cobalt(II) complexes described by Lions, *et al.*[30] The magnetic moment of 4.58 BM (20°) is also indicative of trigonal-bipyramidal rather than square-pyramidal symmetry.[30]

This complex is the first example of a five-coordinate derivative of cobalt(II) in which all of the ligands are identical. It is also the first complex to have a trigonal-bipyramidal CoO_5 chromophore.

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Complexes of Aromatic Amine Oxides. 4-Substituted Quinoline 1-Oxide Complexes of Cobalt(II) and Nickel(II) Perchlorates

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The coordinating properties of a series of 4-substituted quinoline 1-oxides toward nickel(II) and cobalt(II) have been investigated. The substituents studied were CH_3O, CH_3, H, Cl, and NO_2. The compounds were assigned octahedral structures with the general formula $M(4\text{-}Z\text{-}C_9H_6NO)_6(ClO_4)_2$ based upon analytical data and the magnetic moments 3.37–3.61 and 4.91–5.25 BM for nickel(II) and cobalt(II), respectively. The electronic spectra were studied and ligand field parameters were determined. The *Dq* values ranged from 790 to 874 cm^{-1} for the nickel(II) complexes and from 955 to 979 cm^{-1} for the cobalt(II) complexes. For comparison purposes, isoquinoline 2-oxide complexes were also studied. Considerable evidence for $d\pi$–$p\pi$ back-bonding (synergic bonding) is found and discussed.

Introduction

Many studies have been made with complexes of quinoline and substituted pyridines in order to ascertain what factors determine both the stereochemistry and the physical properties of the resultant complexes.[3–7] From these studies it was concluded that the degree of π overlap between metal and heterocyclic amine was greater for quinoline and isoquinoline than for the pyridines.[3] Further, it has also recently been found that, for $Ni(AA)_2 \cdot L$ and $Co(AA)_2 \cdot L$ complexes[8] (L is pyridine 1-oxide, quinoline 1-oxide, or isoquinoline 2-oxide and AA is 2,4-pentanedionate), more electron spin density is delocalized onto the π system of quinoline 1-oxide and isoquinoline 2-oxide than onto pyridine 1-oxide. Hence, as with the quinolines, the quinoline 1-oxides are better acceptors of π-electron density than the corresponding pyridine 1-oxides.

Not only is there a difference in the π-bonding ability of the pyridine and quinoline 1-oxides, but there also should be a difference in the σ-bonding ability owing to steric interactions. The quinoline 1-oxide series should bear the same steric relation to pyridine 1-oxide that quinoline does to pyridine. Where tetrakis-pyridine complexes were found,[4,6] only bisquinoline complexes could be isolated.[5] Therefore, if the hexakisquinoline 1-oxide complexes are isolated, the metal–oxygen bonding should be weakened relative to that of the pyridine 1-oxides by a steric interaction, not only between the metal and the bulkier ligand but also by a ligand–ligand repulsion. This weaker bond should manifest itself as a lowering in the *Dq* value for the quinoline 1-oxides relative to that of the corresponding pyridine 1-oxides.

The availability of many 4-substituted pyridine 1-oxides[9] has given rise to several attempts at correlating substituent constants for the various groups with observable properties of either the ligands themselves or their complexes.[10] Quinoline 1-oxide has the same type of resonance forms as does pyridine 1-oxide and thus similar correlations should be possible for this system.

The ease of formation of hexacoordinated complexes of pyridine 1-oxides[11] coupled with our interest in linear free energy relations[10] of aromatic amine oxides prompted us to investigate the ligational properties of a series of 4-substituted quinoline 1-oxides. The ligands $4\text{-}Z\text{-}C_9H_6NO$ ($Z = CH_3O$, CH_3, H, Cl, and NO_2) and isoquinoline 2-oxide were selected for their constant steric effects and varying basicity. The hexakis complexes of quinoline 1-oxide with nickel(II) and cobalt(II) have previously been reported[12] but have not been extensively characterized.

