanabe-Sugano diagram for the  $d^5$  configuration. The approximation that  $C = 4.48B$  (where  $B$  and  $C$  are the Racah parameters) was made since an insufficient number of peaks were observed to evaluate each parameter separately. (Note:  $C/B = 4.48$  is the ratio often used in construction of  $d^5$  case Tanabe-Sugano diagrams.<sup>16</sup>) The parameters  $Dq$  and  $\beta$  that best fit the data are given in Table IV.

In the electronic spectra of all the manganese complexes two bands appear  $\sim 20,000 \text{ cm}^{-1}$  and are unassigned. Spectra of neither the ligands nor the zinc complexes show bands in this region, so these peaks cannot be attributed to the ligand in either a free or complexed environment. A recent paper by Lever and coworkers<sup>17</sup> has shown that some of the bands in the  $20,000 \text{ cm}^{-1}$  region for PyNO complexes of manganese(II) may be assigned as metal-to-ligand charge transfer transitions. Thus, it is possible that the unassigned peaks observed in the QNO complexes are charge transfer bands.

**Iron(III) Complex.** Only one iron complex was prepared and studied since  $\text{Fe}^{3+}$  is also a  $d^5$  case. The electronic spectrum of  $\text{Fe}(\text{QNO})_6(\text{ClO}_4)_3$  was recorded as a Nujol mull, and the ligand field parameters were calculated as described above for manganese(II).

**Zinc(II) Complexes.** The zinc complexes of the 4-ZQNO and 4-ZPyNO ligands were prepared in order to study the effect of the full d-shell on the metal-oxygen stretching frequency. The  $\text{Zn}(4\text{-ZQNO})_6(\text{ClO}_4)_2$  complexes were also used to aid in the assignment of the electronic spectral bands for the manganese and iron complexes. Since no d-d transitions will be observed from the zinc(II) ion, bands which can be attributed to the ligand in a complexed environment can be located via spectra of the zinc complexes.

## Discussion

There are four basic contributions to the ligand field parameter  $Dq$ : the basicity effect ( $\sigma$ ), the steric effect ( $s$ ), ligand-to-metal  $\pi$ -bonding ( $\pi_{L-M}$ ), and metal-to-ligand  $\pi$ -bonding ( $\pi_{M-L}$ ). The effects of these contributions on  $Dq$  can be expressed as follows:

$$Dq = \sigma - s - \pi_{L-M} + \pi_{M-L}$$

where the positive terms tend to increase  $Dq$  and the negative terms tend to decrease  $Dq$ . Let us compare the PyNO and QNO ligands in light of these four factors. The basicities of the 4-ZPyNO ligands encompass those of the 4-ZQNO ligands,<sup>4</sup> so one would not expect much difference in  $Dq$  values based on this factor. Since the steric hindrance of QNO is greater than PyNO due to the second aromatic

ring, one would predict higher  $Dq$  values for the PyNO complexes. Ligand-to-metal  $\pi$ -bonding is not deemed important in either set of these complexes since all the metal ions studied have electrons in the  $t_{2g}(\pi)$  orbitals and thus ligand donation to these orbitals is unlikely. However, metal-to-ligand  $\pi$ -bonding does seem to be important and the relative ability of the ligands to accept  $\pi$ -electron density from the metal ions will determine the relative magnitude of this effect on the  $Dq$  values. Comparison of the values in Table IV for the  $\text{Cr}(4\text{-ZQNO})_6(\text{ClO}_4)_3$  complexes with the values obtained for the  $\text{Cr}(4\text{-ZPyNO})_6(\text{ClO}_4)_3$  complexes ( $1575$  to  $1613 \text{ cm}^{-1}$ )<sup>12</sup> reveal that the 4-ZQNO  $Dq$  values are as high as those for 4-ZPyNO, indicating that the 4-ZQNO ligands are better  $\pi$ -acceptors than the 4-ZPyNO ligands. This supports the data obtained for the cobalt and nickel 4-ZQNO complexes.<sup>5</sup> The  $Dq$  values of the manganese and iron PyNO complexes have not been reported, so comparison with the values obtained in this work is not possible.

There is a considerable difference in the nitrogen-oxygen stretching frequency,  $\nu_{N-O}$ , for the two ligand systems. There is a linear trend in  $\nu_{N-O}$  for the free 4-ZPyNO ligands<sup>13</sup> but not for the 4-ZQNO ligands. This has been explained<sup>18</sup> by the fact that  $\nu_{N-O}$  is not a pure vibration in the QNO system, but is coupled with the aromatic ring vibrations of the quinoline ring. Consequently no trend is expected in the QNO complexes as was observed in the PyNO complexes.<sup>12,13</sup> One would expect, however, that  $\nu_{N-O}$  would shift to lower energy upon complexation due to a reduction of the nitrogen-oxygen bond order and/or a mass effect. This is not observed (Table II) in the QNO complexes and is probably due to the effect of the above-mentioned coupling.

