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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TABLE I

ANALYTICAL DATA, CONDUCTANCE DATA, AND MAGNETIC MOMENTS FOR COMPLEXES

	Elemental analyses, %							Conductance data in nitromethane at 25°		Magnetic moments at 25°	
	Carbon		Hydrogen		Nitrogen				Λ (molar),		
Compound	Calcd	Found	Calcd	Found	Calcd	Found	Mp, °C[g]	Concn, $M \times 10^4$	cm^2 mho $mole^{-1}$	μ_{eff}, BM	$10^6\chi_g$, cgs units
$CuCl_2 \cdot 2L$[d]	43.24	43.59	4.53	4.75	12.60	12.63	131 dec	8.15	50.4	1.89	2.95
$Cu(NO_3)_2 \cdot 2L$	39.42	39.22	4.14	4.46	17.23	17.02	137 dec	6.96	78.6	1.89	2.73
$Cu(ClO_4)_2 \cdot 3L \cdot 3H_2O$	37.61	37.27	3.95	4.42	10.96	10.77	b	17.2	167	1.39	0.548
$NiCl_2 \cdot L \cdot H_2O$[e]	32.29	32.85	4.06	3.92	9.41	10.13	b	c	c	3.49	16.6
$Ni(NO_3)_2 \cdot 2L \cdot 3H_2O$	35.77	35.42	4.84	5.20	16.27	15.65	160 dec	5.46	105	3.05	3.24
$Ni(ClO_4)_2 \cdot 4L \cdot 2H_2O$	42.97	43.04	4.96	4.83	12.53	12.61	215[a]	6.22	198	3.50	2.32
$CoCl_2 \cdot 2L$[f]	44.71	45.02	4.30	5.07	13.03	12.92	166 dec	2.56	20.3	4.25	17.1
$Co(NO_3)_2 \cdot 2L \cdot 4H_2O$	35.89	36.21	5.23	4.54	15.70	16.03	110–13	6.03	97.6	5.33	19.2
$Co(ClO_4)_2 \cdot 2L \cdot 2H_2O$	31.37	32.07	4.25	4.62	9.15	8.68	b	1.85	122	3.86	9.89
$Zn(ClO_4)_2 \cdot 3L \cdot 4H_2O$	36.64	36.21	4.87	4.36	10.68	10.21	129–130 dec	1.21	204	...	...

[a] Violent decomposition. [b] Mp >360°. [c] Insoluble. [d] Calcd: Cl, 16.35. Found: Cl, 16.40. [e] Calcd: Cl, 23.82. Found: Cl, 24.18. [f] Calcd: Cl, 16.50. Found: Cl, 15.60. [g] Uncorrected melting points.

TABLE II

SPECTRAL DATA

	Infrared (KBr disk)				Visible		
					Soln spectra in nitromethane[c]		
Compound	NO str, cm^{-1}	Free NO_3^- asym str, cm^{-1}	Coord NO_3^-, cm^{-1}	NO bend, cm^{-1}	λ_{max}, mμ	$10^{-4}\epsilon$, l./mole cm	Mull spectra λ, mμ
Ligand	1526 (1523)[b]			822 (827)[b]	426	3.03	388, 401, 445
$CuCl_2 \cdot 2L$	1497			832	430	5.35	406, 430, 515, 774, 920
$Cu(NO_3)_2 \cdot 2L$	1471[a]	1380	1277, 1015, 809	836	424	5.68	408, 458, 540
$Cu(ClO_4)_2 \cdot 3L \cdot 3H_2O$	1510			824	431	2.28	413, 450, 603
$NiCl_2 \cdot L \cdot H_2O$	1497			833	...	...	405, 520, 550, 682, 880
$Ni(NO_3)_2 \cdot 2L \cdot 3H_2O$	1477[a]	1380	1208, 1030, 810	832	427	4.97	405, 465, 550
$Ni(ClO_4)_2 \cdot 4L \cdot 2H_2O$	1494			830	428	10.3	405, 530, 580
$CoCl_2 \cdot 2L$	1499			831	432	5.61	403, 460, 535, 675
$Co(NO_3)_2 \cdot 2L \cdot 4H_2O$	1479[a]	1380	1208, 1039, 810	834	427	5.00	388, 402, 445, 550
$Co(ClO_4)_2 \cdot 2L \cdot 2H_2O$	1515			830	424	4.44	400, 520
$Zn(ClO_4)_2 \cdot 3L \cdot 4H_2O$	1492			834	425	6.84	420

[a] This band is probably a combination band of the nitroso stretch and the asymmetric stretching vibration of coordinated nitrate. [b] In chloroform solution. [c] Concentrations 10^{-5}–10^{-6}*M*.