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TABLE I

ANALYTICAL AND CONDUCTANCE DATA

	% C		% H		% N		% metal				
Complex	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Dec pt,[c] °C	Concn., $M \times 10^{-3}$	Λ_m, cm^2 mho mol^{-1}
4-CH_3O-C_9H_6NO											
$NiX_2 \cdot 6L \cdot 3H_2O$	52.90	52.83	4.40	4.38	6.17	6.27	4.49	4.88	200–205	3.42	160[a]
$CoX_2 \cdot 6L \cdot 5H_2O$	51.51	51.54	4.57	4.13	6.00	5.98	4.22	4.70	137–139	5.40	198[b]
4-CH_3-C_9H_6NO											
$NiX_2 \cdot 6L \cdot H_2O$	58.60	58.20	4.56	4.78	6.85	7.77	4.84	4.78	205–210	1.08	160[a]
$CoX_2 \cdot 6L \cdot 3H_2O$	56.79	57.16	4.76	4.77	6.65	6.52	4.66	4.71	193–196	2.32	255[b]
C_9H_7NO											
$NiX_2 \cdot 6L \cdot 4H_2O$	54.01	54.23	4.17	4.47	7.00	7.02	4.94	5.23	215–218	1.64	141[a]
$CoX_2 \cdot 6L \cdot 3H_2O$	54.86	54.39	4.06	3.76	7.10	7.20	4.97	5.65	161–162	1.80	296[b]
4-Cl-C_9H_6NO											
$NiX_2 \cdot 6L \cdot 3H_2O$	46.69	46.51	3.04	2.77	6.06	6.54	4.40	4.75	204–205	1.95	156[a]
$CoX_2 \cdot 6L \cdot 3H_2O$	46.68	46.43	3.03	2.83	6.05	6.80	4.24	4.50	187–189	4.13	225[b]
4-NO_2-C_9H_6NO											
$NiX_2 \cdot 6L \cdot 6H_2O$	43.05	42.45	3.19	2.91	11.16	11.58	...	...	203–206	2.16	138[a]
$CoX_2 \cdot 6L \cdot 6H_2O$	43.06	42.96	3.21	3.07	11.16	12.60	...	...	240–243	3.67	239[b]
Isoquinoline 2-oxide											
$NiX_2 \cdot 6L$	57.46	57.26	3.72	4.24	7.45	7.53	5.21	5.47	278–282	1.61	119[a]
$CoX_2 \cdot 6L$	57.45	57.10	3.72	3.87	7.45	7.73	5.22	4.80	243–245	3.00	222[b]

[a] Solvent CH_3NO_2. [b] Solvent CH_3CN. [c] Decomposition points are uncorrected.

Experimental Section

Reagents.—Quinoline 1-oxide was prepared once by the method of Ochiai[9] and subsequently was obtained from Aldrich Chemical Co. The 4-chloro, -methyl, and -nitro derivatives were prepared by the method of Ochiai.[9] The 4-methoxy was prepared according to Tanaka.[13] Isoquinoline 2-oxide was prepared according to Robison.[14] The melting points of the ligands all agreed well with the published values. All were recrystallized from acetone.

Synthesis.—The complexes with 4-methyl- and 4-methoxyquinoline 1-oxide, quinoline 1-oxide, and isoquinoline 2-oxide were prepared by mixing ethanolic solutions of the ligand and metal salt. If precipitation did not occur within a few minutes ether was added until precipitation occurred. The complexes were then filtered, washed with anhydrous ether, and dried under vacuum over phosphorus pentoxide. The 4-chloro complexes were prepared from a triethyl orthoformate slurry by the procedure of Van Leeuwen and Groeneveld.[15] The 4-nitro complexes were prepared from nitromethane (nickel(II)) or acetonitrile (cobalt(II)) solutions of approximately a 16:1 ligand to metal ratio, to which triethyl orthoformate had been added. The solutions were stirred overnight, at which time anhydrous ether was added to initiate the precipitation. The product was filtered off, washed with ether, and dried *in vacuo* over phosphorus pentoxide. The analytical data are shown in Table I. All of the complexes are slightly hygroscopic.

Solution Electronic Spectra.—Solution spectra were run in the 350–1500-mμ region on a Cary Model 14 recording spectrophotometer. The solutions contained added ligand to retard dissociation. The spectral data are tabulated in Tables II and III.

