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Nickel(II) Complexes of Some Aromatic Amine Oxides

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The preparation and properties of the complexes of nickel(II) salts with the ligands: 2-methylpyridine N-oxide (2picNO), 2-ethylpyridine N-oxide (2etpyNO), 2,4-dimethylpyridine N-oxide (2,4LNO), 2-methylquinoline N-oxide (2MeQNO), quinoline N-oxide (QNO) and isoquinoline N-oxide (IQNO) are described. The structures of these complexes were determined with the aid of elemental analyses, magnetic and electronic spectral data, infrared data, and conductance data used in conjunction with ligand field theory. Complexes having the following general formulas have been prepared: $NiL_6X_2.nH_2O$, *L*=2etpyNO, *X*=ClO_4, *L*=IQNO, *X*=NO_3; $NiL_4X_2.nH_2O$, *L*=2picNO, *X*=ClO_4, *L*=2etpyNO, 2,4LNO, *X* = NO_3. $NiL_3X_2.nH_2O$, *L* = QNO, *X* = NO_3; $NiLX_2.nH_2O$, *L=all N-oxides, X*=Cl *and* $NiL_2X_2.nH_2O$, *L*=2picNO, 2MeQNO, IQNO, *X*=NO_3. *All the complexes prepared appear to be six-coordinate.*

Introduction

Many studies involving the coordinating properties of various substituted aromatic amines[2-9] toward nickel(II) have been reported. Whereas, the maximum coordination number of pyridine with nickel(II) is four[2] and that of quinoline is generally two,[6] (four in $Ni(quinoline)_4(NCS)_2)$[9], the usual coordination number of both the pyridine N-oxides[10-11] and the quinoline N-oxides is six.[12-14] The N-oxides are able to achieve a greater coordination number than the corresponding amines because of the difference in the steric interactions. We report here the coordinating properties of pyridine N-oxides substituted in the 2-position, 2-methylquinoline N-oxide and some complexes of quinoline N-oxide and insoquinoline N-oxide. These ligands were investigated to ascertain what effect the substituents in the 2-position would have in determining the geometries of the resultant complexes. The following 2-substituted pyridine N-oxides were chosen for this purpose: 2-methylpyridine N-oxide (2picNO), 2-ethylpyridine N-oxide (2etpyNO), and 2,4-dimethylpyridine N-oxide (2,4LNO). Complexes of nickel(II) perchlorate, chloride and nitrate are reported.

Experimental Section

Reagents. 2-Ethylpyridine N-oxide was obtained from Aldrich Chemical Company and purified by vacuum distillation. 2-Methylpyridine N-oxide, 2,4-dimethylpyridine N-oxide and 2-methylquinoline N-oxide were prepared from the corresponding amines (Eastman) by the method of Ochiai.[15] The preparation of quinoline and isoquinoline N-oxides has been previously reported.[12]

Preparation of the Complexes. The perchlorate complexes were prepared from an ethanol solution containing a ligand to metal salt mole ratio of approximately 7:1. The crystals either formed immediately or after standing for several hours at room temperature. They were filtered, washed with cold ethanol and anhydrous ether, and then dried *in vacuo* over phosphorus pentoxide.

The nitrate complexes with the general formulas $NiL_6(NO_3)_2.nH_2O$, $NiL_4(NO_3)_2.nH_2O$ or $NiL_3(NO_3)_2.nH_2O$, and $Ni(IQNO)_2(NO_3)_2$ were all prepared from ethanol solutions using ligand to nickel nitrate mole ratios of 7:1, 5:1, and 2:1, respectively.

The chlorides were all prepared from ethanol solutions containing a ligand to metal salt mole ratio of approximately 7:1. It was found that the nature of the product formed did not depend upon the amount of ligand present, only $NiLCl_2.nH_2O$ type complexes being formed. The elemental analyses appear in Table I.

Physical Measurements and Ligand Field Calculations. The electronic and infrared spectra, magnetic moments, conductance measurements analytical analyses and ligand field calculations were obtained as previously described.[12,13] These data appear in Tables I-V.

