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Complexes of Nickel(II), Cobalt(II), and Silver(I) with 2-, 3-, and 4-Cyanopyridine N-Oxides

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The coordinating properties of 2-, 3-, and 4-cyanopyridine N-oxides have been investigated. With cobalt(II) and nickel(II) all three N-oxides coordinate through the oxygen, giving hexacoordinate complexes in each case. For silver(I), 4-cyanopyridine N-oxide coordinates through the oxygen, while 2-cyanopyridine N-oxide appears either to contain bridging N-oxide groups coordinated through the oxygen or to involve coordination through both the N-oxide oxygen and the nitrile group. The silver complexes have the $\text{AgClO}_4 \cdot 2\text{L}$ stoichiometry.

Introduction

Many studies have appeared regarding the coordinating properties of various substituted pyridine N-oxides.³ In general, coordination occurred through the N-oxide oxygen atom. However, in a few cases with ligands possessing other possible donor groups in the 2 position, coordination has also occurred through these groups giving rise to bidentate ligands.^{4,5} For example, 2-hydroxy- and 2-mercaptopyridine N-oxides readily form complexes with manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II), where the donor acts as a bidentate ligand.⁴ 2-Carboxypyridine N-oxide was also found to act as a bidentate ligand for a series of complexes with the lanthanides.⁵ On the other hand, 2-aminopyridine N-oxide (L) coordinates in a monodentate fashion to give $\text{ML}_6(\text{ClO}_4)_2$ (for $\text{M}^{2+} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Mg}^{2+}$), $\text{ML}_6(\text{ClO}_4)_3$ (for $\text{M}^{3+} = \text{Fe}^{3+}$), and $\text{ML}_4(\text{ClO}_4)_2$ (for $\text{M}^{2+} = \text{Cu}^{2+}, \text{Ba}^{2+}$).⁶

2-, 3-, and 4-cyanopyridines have previously been used as ligands. Coordination has been shown to occur through the pyridine nitrogen in the 3- and 4-cyanopyridine complexes of zinc(II), copper(II), nickel(II), cobalt(II), iron(II), manganese(II), silver(I), copper(I), and gold(I)^{7,8} and through the nitrile nitrogen in the 2-cyanopyridine complexes of silver(I), copper(I), and gold(I).^{7,9}

No reports have yet appeared concerning the donor properties of 2-, 3-, and 4-cyanopyridine N-oxides. Because of the similarity of the cyanopyridine N-oxides to the cyanopyridines, the coordinating properties of the N-oxides (hereafter referred to as 2-, 3-, and 4-CNPyNO) were investigated.

Experimental Section

Materials.—2- and 3-cyanopyridine N-oxides were prepared from the corresponding amines (obtained from Aldrich Chemical Co.) by the method of Ochiai.¹⁰ 4-Cyanopyridine N-oxide was

obtained from Reilly Tar and Chemical Co. and was recrystallized from water. The melting points and infrared spectra of the ligands agreed with the literature values.¹¹⁻¹³

Silver perchlorate (G. F. Smith Chemical Co.) was dried at 70° under vacuum and stored over anhydrous magnesium perchlorate. Cobalt and nickel perchlorates (G. F. Smith Chemical Co.) were used without further purification.

Preparation of the Complexes.—The silver complexes were prepared from an acetone solution containing a 2:1 mole ratio of ligand to metal salt. Precipitation of the complexes usually occurred within a few hours. The complexes were filtered, washed with anhydrous ether, and dried under reduced pressure over phosphorus pentoxide.

The cobalt and nickel complexes were prepared from an ethanol solution containing triethyl orthoformate. A 7:1 ligand to metal salt mole ratio was employed. The complexes usually precipitated immediately. They were filtered, washed with anhydrous ether, and dried under reduced pressure over phosphorus pentoxide.

Elemental Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt Laboratorium, Mülheim, Germany. Cobalt and nickel analyses were obtained by titration with EDTA.¹⁴ Silver was analyzed by the Volhard method.¹⁵ The analytical data appear in Table I.