Magnetic Moments.—The magnetic moments were determined by the Gouy technique using a balance constructed from a Varian epr magnet. The compound $Hg[Co(SCN)_4]$ was used as a calibrant.[16] The diamagnetic corrections were calculated from Pascal's constants.[17] The data are presented in Table III.

Infrared Spectra.—Infrared spectra of the ligands and their complexes as Nujol mulls in the sodium chloride region (650–4000 cm^{-1}) were obtained on a Beckman IR5A recording spectrophotometer. The spectra were calibrated with known frequency bands of polystyrene. The data are listed in Table IV.

Conductance Data.—The conductance measurements were run on an Industrial Instruments conductance bridge, Model RC16B2, using nitromethane and acetonitrile as solvents. These data appear in Table I.

Elemental Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt Laboratorium in Müheim, Germany. Metal analyses were obtained using EDTA.[18]

Ligand Field Calculations.—The secular equations for Ni(II) (d^8) and Co(II) (d^7) were solved in the weak-field formalism; the crystal field matrices have been reported by Orgel.[19] The values of Dq for Ni(II) were taken directly from the wave numbers of the first (lowest energy) spin-allowed absorption band.

The electronic spectra for the cobalt(II) complexes were fitted to the parameters as described by Ballhausen.[20] The experimental and calculated values for ν_2 were matched to within a limit of 1%. For this difference a 3–7% lowering of F–P term splitting (14,500 cm^{-1} in the gaseous ion) was required for the best fit. The per cent lowering of the F–P term splitting for the cobalt(II) complexes (a calculated value) is in good agreement with that of the nickel(II) complexes (a measured value). This gives support to the assignment of the peaks in the cobalt(II) complexes.

Results and Discussion

A trend in basicities of the quinoline 1-oxides was obtained from their pK_a values by plotting these values *vs.* the σ_{PyNO} constants as seen in Figure 1. These values are listed in Table V. This linear correlation indicates that the basicities of the quinoline 1-oxides follow the same order as the corresponding pyridine 1-oxides.[10]

If the pK_a values of the pyridine 1-oxides and quinoline 1-oxides (Table V) are compared, we see that the quinoline 1-oxides are generally slightly stronger bases. This means that they form stronger bonds to the hydrogen ion than do the pyridine 1-oxides. This is a σ bond with no capability for π bonding or for steric interaction. However, when an octahedral complex is formed with the six bulky quinoline 1-oxide groups surrounding a metal ion, the steric interaction should