Reagents.—*p*-Nitroso-N,N-dimethylaniline was prepared by nitrosation of N,N-dimethylaniline with sodium nitrite and hydrochloric acid. Spectrograde Eastman Organic nitromethane was used for visible solution spectra and conductance measurements. Nitrosobenzene was obtained from Aldrich Chemical Co.

Physical Measurements.—Infrared spectra were obtained using a Beckman IR5A recording spectrophotometer calibrated with polystyrene. The spectra were run as Nujol mulls using NaCl plates and as KBr disks. Solution spectra were run using Beckman NaCl solution cells. The visible and near-infrared spectra were obtained with a Cary Model 14 recording spectrophotometer equipped with 1-cm silica cells for solution spectra. The complexes obey Beer's law in the concentration ranges studied. The Nujol mull spectra were taken as smears on filter paper using the technique of Kleinberg, *et al.*[16] The Gouy method was used in obtaining magnetic moments with a Varian epr electromagnet operating at 12,000 G. $Hg[Co(SCN)_4]$ was used as calibrant[17] and diamagnetic corrections were made using Pascal's constants.[18] Conductance measurements were made with an Industrial Instruments Model RC-1 conductance bridge. The electrode was calibrated with standard KCl solution.

Analyses.—C, H, and N analyses were carried out by Alfred Bernhardt Microanalytisches Laboratorium, Mülheim (Ruhr), Hohenweg, Germany. Chloride analyses were obtained by the Mohr method.

Results

The complexes prepared with NODMA are reported in Table I. The stoichiometries of the complexes vary greatly depending on the anion present. A maximum of four ligands was found with nickel perchlorate. The more strongly coordinating anions such as chloride and nitrate are able to compete favorably with the ligand for coordination sites. The molar conductances of the chloride complexes of Cu^{2+} and Co^{2+} are low, indicating a high degree of association in solution. The nickel chloride complex is too insoluble for solution studies. Molar conductances for the nitrate complexes are in the range for 1:1 electrolytes while the perchlorate complexes are in the 2:1 electrolyte range of values in nitromethane. The magnetic moments reported in Table I are in expected ranges except for the slightly low values found for the copper and cobalt perchlorate complexes.

Visible and Infrared Spectra.—Table II shows the visible solution and mull spectra for the ligand and complexes. The intensity of the 420–430-mμ peak in the solution spectra obscured all other visible absorptions, but these absorptions are observable in the Nujol mull spectra. In nitromethane solution, the highly intense peak appears at 426 mμ for the ligand and exhibits a slight shift to longer wavelength in several of

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the complexes. In all of the complexes there is exhibited a large molar absorptivity. The visible and mull spectra of the zinc perchlorate complex have only one absorption and this is due to the ligand.

Also in Table II are the infrared spectral data for the ligand and complexes. The peak appearing at 1526 cm^{-1} in the KBr-disk spectrum of the ligand exhibits shifts of 11–55 cm^{-1} to lower energy in the complexes. Also the peak at 822 cm^{-1} in the ligand shifts to slightly higher energies in the complexes. Infrared bands attributed to nitrate are also reported in Table II. In addition to examining the KBr disk spectra of the ligand and complexes, the solution spectrum of NODMA was observed in chloroform.

Discussion

Visible Spectra.—The basic properties of the nitroso group appear to be enhanced by the contribution of the polar resonance form. The dominating feature of the solution spectra of the ligand and complexes is the high molar absorptivity of the peak appearing at about 400 mμ. This highly intense absorption in the solution spectra of substituted nitrosobenzene derivatives is thought to be due to an intramolecular charge transfer.[19] As the electron-donating ability of the *para* substituent is increased, λ_{max} shifts from 282 mμ in nitrosobenzene to 420 mμ in NODMA along with a corresponding increase in molar absorptivity.[19] This band is also sensitive to the solvent effects with a red shift and a large increase in intensity with increasing polarity of the solvent.[20] Complexing through the nitroso group of NODMA can help to increase the contribution of the charge-transfer resonance structure and cause the corresponding large values for molar absorptivity in the complexes. The peak appearing around 400 mμ in the Nujol mull spectra of all of the complexes has been assigned to the ligand and exhibits a small red shift.

