Complexes of Aromatic Amine Oxides: Nickel(II) Complexes of 6-Substituted Quinoline N-oxides

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The coordinating properties of a series of 6-substituted quinoline N-oxides (6ZQNO) toward nickel-(II) have been investigated. The compounds have been assigned octahedral structures with general formula [Ni(6ZQNO)₆]X₂ where Z=CH₃O, CH₃, H, Cl, Br, or NO₂ and X=ClO₄ or BF₄. The visible and infrared spectra and magnetic properties of these complexes are discussed and compared with the previously reported nickel complexes of the 4-substituted quinoline N-oxides and the 4-substituted pyridine N-oxides. The relative π-acceptor abilities of the three series of ligands are discussed.

Introduction

There has recently been a considerable amount of interest in the donor properties of aromatic amine oxides.[2] These ligands have received much attention because a large change in the basicity with a concomitant minimal change in the steric requirement can be achieved by varying substituents on the aromatic ring.[3] It has been suggested from data available for complexes of 4-substituted pyridine N-oxides[4,5] and 4-substituted quinoline N-oxides[6] that the quinoline N-oxides are better π-acceptor ligands than the 4-substituted pyridine N-oxides. It has recently been demonstrated that the effect of substituents in the 6-position of quinoline N-oxide is small.[7]

Since the 4- and 6-substituted quinoline N-oxides have the same steric requirement, it was of interest to prepare complexes of the 6-substituted quinoline N-oxides to compare their coordinating properties with those of the 4-substituted quinoline N-oxides. No complexes of the 6-substituted quinoline N-oxides have been reported previously. Ligands with the following substituents, CH₃O, CH₃, H, Cl, Br, and NO₂, were selected for this study.

Experimental Section

Reagents. 6-Methoxyquinoline N-oxide was obtained from Aldrich Chemical Company and recrystallized twice from acetone, m.p. 88-89°C.[8] 6-Methylquinoline N-oxide was prepared from 6-methylquinoline (Eastman) by the method of Colonna and Risaliti.[9] 6-Bromo, 6-chloro-, and 6-nitroquinoline N-oxides were prepared from the corresponding quinolines (Aldrich Chemical Company) by the method of Backman and Cooper.[8] All melting points agreed with the literature values.

Synthesis. The coordination compounds were prepared by a previously reported method.[6] The elemental analyses are presented in Table I. Carbon, hydrogen and nitrogen analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mulheim, Germany. Metal analyses were determined by titration with EDTA.[10]

Solution Electronic Spectra. Solution spectra were run in the 350-1500 mμ region on a Cary model 14 recording spectrophotometer. These solutions contained approximately a ten-fold molar excess of added ligand to retard dissociation of the complex. All spectra were run in nitromethane. 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(CNS)₄] was used as a calibrant.[11] The diamagnetic corrections were calculated from Pascal's constants.[12] The data are presented in Table III.

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

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Table I. Elemental Analyses and Physical Constant Data

Complex	Color	m.p. °C[a]	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%Ni Calcd.	%Ni Found
Ni(6MeQNO)₆(ClO₄)₂	peach	234-236	59.42	59.37	4.45	4.78	6.92	6.32	4.84	4.94
Ni(6MeQNO)₆(BF₄)₂	peach	228-230	—	—	—	—	—	—	4.95	5.12
Ni(6MeOQNO)₆(ClO₄)₂	peach	137-139	50.86	50.16	4.66	4.53	5.93	5.80	4.15	4.27
Ni(6NO₂QNO)₆(ClO₄)₂ . 2H₂O	peach	284-286	45.20	45.45	2.79	2.72	11.72	11.88	4.04	3.93
Ni(6NO₂QNO)₆(BF₄)₂	light red	269-271	—	—	—	—	—	—	4.28	4.23
Ni(6BrQNO)₆(ClO₄)₂ . 12H₂O	light red	292-294	35.65	35.87	3.30	2.87	4.62	4.65	3.23	3.54
Ni(6BrQNO)₆(BF₄)₂	light red	129-131	—	—	—	—	—	—	3.72	4.41
Ni(6ClQNO)₆(ClO₄)₂ . H₂O	light red	224-227	47.91	48.15	2.81	3.01	6.21	6.51	4.34	4.61
Ni(6ClQNO)₆(BF₄)₂	red orange	150-153	—	—	—	—	—	—	4.43	4.58

[a] Melting points are uncorrected.