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TABLE II

BAND ASSIGNMENTS IN THE ELECTRONIC SPECTRA

M	4-Z	Solvent	Complex concn, *M*	ν_{max}, cm^{-1}	ϵ_{max}	Assignment
Ni	CH_3O	1.13 × 10^{-2} *M*	1.14 × 10^{-3}	26,000	176	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
		$CH_3OC_9H_6NO$		13,700	22.0	$\rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		12,700	20.0	$\rightarrow {}^1E_g$
				8,350	13.9	$\rightarrow {}^3T_{2g}$
Co	CH_3O	9.14 × 10^{-2} *M*	2.16 × 10^{-3}	20,900	305	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		$CH_3OC_9H_6NO$		18,500	185	$\rightarrow {}^4A_{2g}$
		in CH_3CN		8,180	10.2	$\rightarrow {}^4T_{2g}$
Ni	CH_3	1.35 × 10^{-2} *M*	1.21 × 10^{-3}	23,600	290	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
		$CH_3C_9H_6NO$		14,000	24.0	$\rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		12,700	22.3	$\rightarrow {}^1E_g$
				8,260	17.3	$\rightarrow {}^3T_{2g}$
Co	CH_3	9.8 × 10^{-2} *M*	4.67 × 10^{-3}	20,700	192	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		$CH_3C_9H_6NO$		18,300	102	$\rightarrow {}^4A_{2g}$
		in CH_3CN		8,290	11.5	$\rightarrow {}^4T_{2g}$
Ni	H	6.84 × 10^{-2} *M*	1.04 × 10^{-2}	23,800	183	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
		C_9H_7NO		13,700	12.5	$\rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		12,700	13.0	$\rightarrow {}^1E_g$
				7,900	12.5	$\rightarrow {}^3T_{2g}$
Co	H	9.9 × 10^{-2} *M*	3.60 × 10^{-3}	21,500	199	$^4T_{1g}(F) \rightarrow 4T_{1g}(P)$
		C_9H_7NO		18,500	95.8	$\rightarrow {}^4A_{2g}$
		in CH_3CN		8,700	13.9	$\rightarrow {}^4T_{2g}$
Ni	Cl	8.20 × 10^{-2} *M*	3.08 × 10^{-3}	25,300	650	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
		ClC_9H_6NO		14,300	42.2	$\rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		12,900	22.7	$\rightarrow {}^1E_g$
				8,420	16.2	$\rightarrow {}^3T_{2g}$
Co	Cl	7.15 × 10^{-2} *M*	4.13 × 10^{-3}	20,600	436	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		ClC_9H_6NO		18,000	390	$\rightarrow {}^4A_{2g}$
		in CH_3CN		8,260	30.0	$\rightarrow {}^4T_{2g}$
Ni	NO_2	2.54 × 10^{-1} *M*	2.60 × 10^{-2}	24,300	352	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
		$NO_2C_9H_6NO$		13,400	13.8	$\rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		8,740	7.3	$\rightarrow {}^3T_{2g}$
Co	NO_2	4.55 × 10^{-1} *M*	1.24 × 10^{-2}	21,700	136	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		$NO_2C_9H_6NO$		18,100	56.4	$\rightarrow {}^4A_{2g}$
		in CH_3CN		8,770	14.5	$\rightarrow {}^4T_{2g}$
Ni	Isoquin-	9.66 × 10^{-3} *M*	2.33 × 10^{-3}	23,900	36.5	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
	oline 2-	IQNO IN		14,100	17.6	$\rightarrow {}^3T_{1g}(F)$
	oxide	CH_3NO_2		12,800	14.6	$\rightarrow {}^1E_g$
				8,050	15.9	$\rightarrow {}^3T_{2g}$
Co	Isoquin-	9.90 × 10^{-2} *M*	3.00 × 10^{-3}	21,100	160	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	oline 2-	IQNO in		18,200	33.3	$\rightarrow {}^4A_{2g}$
	oxide	CH_3CN		8,660	13.2	$\rightarrow {}^4T_{2g}$

TABLE III

LIGAND FIELD PARAMETERS AND MAGNETIC MOMENTS

M	4-Z	*Dq*, cm^{-1}	β	ν_2,[a] cm^{-1}		$10^6\chi_m$	$10^6\chi_m^{cor}$	Temp, °K	μ_{eff}, BM
				Calcd	Obsd				
Ni	CH_3O	835	0.94	14,000	13,700	4,063	4,780	296	3.37
Ni	CH_3	826	0.79	14,600	14,000	3,896	4,559	296	3.30
Ni	H	790	0.84	13,200	13,200	4,781	5,412	299	3.61
Ni	Cl	842	0.89	14,000	13,400	4,132	4,853	297	3.41
Ni	NO_2	874	0.78	14,200	13,400	4,105	4,830	298	3.41
Ni	Isoquinoline 2-oxide	805	0.83	13,400	13,500	4,180	4,759	298	3.38
Co	CH_3O	976	0.96	18,400	18,500	10,847	11,590	296	5.25
Co	CH_3	971	0.94	18,200	18,300	9,374	10,063	298	4.91
Co	H	976	0.97	18,300	18,500	10,426	11,044	298	5.14
Co	Cl	955	0.93	17,900	18,000	10,581	11,302	298	5.22
Co	NO_2	965	0.98	18,100	18,100	10,215	10,940	298	5.13
Co	Isoquinoline 2-oxide	979	0.94	18,400	18,200	10,467	11,046	297	5.14

[a] Transition band.

become more important. The steric interaction should give rise to a weaker metal–oxygen bond in the quinoline 1-oxide complexes than in the pyridine 1-oxide complexes. Consequently, the electronic effect exhibited by quinoline 1-oxide should be proportional to that of pyridine 1-oxide and the difference in ligational ability should be manifested as a steric effect.

