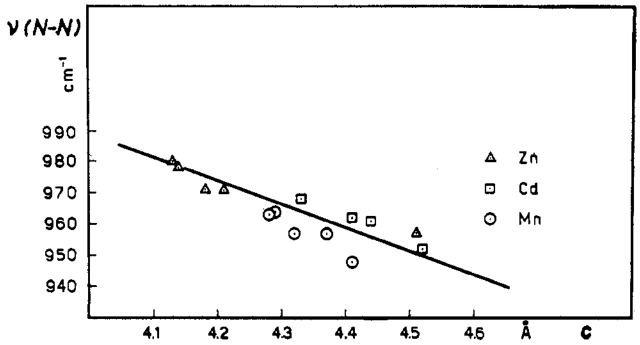

Figure 2.—Relation between stretching band frequency ν (N–N) and repeat distance c in chain complexes $[M^{II}(N_2H_4)_2]_nX_{2n}$.

increased field effect, in the latter, of the positive cations on the lone pairs. Even the small shifts within the set of the chain complexes (Table I) can be related to changing of the repulsion between lone pairs, owing to the electrostatic field effect of the cations. In this set of compounds ν(N–N) is inversely proportional (Figure 2) to the repeat distance along the chain; *i.e.*, the larger is the distance of the attractive positive charges, the weaker is the field effect on the lone pairs.

Acknowledgment.—We thank Consiglio Nazionale delle Ricerche, Rome, for financial aid. We are grateful to Sig. M. Lanfranchi for his assistance in the preparation and analysis of the compounds.

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Coordination Chemistry of 4,4'-Bipyridine[1,2]

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Complexes of 4,4'-bipyridine with Ag(I), Hg(II), Co(II), Cu(II), and Ni(II) have been prepared. Physical properties, stoichiometries, diffuse reflectance spectra, and infrared spectral data indicate that the compounds are coordination polymers in which the ligand acts as a bridging group. Also, the basicity of the ligand has been determined as a function of ionic strength. Acid dissociation constants of quaternized 4,4'-bipyridine are: $K_1 = 6.5 \times 10^{-4}$, 4.9×10^{-4}, and 3.5×10^{-4}; $K_2 = 1.4 \times 10^{-5}$, 1.4×10^{-5}, and 1.2×10^{-5} at molar ionic strengths 0.05, 0.10, and 0.20, respectively.

Introduction

The chemistry of polymeric transition metal complexes is in its infancy. The coordination chemistry of 2,2'-bipyridine has been extensively studied, yet the ligand properties of the isomeric 4,4'-bipyridine molecule have not been investigated. The only references to transition metal–4,4'-bipyridine complexes appear in papers by Peard and Pflaum,[3] who report a compound having the stoichiometric formula $Ag(C_{10}H_8N_2)(NO_3)$, and by Lewis and Mabbs,[4] who report a compound of copper(II) benzoate containing half a 4,4'-bipyridine molecule per formula unit of copper benzoate. As a potential ligand, 4,4'-bipyridine seemed particularly interesting because its structure should preclude chelation and favor coordination of the nitrogen atoms to two different metal ions; *i.e.*, it should coordinate so as to form polymeric complexes. This work was undertaken to determine the basicity of 4,4'-bipyridine as a function of ionic strength and to prepare and characterize 4,4'-bipyridine complexes of transition metal ions.

Experimental Section

Materials.—A modification of the method of Dimroth and Frister[5] was used to prepare 4,4'-bipyridine. Pyridine (50 ml, dried over phosphorus pentoxide), 250 ml of acetic anhydride, and 50 g of zinc dust were stirred together for 2 hr. The yellow precipitate formed was dissolved as completely as possible by heating the mixture on a steam bath for 2 hr. The liquid was filtered off and allowed to crystallize under refrigeration. The yellow crystalline product was then collected by filtration and allowed to oxidize in air for 2–4 days, during which white crystals of 4,4'-bipyridine appeared on the surface of the yellow-brown mixture. The entire mass was then added to 200 ml of water, made slightly acid with hydrochloric acid, and the resulting solution was filtered while hot. The clear filtrate was made basic with sodium hydroxide and set aside on an ice bath to allow crystallization to occur. Recrystallization was repeated until a pure white product was obtained. The yield was approximately 50% based upon pyridine. Other chemicals were reagent grade.

Measurements.—A Sargent Model DR high-precision pH meter equipped with a combination glass–calomel electrode was used for all pH measurements.