Physical Measurements.—The electronic spectra, magnetic moments, conductance data, and ligand field calculations were measured and/or calculated as previously described.¹⁶ Infrared spectra were run as Nujol mulls in the 4000-250-cm⁻¹ region on a Perkin-Elmer Model 421 recording spectrophotometer equipped with a 521 interchange to extend the range of the instrument to 250 cm⁻¹.

Results and Discussion

Cobalt and Nickel Complexes.—The elemental analyses listed in Table I indicate that these complexes are 6-coordinate with the general formula $[\text{M}(\text{CNC}_5\text{H}_4\text{NO})_6](\text{ClO}_4)_2$. The conductance values are in the range normally found for 2:1 electrolytes demonstrating that the perchlorate ion is not coordinated in nitromethane solution. The magnetic moments are in the allowed ranges for high-spin octahedral cobalt and

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 (3) R. G. Garvey, J. H. Nelson, and R. O. Ragsdale, *Coord. Chem. Rev.*, **3**, 375 (1968).
 (4) P. J. Sun, Q. Fernando, and H. Freiser, *Anal. Chem.*, **36**, 2485 (1964).
 (5) H. Yoneda, G. R. Chopin, and J. L. Bear, *Inorg. Chem.*, **4**, 244 (1965).
 (6) H. Sigel and H. Brintzinger, *Helv. Chim. Acta*, **46**, 701 (1963).
 (7) F. Farha, Jr., and R. T. Iwamoto, *Inorg. Chem.*, **4**, 844 (1965).
 (8) D. G. Brewer and P. T. T. Wong, *Can. J. Chem.*, **44**, 1407 (1966).
 (9) L. El-Sayed and R. O. Ragsdale, *J. Inorg. Nucl. Chem.*, **30**, 651 (1968).

(10) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).
 (11) H. Shindo, *Chem. Pharm. Bull. (Tokyo)*, **6**, 117 (1958).
 (12) H. Tani and K. Fukushima, *Yakugaku Zasshi*, **81**, 27 (1961).
 (13) A. R. Katritzky, *Rec. Trav. Chim.*, **78**, 995 (1959).
 (14) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Inc., Princeton, N. J., 1958, pp 230-234.
 (15) A. I. Vogel, "Quantitative Inorganic Analysis," John Wiley & Sons, Inc., New York, N. Y., 1961, p 266.
 (16) J. H. Nelson, L. C. Nathan, and R. O. Ragsdale, *Inorg. Chem.*, **7**, 1840 (1968).

TABLE I
 ELEMENTAL ANALYSES AND CONDUCTANCE DATA

Complex	% C		% H		% N		% metal		Dec pt, ^a °C	Concn × 10 ³ , M	λ _m ^b
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found			
Ni(2-CNC ₅ H ₄ NO) ₆ (ClO ₄) ₂	44.20	44.24	2.47	2.34	17.18	17.11	6.00	5.77	215	2.23	176
Ni(3-CNC ₅ H ₄ NO) ₆ (ClO ₄) ₂	44.20	44.66	2.47	2.64	17.18	17.51	6.00	5.85	245-247	1.38	183
Ni(4-CNC ₅ H ₄ NO) ₆ (ClO ₄) ₂	44.20	44.31	2.47	2.41	17.18	16.65	6.00	5.84	286-287	1.60	161
Co(2-CNC ₅ H ₄ NO) ₆ (ClO ₄) ₂	44.19	44.24	2.47	2.32	17.18	17.31	6.02	5.86	221	1.03	182
Co(3-CNC ₅ H ₄ NO) ₆ (ClO ₄) ₂	44.19	44.79	2.47	2.24	17.18	17.30	6.02	5.61	243-245	1.31	185
Co(4-CNC ₅ H ₄ NO) ₆ (ClO ₄) ₂	44.19	44.16	2.47	2.16	17.18	17.99	6.02	5.91	298-299	1.59	163
Ag(2-CNC ₅ H ₄ NO) ₂ ClO ₄	32.20	32.25	1.80	1.78	12.52	12.22	24.10	23.99	145-148	3.50	91
Ag(3-CNC ₅ H ₄ NO) ₂ ClO ₄ ^c	32.20		1.80		12.52		24.10		131-134	3.48	93
Ag(4-CNC ₅ H ₄ NO) ₂ ClO ₄	32.20	32.07	1.80	1.82	12.52	12.30	24.10	23.79	218-220	3.12	98

^a Decomposition points are uncorrected. ^b Typical values for λ_m in nitromethane are: nonelectrolyte, 0-50; 1:1, 80-100; 2:1, 130-180; 3:1, 200-250. See N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959); J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 1158 (1963). ^c Repeated attempts to prepare this complex resulted in products which consistently yielded unacceptable elemental analyses; e.g., found: C, 27.67; H, 1.57; N, 10.30; Ag, 24.61.