The elemental analyses indicate that the compounds may be formulated as $ML_6(ClO_4)_2 \cdot nH_2O$. The metal analyses were all run immediately after drying at re-

TABLE IV

INFRARED FREQUENCIES (CM^{-1})

M	4-Z	ν(N→O)		δ(N→O)	
		Ligand	Complex	Ligand	Complex
Ni	CH_3O	1280	1287	822	840
Co	CH_3O	1280	1289	822	835
Ni	CH_3	1206	1213	823	831
Co	CH_3	1206	1209	823	830
Ni	H	1229	1224	788	804
Co	H	1229	1227	788	797
Ni	Cl	1302	1300	824	836
		1251	1258		
Co	Cl	1302	1302	824	835
		1251	1256		
Ni	NO_2	1300	1302	845	851
Co	NO_2	1300	1309	845	857
Ni	Isoquinoline 2-oxide	1182	1160	818	834
Co	Isoquinoline 2-oxide	1182	1159	818	829

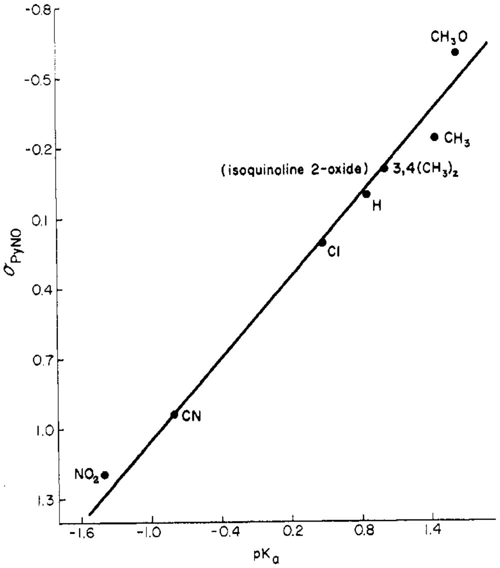

Figure 1.—Correlation of pK_a with σ_{PyNO} for 4-substituted quinoline 1-oxides.

TABLE V

pK_a VALUES OF AROMATIC AMINE OXIDES

Z	4-Z-$C_5H_5NO^a$	4-Z-$C_9H_6NO^b$	σ_{PyNO}
CH_3O	2.05	$\sim$1.62^c	−0.603
CH_3	1.29	1.44	−0.240
H	0.79	0.86	0
Cl	0.36	0.47	0.206
NO_2	−1.7	−1.39	1.19
3,4-$(CH_3)_2$^{d}		1.01	−0.105
CN	−1.17	$\sim$−0.80^c	0.94

[a] Reference 8. [b] Reference 6. [c] Approximate values determined spectrophotometrically in this work. [d] 3,4-$(CH_3)_2$ represents isoquinoline 2-oxide and the σ_{PyNO} constant was determined from the pK_a of this compound.

duced pressure over phosphorus pentoxide and in some cases indicate a different degree of hydration (different value for *n*) from those indicated by the carbon, hydrogen, and nitrogen analyses.

The conductance data suggest the presence of 2:1 electrolytes in nitromethane and acetonitrile, indicating noncoordinated anions in these solvents. Concentration studies showed that the conductances increased nonlinearly with increasing concentration. Although the conductance varied nonlinearly, it never indicated a value less than 1 which was intermediate for 1:1 and 2:1 electrolytes; *e.g.*, for the complex $Ni(4\text{-}CH_3\text{-}C_9H_6NO)_6^{2+}$ the values of λ_m ranged between 310 for 1.86×10^{-5} *M* and 93 for 4.65×10^{-3} *M* solutions. Conductances of solutions containing added ligand were slightly higher than those without but varied in the same manner; *e.g.*, for the complex $Ni(4\text{-}CH_3\text{-}C_9H_6NO)_6^{2+}$ the values of λ_m ranged between 361 for 2.2×10^{-4} *M* and 102 for 5.49×10^{-3} *M* solutions containing 9.15×10^{-3} and 2.28×10^{-2} *M* ligand, respectively.