Diffuse reflectance spectra were obtained with a Beckman DU spectrophotometer equipped with a No. 2580 diffuse reflectance attachment. A 1-in. magnesium carbonate reference block was used for standardization.

A Perkin-Elmer Model 337 grating infrared spectrophotometer was used to determine infrared spectra.

Analyses.—Cobalt, nickel, and copper were determined by conventional complexometric titration with EDTA. Mercury(II) was determined by thiocyanate titration to a ferric ion end point, and silver(I) was determined gravimetrically by precipitation as silver chloride. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories of Knoxville, Tenn.

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(1) Abstracted in part from a thesis submitted by C. E. Mattson to the Graduate School of Colorado State University in partial fulfillment of the requirements for the Master of Science degree.

(2) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(3) W. J. Peard and R. T. Pflaum, *J. Am. Chem. Soc.*, **80**, 1593 (1958).

(4) J. Lewis and F. Mabbs, *J. Chem. Soc.*, 3894 (1965).

(5) O. Dimroth and F. Frister, *Ber.*, **55**, 1223 (1922).

The Basicity of 4,4′-Bipyridine.—In order to obtain an estimate of the probable magnitude of stability constants of 4,4′-bipyridine complexes and as a precursor to possible future complex equilibria studies, the acid dissociation constants of 4,4′-bipyridine were determined as a function of ionic strength.

Appropriate amounts of the anhydrous base were weighed and dissolved in water to prepare standard solutions. Ionic strength adjustments were made with reagent grade potassium chloride, and 4,4′-bipyridine solutions were then titrated with standard hydrochloric acid in which the ionic strength had also been adjusted by addition of potassium chloride. All titrations were carried out at 26°.

The titration data were treated by the following method. The acid dissociation constants of the quaternized base were defined as

$$K_1 = \frac{[\mathrm{H^+}][\mathrm{HB^+}]}{[\mathrm{H_2B^{2+}}]} \text{ and } K_2 = \frac{[\mathrm{H^+}][\mathrm{B}]}{[\mathrm{HB^+}]}$$

where B represents unquaternized 4,4′-bipyridine. During the course of a titration, the total 4,4′-bipyridine concentration was set equal to

$$C_\mathrm{B} = [\mathrm{B}] + [\mathrm{HB^+}] + [\mathrm{H_2B^{2+}}] \qquad (1)$$

and the total hydrogen ion concentration was given by

$$C_{\mathrm{H^+}} = [\mathrm{H^+}] + [\mathrm{HB^+}] + 2[\mathrm{H_2B^{2+}}] \qquad (2)$$

At any point during a titration the hydrogen ion concentration was measured, and C_B and $C_{\mathrm{H^+}}$ were easily calculated from original total concentrations and volume changes. A fraction, *a*, was defined as

$$a = \frac{C_{\mathrm{H^+}} - [\mathrm{H^+}]}{C_\mathrm{B}} = \frac{[\mathrm{HB^+}] + 2[\mathrm{H_2B^{2+}}]}{[\mathrm{B}] + [\mathrm{HB^+}] + [\mathrm{H_2B^{2+}}]} \qquad (3)$$

The fraction, *a*, represents an average number of hydrogen ions bound per 4,4′-bipyridine, and it was assumed that when $a < 0.50$, $[\mathrm{H_2B^{2+}}]$ was negligible and eq 3 could be simplified to

$$a = \frac{1}{(K_2/[\mathrm{H^+}]) + 1} \qquad (4)$$

upon substitution of the expression for K_2. Equation 4 can be rearranged to give

$$\frac{a}{1-a} = (1/K_2)[\mathrm{H^+}] \qquad (5)$$

and plots of the left side of eq 5 *vs.* $[\mathrm{H^+}]$ should be linear with slopes of $1/K_2$ and intercepts of zero. Similarly, when $a < 1.0$, [B] should be negligible, and eq 3 can be arranged to give

$$\frac{a-1}{2-a} = (1/K_1)[\mathrm{H^+}] \qquad (6)$$

and plots of the left side of eq 6 should be linear with slopes of $1/K_1$ and intercepts at zero.

Preparation of Complexes. (A). Ag(bipy)NO₃ and Hg(bipy)(NO₃)₂.—The complexes were prepared by dissolving 0.1 mol of the metal nitrate in approximately 70 ml of water, adjusting the pH to 5–6, and adding excess (0.2–0.5 mol) 4,4′-bipyridine (bipy) dissolved in a 50:50 ethanol–water mixture. A white precipitate formed immediately. The reaction mixture was cooled in an ice bath, and the product was collected on a Büchner funnel. The precipitate was washed with an ethanol–ether mixture and dried in a desiccator over anhydrous calcium chloride. The silver complex was light sensitive. Both complexes were insoluble in water and common organic solvents.