The visible spectrum of the nickel chloride complex is characteristic of octahedral coordination but the stoichiometry indicates a low coordination number. The octahedral coordination may be achieved by a polymeric species involving chloride bridges and a polymer is indicated by the insolubility of the complex. The peaks at 460, 535, and 675 mμ in the spectrum of $CoCl_2 \cdot 2NODMA$ as well as the magnetic moment of 4.25 BM indicate a tetrahedral complex.[21] The complex with copper(II) chloride shows transitions corresponding to the usual tetragonally distorted state. The visible mull spectrum of the complex $Cu(NO_3)_2 \cdot 2NODMA$ has two transitions occurring at 458 and 540 mμ corresponding to those found in square-planar complexes.[22,23] The visible spectra of the cobalt nitrate and nickel nitrate complexes as well as their magnetic moments indicate octahedral coordination. The perchlorate complexes have spectra typical of octahedral coordination but the reason for the low magnetic moments of the copper and cobalt perchlorate adducts is not clear.

Infrared Spectra.—The interpretation of the infrared spectra of aromatic nitroso compounds is not entirely clear. The peak appearing at 1500–1550 cm^{-1} has been assigned as $\nu_{N=O}$.[13,24] However, Nakamoto and Rundle have assigned the peak at 1500–1550 cm^{-1} as $\nu_{N=O}$ conjugated with the carbon–carbon double bonds in the benzene ring and the peak at 1340–1360 cm^{-1} as $\nu_{N=O}$.[12] The N—O bending vibration was assigned at 822 cm^{-1}.[12] The infrared spectrum of the ligand in chloroform was observed since the N—O stretching and bending vibrations should shift as the hydrogen bonding increased. The vibration at 1527 cm^{-1} in KBr shifted to 1523 cm^{-1} in chloroform and that at 822 cm^{-1} shifted to 827 cm^{-1}. The shifts were in the directions to be expected with increased hydrogen bonding. The 1527-cm^{-1} peak in the ligand shifts to lower energies in the complexes, as would be expected when double-bond character decreases on coordination. Also the band at 1339 cm^{-1} appears to shift to lower energies in the complexes but it is very difficult to make definite assignments in this region owing to strong absorptions nearby.

The infrared spectra of the nitrate complexes indicate the presence of coordinated nitrate with the appearance of new bands in the regions 810, 1015–1070, 1208–1277, and 1471–1479 cm^{-1}.[25] The band at about 1470 cm^{-1} in the nitrate complexes is interesting because it is the only band in the region where the nitroso group should absorb. The band at 1470 cm^{-1} is at a lower frequency than the nitroso absorptions in the perchlorate and chloride complexes. This leads to the conclusion that this is a combination band consisting of the nitroso frequency and the asymmetric stretching frequency of coordinated nitrate.[25] There is also a band in the spectra of the nitrate complexes appearing at 1380 cm^{-1}. This is in the region of asymmetric stretch for the free nitrate ion. The molar conductance values are in the range of 1:1 electrolytes for the nitrate complexes. These conductance values as well as the stoichiometries and the 1380-cm^{-1} absorption are evidence for the presence of both coordinated and uncoordinated nitrate.

Conclusions

It has been found through nmr studies that NODMA in trifluoroacetic acid protonates predominantly on the oxygen.[26] Also a related compound, N-nitrosodimethylamine, protonates on the oxygen in fluorosulfonic acid.[27] This indicates that the oxygen is the basic site in these nitroso compounds. The decrease of the energy of the nitroso stretching frequency in the infrared spectra of the complexes is evidence, along with the protonation studies, that coordination with NODMA takes place through the nitroso oxygen.