 TABLE II
 ABSORPTION MAXIMA (CM⁻¹) IN THE ELECTRONIC SPECTRA AND LIGAND FIELD PARAMETERS

Complex	³ A _{2g} → ³ T _{1g} (P)	³ A _{2g} → ³ T _{1g} (F) ^a	³ A _{2g} → ¹ E _g	³ A _{2g} → ³ T _{2g}	Dq	β	ν ₂ (calcd)
Ni(2-CNPYNO) ₆ (ClO ₄) ₂	24,500	14,100	12,700	8080	808	0.87	13,500
Ni(3-CNPYNO) ₆ (ClO ₄) ₂	25,100	14,300	12,500	8260	826	0.89	13,800
Ni(4-CNPYNO) ₆ (ClO ₄) ₂	23,900	14,400	12,600	8130	813	0.82	13,400
Complex	⁴ T _{1g} (F) → ⁴ T _{1g} (P)	⁴ T _{1g} (F) → ⁴ A _{2g} ^a	⁴ T _{1g} (F) → ⁴ T _{2g}	Dq	β	ν ₂ (calcd)	
Co(2-CNPYNO) ₆ (ClO ₄) ₂	18,800	18,800	8220	996	0.80	18,800	
Co(3-CNPYNO) ₆ (ClO ₄) ₂	20,700	19,000	8270	1010	0.94	19,000	
Co(4-CNPYNO) ₆ (ClO ₄) ₂	18,700	18,700	8220	986	0.80	18,700	

^a ν₂ observed.

nickel complexes and are similar to the values found for other aromatic amine oxide complexes.^{16,17}

The perchlorate ions are not coordinated in solution (*vide supra*) nor are they coordinated in the solid state, as the infrared spectra of these complexes all possess a sharp singlet around 620 cm⁻¹ and a broad strong singlet around 1110 cm⁻¹.¹⁸ The nitrogen-oxygen stretching frequency ν_{N-O} of these complexes shifts to lower energy upon coordination by some 23-48 cm⁻¹ suggesting a reduction in the nitrogen-oxygen bond order. Similar shifts have been noted in all other complexes of pyridine N-oxides,^{3,17,19} where coordination occurs through the oxygen. The nitrile stretching frequency ν_{C≡N} shifted to higher energy by some 15 cm⁻¹ or remained the same. ν_{C≡N} has been shown to shift to higher energy when coordination occurs through the nitrile (see ref 7 and references contained therein). However, when 3- and 4-cyanopyridine coordinated through the pyridine nitrogen, ν_{C≡N} still increased in energy.⁷ Apparently a shift in ν_{C≡N} to higher energy does not necessarily demonstrate nitrile coordination.

The electronic spectra of the nickel complexes are typical of nickel(II) in an octahedral field and are very similar in appearance to spectra previously reported for aromatic amine oxide complexes of this metal ion.^{16,17,19} While the electronic spectrum of Co(3-CNPYNO)₆(ClO₄)₂ possesses the three peaks typical of octahedral cobalt(II), the spectra of Co(2-CNPYNO)₆(ClO₄)₂ and Co(4-CNPYNO)₆(ClO₄)₂ appear to have only two peaks.