Assignment of the metal-oxygen vibrations would appear to be quite straight forward for complexes of the type studied here. If one compared a spectrum of a given complex with that of the corresponding ligand, the ligand peaks should match up reasonably well and a new band appearing in the  $450$  to  $250 \text{ cm}^{-1}$  region would probably be  $\nu_{M-O}$ . Unfortunately this is not always the case, since various vibrations are shifted, activated, deactivated and/or changed in intensity due to changes in symmetry upon complexation. In fact, only the complexes of the unsubstituted PyNO and QNO provide spectra where  $\nu_{M-O}$  can be assigned in a very straight forward manner.

Herlocker, *et al.*<sup>13</sup> found that  $\nu_{M-O}$  for the  $\text{Ni}(4\text{-ZPyNO})_6(\text{ClO}_4)_2$  complexes gave a linear relationship when plotted versus sigma substituent constants. Whyman, *et al.*<sup>12</sup> studied the same complexes and agree with Herlocker's  $\nu_{M-O}$  assignments except in the case of  $\text{Ni}(4\text{-CH}_3\text{PyNO})_6(\text{ClO}_4)_2$ . The latter's assignment of  $\nu_{M-O}$  for this complex, being some  $70 \text{ cm}^{-1}$  higher than Herlocker's, destroys the linear correlation. Whyman<sup>12</sup> also studied the 4-ZPyNO complexes of chromium, iron, and cobalt, and found a somewhat linear trend in each series except for  $Z = \text{CH}_3$ , where  $\nu_{M-O}$  was always high.

(16) B. N. Figgis, « Introduction to Ligand Fields », Interscience Publishers, New York, N. Y., 1966, p. 163.

(17) W. Byers, B. F. Chou, A. B. P. Lever, and R. V. Parish, *J. Amer. Chem. Soc.*, **91**, 1329 (1969).

(18) H. Shindo, *Chem. Pharm. Bull. (Tokyo)*, **8**, 845 (1960).

In our investigation of the 4-ZQNO complexes, we find that  $\nu_{M-O}$  is lowest for  $Z = H$  and increases in going from  $Z = H$  to  $CH_3$  and  $CH_3O$ . We find that  $\nu_{M-O}$  also increases in going from  $Z = H$  to  $Cl$  and  $NO_2$ , thus giving somewhat of a V-shaped trend. One can rationalize a trend such as this by considering that two competing effects are being observed. First, for the electron donating substituents  $CH_3$  and  $CH_3O$ , one is seeing predominantly the basicity effect, where the stronger bases give higher values of  $\nu_{M-O}$ . This is the effect observed for the  $TiF_4 \cdot 2(4-ZPyNO)$  complexes.<sup>19</sup> Secondly, for the electron withdrawing substituents  $Cl$  and  $NO_2$ , one is seeing predominantly the  $\pi$ -bonding effect observed by Herlocker.<sup>13</sup> The combination of these effects produces a V-shaped trend.

It is difficult to visualize why the 4-ZPyNO and 4-ZQNO systems would show differing trends, but it is more difficult to visualize why  $\nu_{M-O}$  for 4-ZPyNO complexes in which  $Z = CH_3$  should be higher than the others. In view of this, we reinvestigated the 4- $CH_3OPyNO$  complexes of  $Ni^{2+}$  and  $Co^{2+}$  as well as studying the corresponding  $Zn^{2+}$  complex. We

(19) F. E. Dickson, E. W. Gowling, and F. F. Bentley, *Inorg. Chem.*, 6, 1099 (1967).

observed the band *ca.* 280 to 300  $cm^{-1}$  which the previous workers assigned as  $\nu_{M-O}$  and agree that it is a reasonable choice. However, there is another band *ca.* 410 to 422  $cm^{-1}$  in each of these complexes which has all the characteristics of  $\nu_{M-O}$ . Where either of these bands would be a reasonable choice for the 4- $CH_3OPyNO$  complexes, no bands appear in the 320 to 250  $cm^{-1}$  region in the 4- $CH_3OQNO$  complexes, leaving us with only one choice for  $\nu_{M-O}$ , that in the 405 to 440  $cm^{-1}$  region.

In conclusion, the data presented here indicate the presence of a metal-to-ligand  $\pi$ -bonding effect in the  $Cr^{3+}$ ,  $Fe^{3+}$ , and  $Mn^{2+}$  complexes of 4-ZQNO and support the conclusions obtained for the cobalt and nickel complexes previously studied. In addition, the zinc complexes of both ligand systems follow the trends established by the other transition metal complexes, so apparently some  $\pi$ -bonding does occur even though zinc has a full d-shell.

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