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Table I. Elemental Analyses and Physical Constant Data

Complex	m.p. °C	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%Ni Calcd.	%Ni Found
$Ni(2etPyNO)_6(ClO_4)_2 . 2H_2O$	128-130	48.80	48.69	5.62	5.70	8.13	7.55	5.68	6.41
$Ni(2etPyNO)_4(NO_3)_2$	128-130	49.70	49.01	5.35	5.30	12.44	12.31	8.70	9.10
$Ni(2picNO)_4(ClO_4)_2$	113-117	41.52	41.60	4.05	4.04	8.07	7.64	8.46	8.15
$Ni(2picNO)_2(NO_3)_2 . H_2O$	133-135	34.37	34.26	3.82	4.21	13.36	13.21	14.00	13.82
$Ni(2,4LNO)_4(NO_3)_2$	170-173	49.70	49.63	5.33	5.51	12.44	12.90	8.70	8.92
$Ni(2MeQNO)_2(NO_3)_2 . \frac{1}{2}H_2O$	230-231	47.21	47.20	3.74	3.94	11.00	10.91	11.50	11.68
$Ni(IQNO)_2(NO_3)_2$	230-232	45.68	45.47	2.96	3.23	11.84	11.79	12.41	12.29
$Ni(IQNO)_6(NO_3)_2 . \frac{1}{2}H_2O$	205-210	61.02	60.89	4.08	3.93	10.55	10.11	5.53	5.68
$Ni(QNO)_3(NO_3)_2 . \frac{1}{2}H_2O$	146-150	51.69	51.63	3.99	4.17	11.18	11.09	9.36	9.79
$Ni(2etPyNO)Cl_2 . 2H_2O$	290	29.10	29.65	4.50	4.49	4.85	4.73	20.32	20.32
$Ni(2picNO)Cl_2 . 2H_2O$	>360	27.80	27.62	4.20	3.83	5.40	5.32	22.70	23.05
$Ni(QNO)Cl_2 . 2H_2O$	>360	37.00	37.26	3.08	3.57	4.80	4.79	18.89	18.76
$Ni(IQNO)Cl_2 . \frac{1}{2}H_2O$	>360	38.06	38.40	3.52	3.48	4.93	4.98	20.69	20.52

Table II. Conductance, Infrared and Magnetic Moment Data

Complex	Conc., $M \times 10^3$	λm [a] cm^2 mho $mole^{-1}$	ν_{NO}	$\Delta\nu_{NO}$	$10^6\chi_m$	$10^6\chi_m$	$\mu_{eff.}$ BM [b]
$Ni(2etPyNO)_6(ClO_4)_2 . 2H_2O$	3.78	174	1208	−51	3602	4204	3.17
$Ni(2etPyNO)_4(NO_3)_2$	2.06	20	1201	−58	5590	5951	3.78
$Ni(2picNO)_4(ClO_4)_2$	1.28	141	1210	−36	4207	4534	3.16
$Ni(2picNO)_2(NO_3)_2 . H_2O$	1.79	27	1205	−41			
$Ni(2,4LNO)_4(NO_3)_2$	1.32	44	1210	−40			
$Ni(2MeQNO)_2(NO_3)_2 . \frac{1}{2}H_2O$	2.45	27	1190	−50	4963	5205	3.52
$Ni(IQNO)_2(NO_3)_2$	1.90	28	1162	−18	4016	4228	3.18
$Ni(IQNO)_6(NO_3)_2 . \frac{1}{2}H_2O$	1.32	69	1160	−20	4247	4800	3.39
$Ni(QNO)_3(NO_3)_2 . \frac{1}{2}H_2O$	4.31	21	1209	−26			
$Ni(2etPyNO)Cl_2 . 2H_2O$		[c]	1189	−70	4185	4315	3.10
$Ni(2picNO)Cl_2 . 2H_2O$		[c]	1195	−51			
$Ni(QNO)Cl_2 . 2H_2O$		[c]	1210	−25	4190	4359	3.23
$Ni(IQNO)Cl_2 . \frac{1}{2}H_2O$		[c]	1160	−20			

[a] Typical values[16,17] of λ_m in nitromethane are: non-electrolyte, 0-50; 1:1, 80-100; 2:1, 130-180. [b] Temperatures ranged from 296° to 299°K. [c] Insoluble.