In the more concentrated solutions the lower conductance values can be accounted for on the basis of ion pairing; whereas in the more dilute solutions this phenomenon was not as important. In the solutions with added ligand the solvating ability of the mixed solvent probably decreased the extent of ion pairing.

Correlations have been obtained between the nitrogen–oxygen stretching frequency and Hammett σ values for both the free ligand[11,21] and for nickel(II),[11,21] cobalt(II),[11,22] copper(II),[11,22] chromium(III),[11,22] iron(III),[11,22] and titanium(IV)[11,23] complexes of 4-substituted pyridine 1-oxides. As mentioned earlier, the quinoline 1-oxides should exhibit the same electronic effects as those found for pyridine 1-oxides and correlations with the nitrogen–oxygen stretching frequency, ν_{N-O}, of the quinoline 1-oxides would be expected. However, as Shindo[24] has pointed out, no correlation could be found. He offered as an explanation that ν_{N-O} is not a pure vibration in quinoline 1-oxides but is coupled with the aromatic ring vibrations of the quinoline ring. This coupling amounts to a lowering of the energy of the π system in quinoline 1-oxides relative to that of the pyridine 1-oxides. We found also that no correlations could be made for the nitrogen–oxygen stretching frequency of the cobalt(II) or nickel(II) complexes. The values of the infrared frequencies for the ligands presented in Table IV are consistent with those already reported[24] except in the case of isoquinoline 2-oxide. Shindo[24] assigned a value of 1256 cm^{-1} for the nitrogen–oxygen stretching frequency and Kluiber and Horrocks[8] assigned a value of 1180 cm^{-1}. We agree with the latter (1180 cm^{-1}) as it is this peak which shifts upon complexation.

For the nickel and cobalt complexes ν_{N-O} is either found at the same frequency as in the free ligand or shifted to higher energy by some 5 cm^{-1} for all cases except for isoquinoline 2-oxide. In the latter case, the N–O stretching frequency is shifted to lower energy. We anticipated a shift to lower energy upon complex formation for two reasons, the first being a simple mass effect and the second, a lowering of the nitrogen–oxygen bond order. This occurred in the complexes of pyridine

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1-oxides where shifts of some 10–50 cm^{-1} were observed.[19,21–23] Also for interactions with quinoline 1-oxides where only a σ bond is formed, *e.g.*, the hydrogen-bonding interaction with methanol,[22] the nitrogen–oxygen stretching frequency was shifted to lower energy by some 4–28 cm^{-1}. Hence, for the metal complexes, if only a σ bond were formed, then ν_{N-O} should represent a decrease in energy. Since we find no shift or a shift to higher energy, we conclude that the nitrogen–oxygen bond order remains essentially the same or increases slightly. In order for this to happen, there must be metal-to-ligand back-donation of electron density to replace the electron density on the oxygen atom lost by σ donation of an electron pair from the oxygen to the metal atom upon formation of the dative bond.

The electronic spectral data in Tables II and III are typical of octahedral nickel(II) and cobalt(II) complexes. Solid-state mull spectra showed no gross differences from the solution spectra, indicating that $M(4\text{-}Z\text{-}C_9H_6NO)_6{}^{2+}$ are the species present in solution with excess ligand. Figures 2 and 3 illustrate representative spectra of the nickel(II) and cobalt(II) complexes studied. The familiar doublet appearing at *ca.* 14,000 cm^{-1} is characteristic of an octahedral nickel(II) complex. The lack of fine structure and the appearance of a peak at *ca.* 20,000 cm^{-1} in the cobalt(II) spectra is typical of cobalt(II) in an octahedral field. The electronic transition attributable to $10Dq$ decreases continuously with added ligand, and since nitromethane and acetonitrile both have higher Dq values than the N-oxides and the perchlorate ion is suspected to have a lower value, the species must have undergone some solvolysis. To retard the solvolysis and to ensure that spectra of the hexakis N-oxide complexes were recorded, all solution spectra were run with at least a tenfold excess of ligand. As the amount of excess ligand was increased, the peaks were found to shift progressively to lower energy until a ratio of approximately 10:1 was obtained. Spectra with more excess ligand than this all gave similar results. Thus, if the spectra were recorded, with a ratio of less than 10:1, the Dq values would have been too high by virtue of the average environment rule. Similar results have previously been reported for the pyridine 1-oxide complexes.[19] The extinction coefficients for ν_3 in the case of nickel(II) and ν_2 and ν_3 for cobalt(II) are much higher than those normally found for Laporte forbidden d–d transitions in octahedral complexes. These peaks appear as shoulders (Figures 2 and 3) on intense charge-transfer bands and, hence, "borrow" intensity from these bands. To date, all of the N-oxide complexes previously studied exhibit this charge-transfer band.[11]