(B). Co(bipy)(NO₃)₂, Ni(bipy)Cl₂, and Cu(bipy)(NO₃)₂.—Approximately 0.1 mol of the hydrated metal salt was dissolved in 95% alcohol and excess (0.4–0.8 mol) bipy in 95% ethanol was added with stirring. Precipitation was immediate. The products were filtered, washed with an ethanol–ether mixture, and dried at 70–80°. A nickel(II) nitrate–bipy product could not be produced by this method.

(C). Cu(bipy)₂(NO₃)₂, Ni(bipy)₂(NO₃)₂, and Co(bipy)₂(NO₃)₂.—Approximately 0.1 mol of the dried metal salts was ground by mortar and pestle with a 50–100-fold excess of bipy in an anhydrous methanol slurry. After grinding for 10 min, the slurry was set aside for 1 hr. Excess bipy was then dissolved by multiple washings with anhydrous methanol, and the remaining product was filtered and washed repeatedly with anhydrous methanol and ether. The product was air dried.

Results and Discussion

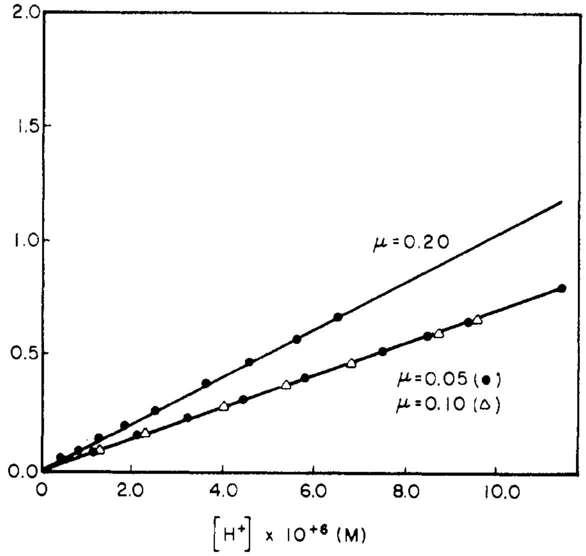

Figure 1.—Determination of K_2.

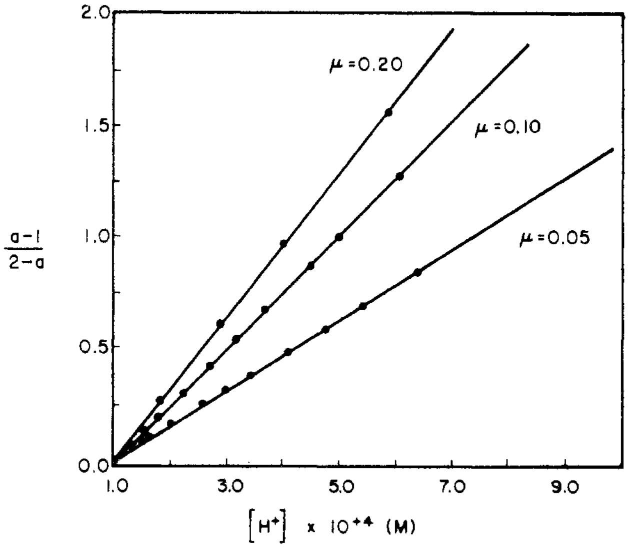

Figure 2.—Determination of K_1.

Data pertaining to the determination of K_1 and K_2 for 4,4′-bipyridine are available as an appendix filed with the American Documentation Institute.[6] Figure 1 shows plots of the variables in eq 5 and Figure 2 depicts plots of the variables in eq 6. The slopes of the straight-line plots gave values of K_1 equal to 6.5×10^{-4}, 4.9×10^{-4}, and 3.5×10^{-4} and K_2 equal to

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[6] Material supplementary to this article has been deposited as Document No. 9998 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I