Table III. Electronic Absorption Maxima [a]

Complex	State	$^3A_{2g} \rightarrow {}^3T_{2g}$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^1E_g$	Unassigned
$Ni(2etPyNO)_6(ClO_4)_2 . 2H_2O$	Mull	7750	12600	27600		19800
$Ni(2etPyNO)_4(NO_3)_2$	Mull	8370	13800	27600	12600	
$Ni(2picNO)_4(ClO_4)_2$	Mull	8380	13500	26500	12600	19400
$Ni(2picNO)_2(NO_3)_2 . H_2O$	Mull	8790	13800	28100	13000	
$Ni(2,4LNO)_4(NO_3)_2$	Mull	8350	13700	26000		
$Ni(2MeQNO)_2(NO_3)_2 . \frac{1}{2}H_2O$	CH_3NO_2	8850 (18)	15100 (36)	25200 (84)	12700 (24)	20600
$Ni(IQNO)_2(NO_3)_2$	Mull	8180	14400	24300	12800	
$Ni(IQNO)_6(NO_3)_2 . \frac{1}{2}H_2O$	CH_3NO_2	8710 (9)	14400 (25)	23900 (161)	12600 (18)	18000
$Ni(QNO)_3(NO_3)_2 . \frac{1}{2}H_2O$	Mull	8140	13600	27000		19400

[a] ν in cm^{-1} (extinction coefficients $l\ mole^{-1}\ cm^{-1}$).

Table IV. Infrared Frequencies of the Nitrate Group for Some Nickel Nitrate Complexes, cm^{-1}

Compound	assym. stretch ν_3	sym. stretch ν_3'	NO stretch ν_1	non-planar def. ν_4
Coordinated Nitrate [a]	(1530-1480)	(1290-1250)	(1030-970)	(800-780)
Ionic Nitrate [a]	(1390-1350)	(1020-1150)	(830-810)	720
$Ni(2etPyNO)_4(NO_3)_2$	1511	1270	1031	782
$Ni(2picNO)_2(NO_3)_2 . H_2O$	1492	1282	1023	810
$Ni(2,4LNO)_4(NO_3)_2$	1495	1280	995	792
$Ni(QNO)_3(NO_3)_2 . \frac{1}{2}H_2O$	1480	1297	1030	780
$Ni(IQNO)_2(NO_3)_2$	1515	1270	1032	805
$Ni(IQNO)_6(NO_3)_2 . \frac{1}{2}H_2O$	1357	1048	815	720
$Ni(2MeQNO)_2(NO_3)_2 . \frac{1}{2}H_2O$	1502	1270	1033	804

[a] Data from references 18 and 19.

Results and Discussion

The elemental analyses in Table I indicate that in general substitution in the 2-position is sufficient to reduce the number of coordinated N-oxide ligands to four or less. In contrast, six 2-ethylpyridine N-oxide ligands coordinated with nickel perchlorate. Several attempts to prepare the hexakis(2-methylpyridine N-oxide) complex were unsuccessful. It is surprising that 2-methylpyridine N-oxide does not form a hexakis complex while 2-ethylpyridine N-oxide does, especially since hexakis complexes are easily formed by both the 4- and 6-substituted quinoline N-oxides.[12,13] There does not seem to be any apparent explanation for this phenomenon. Certainly one would expect greater steric interaction with 2-ethylpyridine N-oxide than with 2-methylpyridine N-oxide.

The elemental analyses of the chloride complexes showed that only complexes of the type $NiLCl_2 . nH_2O$ were formed. Complexes of this formulation were prepared with 2-ethyl and 2-methylpyridine N-oxide and with quinoline N-oxide and isoquinoline N-oxide. Pyridine N-oxide has also been reported to form a complex with nickel chloride having the same stoichiometry.[20]

The conductance data indicate that the perchlorate complexes are 2:1 electrolytes, the nitrate complexes non-electrolytes and that $Ni(IQNO)_6(NO_3)_2$ is intermediate between a non-electrolyte and a 1:1 electrolyte. Apparently the nitrate ion displaces isoquinoline N-oxide from solutions of the latter complex. Conductance measurements on the chloride complexes were not carried out since these compounds were insoluble in solvents which did not decompose them.