The donor strength of a nitroso group on a benzene

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ring can be significantly increased by substitution of a strongly electron-donating group *para* to the nitroso moiety. However, even with this enhancement, the complexes formed are of low coordination number with respect to the ligand. It appears that even weakly coordinating anions such as nitrate and chloride can compete favorably with NODMA for coordination sites. It is interesting to compare this type of ligand with the pyridine N-oxides which have received much interest. The same resonance forms are available to nitrosobenzene as to pyridine N-oxide and coordination is through the N–O group. However, the infrared stretching frequencies indicate considerably more double-bond character in the nitroso compound. The N–O stretching frequency appears at around 1250 cm^{-1} in pyridine N-oxide[28] and at about 1500 cm^{-1} in nitrosobenzene.[13] The phenyl group seems to act as more of an electron sink to the nitroso compound whose dipole moment of 3.14 D[15] is less than that of pyridine N-oxide in which the value is 4.24 D.[29] Apparently this stabilization of the double-bonded N–O group decreases the basicity of the nitroso group toward metal ions relative to pyridine N-oxide. This decrease in basicity does not seem to be a steric problem since the N–O group is well removed from the benzene ring. Complexes with pyridine N-oxide easily exhibit coordination numbers of 6 with metal ions except when a strongly electron-withdrawing group such as nitro is substituted in the *para* position in pyridine N-oxide. Substitution of the dimethylamino group in the *para* position in nitrosobenzene greatly increases the dipole moment and seems to enhance the relative basicity of the nitroso group. This increased basicity is reflected in the fact that we were unable to obtain complexes using similar experimental techniques with nitrosobenzene.

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A Novel Series of Six-Coordinated Iron(II) Diimine Complexes with Half-Quenched Spin

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The magnetic behavior of seven new six-coordinated iron(II) complexes having the general formula $Fe^{II}(diimine)_2X_2$, where X_2 stands for bidentate oxalate^{2-} and malonate^{2-} or two F^- ligands, has been studied. Between 77 and 300°K, the susceptibilities follow the Curie–Weiss law, $\chi_m = C_m/(T - \Theta)$, with Θ between -9 and $-51°$. The magnetic moments at 293°K are ~3.90 BM, corresponding to two unpaired electrons with a contribution of ~1.0 BM from second-order Zeeman effect. The agreement between corresponding moment values of the solid and in solution excludes the possibility that the rare $S = 1$ condition of iron(II) arises from intermolecular exchange interactions. Mössbauer effect studies result in isomer shifts $\delta = 0.33 \pm 0.04$ mm/sec, consistent with $S = 1$, and ΔE_Q between 0.18 and 0.31 mm/sec giving evidence for a very small electric field gradient. The electronic and epr spectra are briefly reported. The two Fe–O and the Fe–F stretching modes located in the infrared spectrum at 522, 340, and *ca.* 495 cm^{-1}, respectively, indicate that the compounds are *cis* monomeric. The unit cell of $[Fe(phen)_2ox] \cdot 5H_2O$ is extended along the b axis; the crystals are triclinic, with space group $P\bar{1}$ or P1 and $Z = 16$.

Introduction

Most simple mononuclear iron(II) complexes may be divided into two classes on the basis of their magnetic behavior: (i) high-spin compounds with four unpaired electrons exhibiting a quintet ground state ($S = 2$), *e.g.*, $Fe(H_2O)_6^{2+}$ and $FeCl_4^{2-}$, in which case the magnetic moment is 4.9–5.5 BM at room temperature and temperature dependent, following a curve as described previously;[3] (ii) low-spin compounds with all electrons paired and thus with a singlet ground state ($S = 0$) as in $Fe(CN)_6^{4-}$, compounds of this type showing a contribution from second-order Zeeman effect resulting in μ_{eff} values of up to 1.0 BM. Deviations from the normal high-spin and low-spin patterns may be encountered in six-coordinated iron(II) if the ligand field strength Δ approaches the mean spin-pairing energy π for the d^6 configuration, where $\pi = (5/2)B + 4C$, B and C being the Racah parameters. Thus the unusual μ_{eff} *vs.* T curves of certain diisothiocyanato- and diisoselenocyanatobis(diimine) complexes of iron(II), which were recently studied by the present authors,[4-6] are caused by transitions between the ground states $^5T_2$ and $^1A_1$.[7]

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