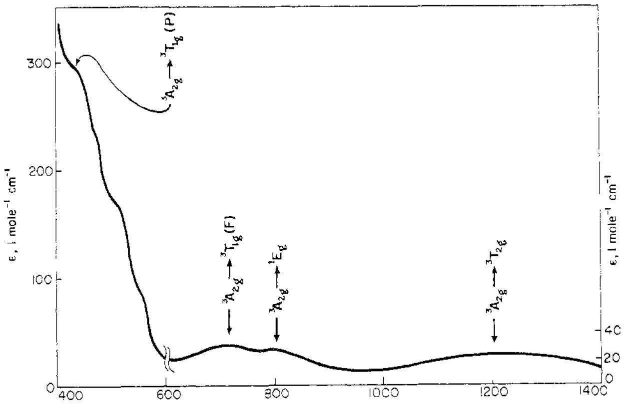

Figure 2.—Electronic spectra for $[Ni(4\text{-}CH_3\text{-}C_9H_6NO)_6](ClO_4)_2$ in CH_3NO_2 with excess $4\text{-}CH_3\text{-}C_9H_6NO$.

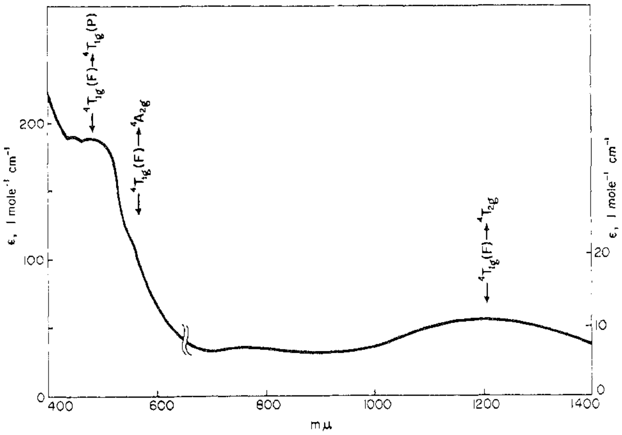

Figure 3.—Electronic spectra for $[Co(4\text{-}CH_3\text{-}C_9H_6NO)_6](ClO_4)_2$ in CH_3CN with excess $4\text{-}CH_3\text{-}C_9H_6NO$.

Although the Dq values were expected to be lowered by the previously discussed steric effect, they were found to be in the same range as those of the pyridine 1-oxides.[21,22] One explanation for the magnitude of the Dq values of the quinoline 1-oxides involves considering a lowering of the N-oxide π^* orbitals relative to those in pyridine 1-oxides, so that there would be more metal-to-ligand back-bonding in these complexes, thus raising the values of Dq. This is in essence a lowering of the metal t_{2g} orbitals relative to the e_{1g} causing a concomitant raising of Dq. The β values for all complexes are quite high suggesting little covalency in the metal–oxygen bond.

Whereas one investigator found that the Dq values for pyridine 1-oxide complexes of nickel(II) could be correlated to Hammett σ values,[21] another found the Dq values to be essentially constant.[22] We found no trend whatsoever in the Dq values of the quinoline 1-oxide complexes.