The first of the two peaks is in the near-infrared region as expected while the second is in the visible region where two bands are normally found. Qualitative treatment of the spectra with a Du Pont 310 curve resolver shows that this second peak is actually composed of more than one band. Two possible explanations are offered for this observation. First, the ⁴T_{1g}(F) → ⁴A_{2g} transition is a two-electron transition and is relatively weak in intensity. Since this transition appears quite near the more intense ⁴T_{1g}(F) → ⁴T_{1g}(P) transition, it is not unreasonable that the ⁴T_{1g}(F) → ⁴A_{2g} band might be masked by the ⁴T_{1g}(F) → ⁴T_{1g}(P) band. Second, from the Tanabe-Sugano diagram for a d⁷ case²⁰ one would predict three peaks in the spectrum of octahedral cobalt(II) except where the ⁴A_{2g} and ⁴T_{1g}(P) energy levels cross, giving rise to only two peaks. The crossover point for these two energy levels occurs at Dq/B ≈ 1.2-1.3. Since the experimental values of Dq/B are 1.29 for Co(2-CNPYNO)₆(ClO₄)₂ and 1.28 for Co(4-CNPYNO)₆(ClO₄)₂ (in contrast to 1.11 for Co(3-CNPYNO)₆(ClO₄)₂), it is suggested that the apparent accidental degeneracy of the ⁴A_{2g} and ⁴T_{1g}(P) energy levels also accounts for the single band in the visible region.

Low-frequency infrared spectra should offer substantial evidence concerning oxygen or nitrogen coordination. Metal-oxygen stretching frequencies of aromatic amine oxide coordination compounds are generally found in the region 250-450 cm⁻¹.^{17,19,21} Typical metal-nitrogen stretching vibrations are usually found

(17) R. Whyman, W. E. Hatfield, and J. S. Paschal, *Inorg. Chim. Acta*, **1**, 113 (1967).

(18) W. E. Bull and L. E. Moore, *J. Inorg. Nucl. Chem.*, **27**, 1341 (1965).

(19) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).

(20) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966, pp 165-167.

(21) F. E. Dickson, E. W. Gowling, and F. F. Bentley, *Inorg. Chem.*, **6**, 1099 (1967).

below 300 cm^{-1} .²²⁻²⁴ In all of the pyridine N-oxide complexes of cobalt and nickel, where only one donor site is available for coordination (the N-oxide oxygen) the reported metal-oxygen vibrations are in the region $299\text{--}393\text{ cm}^{-1}$ and vary over a limited range for each metal ion.^{17,19} For the nickel complexes, $\nu_{\text{Ni-O}}$ was inversely proportional to pK_a of the 4-substituted pyridine N-oxide ligands.¹⁹ On the basis of this correlation, $\nu_{\text{Ni-O}}$ for the 4-cyanopyridine N-oxide-nickel complex is predicted to occur at 370 cm^{-1} . A peak is present in the spectrum of the complex and not in the spectrum of the ligand at 378 cm^{-1} . The spectra of the nickel 2- and 3-cyanopyridine N-oxide complexes and the cobalt 2-, 3-, and 4-cyanopyridine N-oxide complexes each have a band in this region which is not present in the spectra of the free ligands (see Table III).

The infrared data showing a shift in $\nu_{\text{N-O}}$ to lower energy upon complexation, the low-frequency infrared spectra showing the presence of a peak attributable to $\nu_{\text{M-O}}$, and the electronic spectra giving Dq values in the range for oxo donors all clearly demonstrate that the cobalt and nickel cyanopyridine N-oxide complexes involve coordination through oxygen.

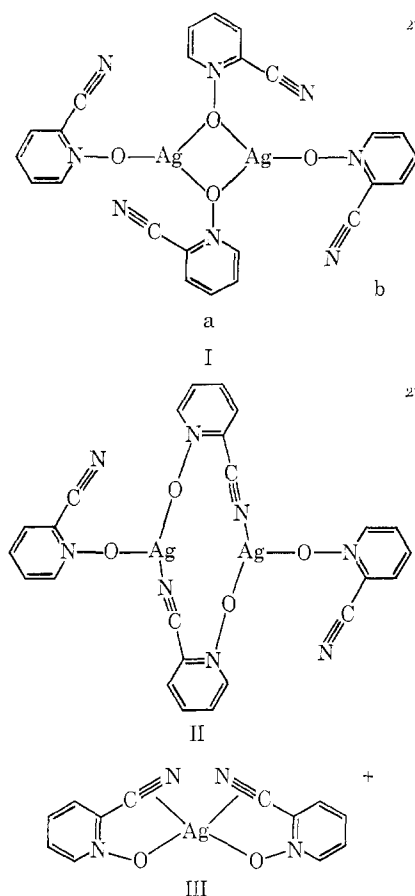
Silver Complexes.—Elemental analyses (Table I) show that the 2- and 4-cyanopyridine N-oxide complexes of silver have the $\text{Ag}(\text{CNC}_5\text{H}_4\text{NO})_2\text{ClO}_4$ stoichiometry. Conductance data indicate the presence of 1:1 electrolytes in nitromethane.