Table II. Electronic Absorption Maxima of [Ni(6ZQNO)₆]X₂ Complexes [a]

6Z	X	$^3A_{2g} \rightarrow {}^3T_{2g}$ [b]	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^1E_g$	Conc. M
CH₃O	ClO₄	8130 (11)	14200 (27)	24700 (1440)	12900 (21)	1.39 × 10⁻³
CH₃	ClO₄	8090 (11)	13900 (11)	23900 (143)	12900 (11)	1.47 × 10⁻³
CH₃	BF₄	8010 (11)	13900 (12)	23900 (578)	12900 (12)	1.73 × 10⁻³
Br	ClO₄	8110 (16)	14000 (17)	23400 (1320)	12800 (15)	2.42 × 10⁻³
Br	BF₄	7900 (17)	13900 (19)	23600 (256)	12700 (18)	1.51 × 10⁻³
Cl	BF₄	7850 (17)	13900 (16)	23800 (950)	12900 (16)	2.11 × 10⁻³
NO₂	ClO₄	8240 (12)	14440 (16)	24700 (1590)	12900 (12)	1.26 × 10⁻³
NO₂	BF₄	8170 (11)	14200 (14)	24700 (840)	12900 (14)	2.38 × 10⁻³
H [c]	ClO₄	7900 (13)	13700 (13)	23800 (183)	12700 (13)	1.04 × 10⁻²

[a] The spectra were run in nitromethane solution; both 1 and 10 cm cells were used. [b] ν In cm⁻¹ (extinction coefficient; l.mole⁻¹.cm⁻¹). [c] Data from reference 6.

Table III. Ligand Field Parameters and Magnetic Moments of [Ni(6ZQNO)₆]X₂ Complexes

6Z	X	Dq	β	$\nu_{2\,obs.}$ [a]	$\nu_{2\,calc.}$	$10^6 X_m$	$10^6 X_{m'}$	T°K	μ_{eff}BM
CH₃O	ClO₄	813	0.88	13500	13600	4110	4866	297°	3.41
CH₃	ClO₄	809	0.88	13400	13400	4399	5048	297°	3.48
CH₃	BF₄	801	0.83	13400	13300	—	—	—	—
H [b]	ClO₄	790	0.84	13200	13200	4781	5412	299°	3.61
Br	ClO₄	811	0.79	13300	13400	4295	5120	298°	3.48
Br	BF₄	790	0.84	13400	13000	—	—	—	—
Cl	BF₄	785	0.84	13400	13100	4339	5033	298°	3.48
NO₂	ClO₄	824	0.87	13600	13700	4128	4802	297°	3.39
NO₂	BF₄	817	0.87	13600	13600	—	—	—	—

[a] Transition band ν_2, cm⁻¹. [b] Data from reference 6.

Table IV. Infrared Frequencies (cm⁻¹) for [Ni(6ZQNO)₆]X₂ Complexes

Z	ν_{NO} Ligand	ν_{NO} Complex	δ_{NO} Ligand	δ_{NO} Complex
CH₃O	1242	1213	852	866
CH₃O	1207	1180		
CH₃	1305 [a]	1205	844 [a]	845
CH₃	1243 [a]	1170		
H	1229 [a]	1224	788 [a]	804
Cl	1300	1267	875	905
Cl	1269	1223		
Br	1268	1268	864	871
Br	1224	1221		
NO₂	1290	1300	830	857
NO₂	1268	1265		

[a] Data from reference 14.

Ligand Field Calculations. The secular equations for nickel(II) (d⁸) were solved in the weak field formalism; the crystal field matrices have been reported by Orgel.[13] The values of Dq were obtained directly from the first (lowest energy) spin allowed absorption band.

Results

The elemental analyses indicate that the compounds may be formulated as NiL₆X₂.nH₂O. The metal analyses were all run immediately after drying the compounds at reduced pressure over phosphorus pentoxide and in some cases indicate a different degree of hydration (different value for n) than what is indicated by the carbon, hydrogen and nitrogen analyses.

The nitrogen-oxygen stretching frequency, ν_{NO}, of the 6-substituted quinoline N-oxides like that of the 4-substituted quinoline N-oxides is coupled with the aromatic ring vibrations[6,14] and therefore, shows no correlation to the structure. The values for ν_{NO} and δ_{NO} for the ligands and complexes are presented in Table IV. The values for quinoline N-oxide and 6-methylquinoline N-oxide have been previously reported.[14] The assignment of ν_{NO} is not unequivocal as there are several peaks which appear in this region for both the 6-substituted quinolines and the 6-substituted quinoline N-oxides. However, δ_{NO} may be

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assigned with fair certainty. ν_{NO} was assigned by using the spectra of quinoline N-oxide and 6-methyl-quinoline N-oxide, which have been assigned as guides and comparing the spectra of the quinolines to those of the quinoline N-oxides. Most of the peaks assigned as ν_{NO} shift to lower energy upon complexation. A shift to lower energy was also found for the complexes of the pyridine N-oxides[4,5] but not for the complexes of the 4-substituted quinoline N-oxides.[6]