The magnetic moments are all in the allowed ranges for high-spin octahedral complexes. In most cases, the magnetic moments are higher than what is normally reported for cobalt(II) and nickel(II) complexes and considerably higher than the spin-only value. Reported[22] magnetic moments for pyridine 1-oxide complexes of cobalt(II), 4.71–4.84 BM, and nickel(II), 3.30–3.34 BM, are lower than what we report here, 4.91–5.25 and 3.30–3.61 BM, for cobalt(II) and nickel(II), respectively. This indicates a greater orbital contribution to the magnetic moment in the quinoline 1-oxide complexes than in those of pyridine 1-oxides. The greater orbital contribution comes from a lowering of the π^* orbitals in quinoline 1-oxides relative to pyridine 1-oxides. Hence, π back-bonding (metal to ligand) becomes increasingly important in the quinoline 1-oxide complexes.

Conclusions

The data indicate the importance of a π-back-bonding (metal-to-ligand) interaction. It is interesting that this interaction is much more important in quinoline 1-oxides than in pyridine 1-oxides. In addition π bonding seems to be more important for isoquinoline 2-oxide than for pyridine 1-oxide. The addition of the aromatic ring in the quinoline ring system helps to delocalize electrons and lowers the π^* molecular orbitals in this system significantly, thereby creating more effective π overlap with the metal ion.

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The Donor Properties of Nitroso Compounds. I. Complexes with *p*-Nitroso-N,N-dimethylaniline

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The donor properties of nitroso compounds with metal ions have not been well characterized. Complexes of copper, cobalt, and nickel salts and zinc perchlorate with the ligand *p*-nitroso-N,N-dimethylaniline have been prepared and studied. The infrared spectra, solution and mull visible spectra, magnetic moments, and molar conductances are reported. The basicity of nitrosobenzene is sufficiently increased by substitution of the dimethylamino group in the *para* position to allow the isolation of stable complexes. Even with this enhancement of the basicity, nitrosobenzene derivatives appear to be relatively weak bases. Coordinated nitrate ion is observed in the complexes with the nitrate salts.

Introduction

The donor properties of aromatic nitroso compounds acting as monodentate Lewis bases have not been systematically investigated although a literature search shows several instances of coordination occurring. In 1921, Baudisch reported a complex with ferrocyanide having the stoichiometry $Fe(CN)_5C_6H_5NO^{3-}$.[1] Further complexes of this nature have been reported with several *para*-substituted nitrosobenzene derivatives.[2] Also, nitrosobenzene has been reported to replace carbon monoxide in iron pentacarbonyl to yield $[(C_6H_5NO)Fe(CO)_3]_2$.[3] An adduct of nitrosobenzene with tin tetrachloride was reported to have the stoichiometry $SnCl_4 \cdot 2C_6H_5NO$.[4] *p*-Nitroso-N,N-dimethylaniline has been used as a color-producing reagent in the spectrophotometric determination of palladium,[5] iridium,[6] platinum,[7] and rhodium.[8] The fungicidal properties of several complexes with *p*-nitroso-N,N-dimethylaniline have been reported in several patents.[9-11] This study was undertaken in order to help characterize the donor properties of nitrosobenzene derivatives.

The ligand chosen was *p*-nitroso-N,N-dimethylaniline (NODMA). The dipole moment of the ligand is 6.90 D,[12] which indicates a large contribution of the polar resonance form to the structure.[13,14] This resonance form places a formal negative charge on the nitroso oxygen. The nitroso group is sensitive to *para* substitution on the benzene ring as evidenced by the increase in dipole moment from 3.14 D[15] in nitrosobenzene to the 6.90 D value for NODMA. The large dipole moment of NODMA and a nmr study by Korver, Vanderhaak, and deBoer[14] showing hindered rotation of the nitroso group are good evidence for the considerable contribution of the polar resonance form to the structure. The evidence presented above and steric considerations decrease the possibility that coordination could occur through the dimethylamino group.

Experimental Section

Preparation of Complexes.—The nickel chloride complex was prepared by dissolving the metal salt in absolute alcohol and adding a 6:1 molar excess of ligand dissolved in acetone. Precipitation was completed by the addition of ether. The remaining complexes were prepared by stirring the metal salt with 2,2-dimethoxypropane for 20–30 min and adding to this an acetone–NODMA solution containing a 6:1 molar excess of ligand. Precipitation was again completed by the addition of ether. The complexes were washed with ether and dried *in vacuo* overnight.

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