The magnetic moments (Table III) establish that the nickel(II) complexes are spin free, but the values are high for six-coordinate complexes (*vide infra*) indicating that there is a large orbital contribution to the magnetic moment. High magnetic moments have also been reported for other N-oxide complexes of nickel(II).[10-14]

The infrared data presented in Table II, is consistent with that reported for other N-oxide complexes[10,11,20,22] in that ν_{NO} shifts as expected to lower energy upon complexation. The shift in ν_{NO} ($\Delta\nu_{NO}$) ranges from -18 to -70 cm^{-1}. The perchlorate ion is not coordinated in the solid state as the infrared spectra[7] of these complexes possess a sharp singlet around 620 cm^{-1} and a broad strong singlet around 1110 cm^{-1}. The infrared frequencies for the nitrate group are given in Table IV. Comparison of this data with reported ranges for previous studies[18,19] shows that all the nitrate complexes reported here contain coordinated nitrate except $Ni(IQNO)_6(NO_3)_2$. It is not usually possible from infrared data alone to distinguish between monodentate and bidentate coordinated nitrate ions.[18] However, from a consideration of the stoichiometries of the nitrate complexes and the conclusion (*vide infra*) that the electronic spectral data are typical of six-coordinate nickel(II) compounds, we can suggest that some nitrate ions may be coordinating in a monodentate and others in a bidentate fashion. For example, the nitrate group could function as a bidentate ligand in the complex $Ni(IQNO)_2(NO_3)_2$ and as a monodentate ligand in the compound $Ni(2etPyNO)_4(NO_3)_2$.

Table V. Ligand Field Parameters for Some Nickel(II) Nitrate Complexes

Complex	Dq	β	$\nu_2$obs.[a]	ν_2Calcd.
$Ni(2etPyNO)_4(NO_3)_2$	852	0.97	13800	14300
$Ni(2picNO)_2(NO_3)_2 . H_2O$	879	0.95	13800	14700
$Ni(2,4LNO)_4(NO_3)_2$	835	0.94	13700	14000
$Ni(QNO)_3(NO_3)_3 . \frac{1}{2}H_2O$	814	0.93	13600	13800
$Ni(IQNO)_2(NO_3)_2$	817	0.84	14400	13600
$Ni(IQNO)_6(NO_3)_2 . \frac{1}{2}H_2O$	871	0.76	14400	14200
$Ni(2MeQNO)_2(NO_3)_2 . \frac{1}{2}H_2O$	885	0.83	15100	14600

[a] ν in cm^{-1}, $\nu_2$obs. is taken as the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition.

The electronic spectral data for the complexes listed in Table III are typical of octahedral nickel(II) complexes. Ligand field calculations were made on the nitrate complexes for supporting evidence that these comlpexes are six-coordinate using the weak field formalism and assuming octahedral symmetry.[21] The results appear in Table V. The agreement of the calculated and experimental values of ν_2 upholds the suggestion that these complexes are at least pseudo octahedral. The assignments of the electronic transitions listed in Table III were made assuming octahedral symmetry. The Dq values indicate that in general the nitrate ion and the aromatic amine oxides occupy very close positions in the spectrochemical series. The values for β are quite similar to those reported for nickel N-oxide complexes[10-13] and suggest little covalency in the metal-oxygen bond. The compounds, $NiL_6(NO_3)_2$, $NiL_4(NO_3)_2$, $NiL_3(NO_3)_2$, and $NiL_2(NO_3)_2$ have all been found and thus far the nitrate ligand is the only anion with which various stoichiometries have been formed with the aromatic amine oxides. Another indication that the amine oxides and the nitrate ion have similar coordinating abilities is the isolation of the two complexes $Ni(IQNO)_6(NO_3)_2$ and $Ni(IQNO)_2(NO_3)_2$.

The chloride and perchlorate comelpxes also appear to be octahedrally coordinated. Octahedral coordination may result *via* N-oxide bridges,[22] chloride bridges, or aquo bridges, all of which are known for coordination compounds. The mode of bridging for the complexes reported here is not known. If there were both bridging N-oxides and terminal N-oxides to give a coordination number of six, one might expect to see two absorptions for the nitrogen-oxygen stretch-

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to contain only bridging N-oxide groups sometimes exhibit two nitrogen-oxygen stretching frequencies.[22] On the other hand, those copper compounds which contain both types of N-oxides (terminal and bridging) do not consistently exhibit either one or two stretching modes. In this work only one N-oxide stretching frequency was found. For the Ni(2picNO)$_4$-(ClO$_4$)$_2$ complex N-oxide bridges are almost certainly necessary for octahedral coordination, however, for the chloride complexes N-oxide bridges are not necessary for octahedral coordination as this may be achieved by chloro-bridges.