The electronic spectra (Table II) were interpreted by the aid of ligand field theory[15,17] using the weak field formalism. The data presented in Tables II and III are typical of octahedral nickel(II) complexes. These complexes undergo solvolysis reactions in solution.[4,6] To retard the solvolysis and to ensure that spectra of the *hexakis*(N-oxide) complexes would be recorded, the spectra were all run with the presence of approximately a 10:1 mole ratio of excess ligand. Solid state mull spectra showed no gross differences from the solution spectra containing excess ligand. The charge transfer bands present in the other N-oxide complexes[4-6] were also noted here; and because of this, the extinction coefficients for ν_3 were higher than those normally found for Laporte forbidden d-d transitions. The Dq values (Table III) are all around 800 cm^{-1}, and vary over a very limited range. The β values are relatively high, suggesting little covalency in the metal oxygen bond.

The magnetic moments are all in the allowed range for high spin octahedral nickel(II) complexes. The magnetic moments (3.39-3.61 BM) are very similar to what has been reported[6] for the nickel(II) complexes of the 4-substituted quinoline N-oxides (3.30-3.61 BM).

Discussion

The steric interactions involved in forming an octahedral complex should be the same for the 4- and 6-substituted quinoline N-oxides. Thus, any difference in ligational ability for the two series of ligands should be a consequence of a difference in basicity and/or a difference in the π-acceptor ability. There have only been two pK$_a$ values (quinoline N-oxide[18] and 6-methylquinoline N-oxide[18]) determined for the 6-substituted quinoline N-oxides. Nevertheless, an ordering of pK$_a$ values for the 6-substituted quinoline N-oxides may be obtained from Hammett sigma constants[7,19] and these two pK$_a$'s. Using this data, one obtains the equation pK$_a$ = -0.882σ + 0.86, relating pK$_a$ and σ.

The approximate pK$_a$ values of the other 6-substituted quinoline N-oxides were calculated from this equation and are listed in Table V, along with the pK$_a$ values of the 4-substituted quinoline N-oxides for comparison.

Table V. pK$_a$ Values of Quinoline N-Oxides

Z	pK$_a$ 6ZQNO	pK$_a$ 4ZQNO[3]	σ
CH$_3$O	1.1	1.62	-0.268
CH$_3$	1.01 [a]	1.44	-0.170
H	0.86 [a]	0.86	0
Cl	0.7	0.47	0.227
NO$_2$	0.2	-1.39	0.778

[a] Experimental values, reference 18.

The pK$_a$ values demonstrate that the effect of substitution in the 6-position is not as great as that found for substitution in the 4-position. This might be expected as substituents in the 4-position may conjugate directly with the oxygen atom while the conjugation of the 6-position proceeds only to a position one atom removed (the ring nitrogen) from the oxygen atom. This difference in the substituent effect has previously been demonstrated for the hydrogen bonding interaction of the N-oxides with phenols.[7] The calculated pK$_a$'s show that the 6-substituted quinoline N-oxides are stronger bases than the 4-substituted quinoline N-oxides when the substituents are deactivating and weaker bases when the substituents are activating. The difference in the pK$_a$ values for the 6-substituted quinoline N-oxides is not very large, and the basicities are not significantly different from that of quinoline N-oxide itself. Consequently, the bonding abilities of the various 6-substituted quinoline N-oxides should not be very different from that of quinoline N-oxide.

The ligational ability of the quinoline N-oxides should be less than that of the pyridine N-oxides owing to a greater steric interaction, not only between the ligand and the metal ion, but also among the ligands themselves. However, the 4-substituted quinoline N-oxides and the 4-substituted pyridine N-oxides were found to be very similar in ligational ability.[6] This was explained by the greater π-acceptor strength of the 4-substituted quinoline N-oxides. The Dq values of the 6-substituted quinoline N-oxides (785-824 cm^{-1}) are very similar to those found for the 4-substituted quinoline N-oxides[6] (790-874 cm^{-1}). The metal-oxygen stretching frequencies[20] for the 4-substituted quinoline N-oxide complexes of nickel(II) varied from 340 cm^{-1} to 368 cm^{-1} and the metal-oxygen stretching frequencies of the 6-substituted quinoline N-oxide complexes of nickel(II) varied from 345 cm^{-1} to 360 cm^{-1}. The similarity of Dq and the metal-oxygen stretching frequencies for these two series of ligands indicate that their ligational ability is very nearly the same. As a result, the 6-substituted quinoline N-oxides like the 4-substituted quinoline N-oxides, must be better π-acceptors than the pyridine N-oxides. While it was mainly the π-acceptor ability of the 4-substituted quinoline N-oxides that made their ligational ability comparable to that of the 4-substituted pyridine N-oxides, it is a combination of the greater basicity and π-acceptor ability of the 6-substituted quinoline N-oxides which makes their ligational ability similar to that of the 4-substituted pyridine N-oxides.

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