The infrared data obtained for $\text{Ag}(4\text{-CNPYNO})_2\text{ClO}_4$ closely parallel those found for the cobalt and nickel complexes in this study as evidenced by the consistency in the magnitude and direction of the shift in $\nu_{\text{N-O}}$ (Table III). Furthermore, the low-frequency infrared spectrum of $\text{Ag}(4\text{-CNPYNO})_2\text{ClO}_4$ possesses a peak at 372 cm^{-1} which is not present in the spectrum of the ligand. Since this band is in the same range as those found for the cobalt and nickel complexes, it is assigned as $\nu_{\text{Ag-O}}$. Based on the above evidence, it is concluded that coordination occurs through the oxygen in $\text{Ag}(4\text{-CNPYNO})_2\text{ClO}_4$.

The infrared spectrum of $\text{Ag}(2\text{-CNPYNO})_2\text{ClO}_4$ differs markedly from that of $\text{Ag}(4\text{-CNPYNO})_2\text{ClO}_4$. Both $\nu_{\text{C}\equiv\text{N}}$ and $\nu_{\text{N-O}}$ were found to be split, with $\Delta\nu_{\text{C}\equiv\text{N}}$ being $+28$ and -2 cm^{-1} and $\Delta\nu_{\text{N-O}}$ being -42 and -52 cm^{-1} . The $\Delta\nu_{\text{N-O}}$ values imply oxygen coordination. The $\Delta\nu_{\text{C}\equiv\text{N}}$ values possibly indicate nitrile coordination, and the fact that both $\nu_{\text{C}\equiv\text{N}}$ and $\nu_{\text{N-O}}$ are doublets suggests two different ligand environments.

Three structures consistent with the above data are shown below. Structure I is considered for several reasons. (1) Some 3-coordinate silver complexes are known⁷ and recently a report of $\text{Ag}(\text{CH}_3\text{PyNO})_3\text{ClO}_4$ complexes has appeared.²⁵ The $\text{Ag}(\text{CH}_3\text{PyNO})_3\text{ClO}_4$ complexes possess two different N-oxides as shown by infrared data. Two nitrogen-oxygen stretching frequencies were assigned, both of which were found at

lower energy than $\nu_{\text{N-O}}$ of the free ligand. (2) A copper complex of pyridine N-oxide has been shown by X-ray data²⁶ to have a structure possessing N-oxide bridges similar to that shown in I. (3) Copper complexes of pyridine N-oxides with the general formula CuL_2X_2 showed two nitrogen-oxygen stretching frequencies, and chemical evidence suggested that they were the N-oxide-bridged species with the other N-oxide weakly bonded in some manner.²⁷ (4) In I, $\nu_{\text{N-O}}$ for ligand type a should appear at lower energy than that for ligand type b. It is more difficult to say why $\nu_{\text{C}\equiv\text{N}}$ should increase for one type of ligand and not for the other, although it is not unreasonable that $\nu_{\text{C}\equiv\text{N}}$ is a doublet.



In structure II, there are two nonequivalent ligands, one of which would have an increase in $\nu_{\text{C}\equiv\text{N}}$ and a decrease in $\nu_{\text{N-O}}$ over that found in the free ligand. The other would have a decrease in $\nu_{\text{N-O}}$ coupled with a small or no change in $\nu_{\text{C}\equiv\text{N}}$. Another argument in support of II concerns the position of the cyano substituent. Whereas 2-cyanopyridine N-oxide is the only ligand which could form a structure similar to II, it is conceivable that all three ligands could form a structure similar to I. There is, however, no precedence for structure II, and the chelate would be a highly unstable 12-membered ring.

The conductance data for $\text{Ag}(2\text{-CNPYNO})_2\text{ClO}_4$ do not support either I or II, since both of these structures

(22) N. S. Gill and H. J. Kingdon, *Australian J. Chem.*, **19**, 2197 (1966).

