Interactions of Nickel (II) with Sterically Hindered Amine N-oxides

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Received December 2, 1982

In the past few years a number of authors have begun to investigate the effects of ortho-substitution on the ability of pyridine N-oxide to coordinate with metal ions such as nickel (II). Studies involving 2-substituted pyridine N-oxides [1–7], 2,6-lutidine N-oxide [1, 3, 4, 8–12], quinoline N-oxide, isoquinoline N-oxide, and various methyl-substituted derivatives [2, 13–15], and acridine N-oxide [16] have produced complexes with geometries other than octahedral and coordination spheres containing ligands other than monodentate N-oxide ligands—such as anions, water molecules, and potentially bidentate or bridging N-oxides—thus making comparisons of the donor strengths of these ligands as compared to that of pyridine N-oxide [17] often impossible.

Since the spectrochemical parameter, Dq, is easily obtained for nickel (II) complexes, we decided to attempt to compare the Dq values of 2-picoline N-oxide (2-picNO) and 2-ethylpyridine N-oxide (2-EtpyNO) with those of pyridine N-oxide (pyNO = 794 cm^{-1} [17]), 4-picoline N-oxide (4-picNO = 794 cm^{-1} [17], and 2,6-lutidine N-oxide (2,6-LuNO = 765 cm^{-1} [8]). These mono-substituted ligands were chosen because their electronic effects on the donor site would be expected to be similar to and their steric effects would be expected to be in between those of the other ligands.

Although $[Ni(2\text{-}EtpyNO)_6](ClO_4)_2$ has been studied in both solid [2] and solution [1] states by previous workers, the Dq values obtained differ, a situation noted earlier [17, 18] for a series of 4-substituted pyNO complexes of nickel (II). In addition two different complexes with 2-picoline N-oxide, $[Ni(2\text{-}picNO)_4](ClO_4)_2$ [2] and $[Ni(2\text{-}picNO)_6](ClO_4)_2$ [1], have been prepared. Since the former complex appears to contain hexacoordinated nickel (II) ion, Nelson and Ragsdale [2] have proposed that both bridging and non-bridging 2-picoline N-oxide ligands are present. Recently, however Karayannis *et al.* [19] have described this compound as containing five-coordinate nickel (II), with two ligands bridging to form a dimeric cation.

Experimental

Five grams of hydrated nickel perchlorate were dissolved in a mixture of 10 ml of ethanol and 40 ml of triethylorthoformate and stirred for 2½ hours at room temperature. The addition of 10 ml of neat 2-ethylpyridine N-oxide (or 20 ml of a 1:1 mixture of ethanol and 2-picoline N-oxide) to the dehydrated nickel (II) solution produced yellow precipitates almost immediately. The mixtures were stirred for 30 minutes, after which time anhydrous ether was added. The products were filtered, washed with ether, and dried under vacuum. They do not appear to be hygroscopic.

The analyses were performed by Galbraith Laboratories, Inc. at Knoxville, Tennessee. *Anal.* Calcd. for $[Ni(2\text{-}picNO)_6](ClO_4)_2$: C, 47.39%; H, 4.64%; N, 9.21%. Found: C, 47.17%; H, 4.49%; N, 9.07%. Calcd. for $[Ni(2\text{-}EtpyNO)_6](ClO_4)_2$: C, 50.63%; H, 5.46%. Found: C, 50.78%; H, 5.68%.

Infrared spectral data, conductance data, and solution electronic spectral data were obtained as before [20].

Results and Discussion

The stoichiometries of the two complexes are the same as those obtained by Schmauss and Specker [1] and, in the case of the 2-ethylpyridine N-oxide complex, as Nelson and Ragsdale [2]. The infrared spectra contain only one intense band for the N–O stretching frequency (1205 cm^{-1} for 2-picNO and 1202 cm^{-1} for 2-EtpyNO) and only one strong, broad band for the asymmetric perchlorate vibration. These results compare well with those reported before [1, 2]. Thus the complexes appear to contain only coordinated 2-substituted N-oxide in the first coordination sphere, and we characterize them as $[Ni(2\text{-}RpyNO)_6]^{2+}$.

Conductance values of 151 and 129 for the 2-picNO and 2-EtpyNO complexes, respectively, indicate no perchlorate coordination in dilute nitromethane solutions either. We find, however, that the electronic spectra change when excess ligand is added to the nitromethane solutions, an indication that some ligand dissociation is occurring in ligand-free nitromethane solutions.

The spectral data obtained for the two complexes (approximately 0.05 molar with added ligand) are: 2-picNO-ν_1, 1275 nm (14.8); ν_2, 788 nm (17.8); ν_3, 718 nm (15.9); and ν_4, 386 nm (130), and 2-EtpyNO-ν_1, 1280 nm (14.7); ν_2, 787 nm (18.2); ν_3, 718 nm (17.4), and ν_4, 395 nm (180). In these cases ν_1 is assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition, ν_2 is assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition, and ν_3 is assigned to

0020-1693/83/0000-0000/$03.00

the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition. While the ν_4 band may be due to a metal → ligand transfer transition [1, 21], which masks the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition, its high molar absorptivity is certainly typical of those found in many $[Ni(4\text{-}ZpyNO)_6]^{2+}$ complexes [17].

The spectral data obtained are comparable to those of Schmauss and Specker [1], although the values for the molar absorptivities do vary a bit. From this and other [8, 17] studies, the following order of Dq values can be obtained for nickel (II) systems: pyNO (794 cm^{-1}) = 4-picNO (794 cm^{-1}) > 2-picNO (785 cm^{-1}) ≅ 2-EtpyNO (781 cm^{-1}) > 2,6-LuNO (765 cm^{-1}). This order is what one would have predicted on the basis of non-bonded interactions between the coordinated ligands. It is interesting to note that the $[Ni(2,6\text{-}LuNO)_6]^{2+}$ solution species reported by Schmauss and Specker [1] is actually $[Ni(2,6\text{-}LuNO)_5]^{2+}$ [8, 9], and the colorless solid listed as $[Ni(2,6\text{-}LuNO)_6](ClO_4)_2 \cdot 3H_2O$ is actually $[(2,6\text{-}LuNO)_2H](ClO_4)$, first characterized by Reedijk [22] and since found in other systems [7, 8].

Given the relatively small differences between the Dq values of the above ligands, it may be difficult to extend the series. It is especially important that the electronic effects of the ligands remain similar to those already studied. Thus Ragsdale has found that various methyl-substituted quinoline N-oxides, isoquinoline N-oxide, and acridine N-oxide possess higher Dq values towards nickel (II) [13, 14] or chromium (III) [16] than does pyridine N-oxide, a situation which he ascribes to more efficient back-bonding between ligand and metal. We assume that a similar situation exists in the case of 2-cyanopyridine N-oxide (Dq = 808 cm^{-1} for nickel (II)) [5].

Acknowledgement

The authors thank the Faculty Research and Creativity Committee of Western Maryland College for a grant.

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