(23) P. T. T. Wong and D. G. Brewer, *Can. J. Chem.*, **46**, 139 (1968).

(24) C. W. Frank and L. B. Rogers, *Inorg. Chem.*, **5**, 615 (1966).

(25) G. Schmauss and H. Specker, *Naturwissenschaften*, **54**, 442 (1967).

(26) R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).

(27) Y. Muto and H. B. Jonassen, *Bull. Chem. Soc. Japan*, **39**, 58 (1966).

TABLE III
 MAGNETIC MOMENT AND INFRARED DATA

Compound	$10^6\chi_m$	$10^6\chi_m'$	Temp, °K	μ_{eff} , BM	$\nu_{\text{C=N}}$, cm^{-1}	$\nu_{\text{N-O}}$, cm^{-1}	$\nu_{\text{M-O}}$, cm^{-1}
2-CNPyNO					2234	1262	
Ni(2-CNPyNO) ₆ (ClO ₄) ₂	4,320	4,750	296	3.37	2234	1215	381
Co(2-CNPyNO) ₆ (ClO ₄) ₂	9,890	10,320	296	4.96	2232	1214	381
Ag(2-CNPyNO) ₂ ClO ₄					2232, 2262	1220, 1210	<i>a</i>
3-CNPyNO					2223	1269	
Ni(3-CNPyNO) ₆ (ClO ₄) ₂	4,560	4,990	296	3.45	2240	1246	400
Co(3-CNPyNO) ₆ (ClO ₄) ₂	10,050	10,480	297	5.01	2240	1245	395
4-CNPyNO					2223	1276	
Ni(4-CNPyNO) ₆ (ClO ₄) ₂	3,950	4,380	296	3.23	2238	1229	378
Co(4-CNPyNO) ₆ (ClO ₄) ₂	9,210	9,640	296	4.81	2238	1228	369
Ag(4-CNPyNO) ₂ ClO ₄					2231	1239	372

^a $\nu_{\text{Ag-O}}$ masked by ligand peak.

would be 2:1 electrolytes and the experimental data indicate a 1:1 electrolyte. However, either of these structures could easily be broken up in solution to give 1:1 electrolytes. An infrared spectrum taken on a nitromethane solution of the complex would substantiate this premise, but Ag(2-CNPyNO)₂ClO₄ does not have sufficient solubility.

There are three possible geometries for a structure such as III, *trans* planar, *cis* planar, and tetrahedral. Whereas there is no precedence for planar silver(I) complexes, several tetrahedral complexes are known, e.g., bis(8-hydroxyquinoline)silver(I)²⁸ and tetrakis(thioacetamide)silver(I) chloride.²⁹ Symmetry considerations for MA₂B₂ tetrahedral and *cis*-planar species predict two infrared-active bands for both the M-A and M-B vibrations, indicating different environments for each of the A and B atoms. One M-A and one M-B infrared-active band would be predicted for the *trans*-

planar species. Structure III would explain the 1:1 conductivity.

Another possibility has been considered for Ag(2-CNPyNO)₂ClO₄, namely, an equilibrium mixture of an AgL₂⁺ species with ligands coordinated through the oxygen and an AgL₂⁺ species with the ligands coordinated through the nitrile. These species would give 1:1 electrolytes and thus fit the conductance data, but they do not fit the infrared data in that the latter AgL₂⁺ species would have "free" nitrogen-oxygen bonds. Although other equilibrium mixtures might be additional possibilities, it should be pointed out that both peaks in the $\nu_{\text{C=N}}$ doublet are of equal intensity as are the two peaks in the $\nu_{\text{N-O}}$ doublet. This implies that the species in equilibrium would be present in equal amounts—a rather unlikely case. Whereas this last assumption may not hold in every case, it has been shown that for benzonitrile adducts of SnCl₄ the area under the nitrile peak is proportional to the concentration of free nitrile in solution.³⁰

(28) J. E. Fleming and H. Lynton, *Can. J. Chem.*, **46**, 471 (1968).

(29) E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 775 (1936).

(30) T. L. Brown and M. Kubota, *J. Am. Chem. Soc.*, **83**, 331 (1961).