ANALYTICAL AND PHYSICAL DATA OF SOME TRANSITION METAL 4,4′-BIPYRIDINE COMPLEXES

Complex	Color	Dec pt, °C	% M		% C		% H		% N	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Ag(bipy)NO_3$	White	290	33.0	32.9	36.8	37.0	2.2	2.5	12.9	12.8
$Hg(bipy)(NO_3)_2$	White	320	41.7	41.2	25.0	25.3	1.7	1.8	11.6	11.6
$Co(bipy)(NO_3)_2$	Pink	300	17.3	16.6	35.4	35.2	2.4	2.5	16.5	16.0
$Cu(bipy)(NO_3)_2$	Blue-lavender	285	18.5	17.3	34.9	33.5	2.3	2.5	16.3	15.8
$Ni(bipy)_2(NO_3)_2$	Blue-green	>300	11.9	11.9	48.5	47.7	3.2	3.0	17.0	15.4
$Co(bipy)_2(NO_3)_2$	Pink-orange	300	11.9	12.3	48.5	41.3	3.3	3.4	16.8	14.9
$Cu(bipy)_2(NO_3)_2$	Lavender	285	12.7	12.7	48.0	49.9	3.2	4.3	16.8	13.8
$Ni(bipy)Cl_2$[a]	Yellow-green	>300								

[a] % Cl: calcd, 24.8; found, 24.6.

1.4×10^{-5}, 1.4×10^{-5}, and 1.2×10^{-5} at molar ionic strengths of 0.05, 0.10, and 0.20, respectively. The slopes of the plots for K_2 were actually slightly different at ionic strengths 0.05 and 0.10, but the difference was too slight to yield different K_2 values. Plots of the stoichiometric constants *vs.* the square root of ionic strengths gave approximate thermodynamic constants (zero molar ionic strength) of $K_1 = 9.3 \times 10^{-4}$ and $K_2 = 1.5 \times 10^{-5}$. The only previously reported values for the acid dissociation constants of 4,4′-bipyridine were $K_1 = 6.8 \times 10^{-4}$ and $K_2 = 1.5 \times 10^{-5}$ at ionic strength 0.20 and 20°.[7] However, in that study the author used a successive approximation method, and the more rigorous method applied here should yield the more reliable results. Obvious possible sources of error in the method outlined here are the assumption that $[H_2B^{2+}]$ is negligible at $a < 0.5$, and $[B]$ is negligible at $a > 1.0$. From mass balance and the results obtained, these assumptions were checked and proved to be valid. Also, the fact that the plots are, in fact, linear lends credence to the assumptions.

Analytical and physical data for the 4,4′-bipyridine complexes are given in Table I. The compounds listed display a fairly high thermal stability and are virtually insoluble in water and common polar and nonpolar organic solvents, all of which are properties consistent with polymeric structures. The assigned formulas quoted in Table I are the best stoichiometric formulas based upon analytical and spectral data; however, it is obvious, particularly for $Co(bipy)_2(NO_3)_2$ and $Cu(bipy)_2(NO_3)_2$, that the products may be mixtures and/or contain entrapped methanol or water which was not lost during air drying. Unfortunately, the insolubility of the products precluded purification by recrystallization.

Infrared spectra of $Ag(bipy)NO_3$ and $Hg(bipy)(NO_3)_2$ display bands at approximately 1365, 832, and 705 cm^{-1}, attributed to a double degenerate stretch, an out-of-plane bending, and a double degenerate in-plane bending for ionic nitrate ion.[8,9] The properties, stoichiometry of preparation, ir data, and tendency of Ag(I) and Hg(II) to form linear two-coordinate complexes all lead to the conclusion that the Ag(I) and Hg(II) products have linear polymeric structures (–M–bipy–M–bipy–, etc.). An X-ray study by Vranka and Amma has established that solid $Ag(pyrazine)NO_3$ consists of $(\text{–Ag–ligand–})_x$ chains with NO_3^- groups linking the polymer chains.[10] While X-ray data are not yet available on the compounds described here, similarities in the stoichiometry and properties of the compounds and the nature of the ligands indicate analogous structures for $Ag(bipy)NO_3$ and $Hg(bipy)(NO_3)_2$.

To gain some insight into the structure of the $Co(bipy)(NO_3)_2$ complex, visible diffuse reflectance spectra and infrared spectra were obtained. Reflectance spectra each with a maximum at 19,600 cm^{-1} and a shoulder at 21,100 cm^{-1} are typical of an octahedral configuration. Infrared spectra of the complex had NO_3^- bands at 1280, 805, and 725 cm^{-1}, which are consistent with values given for bidentate coordinated nitrate. The data indicate that each Co(II) ion is surrounded octahedrally by two bridging 4,4′-bipyridine molecules and two bidentate coordinated nitrate ions.

The reflectance spectrum of $Ni(bipy)Cl_2$ is identical with the diffuse reflectance spectrum of the octahedral $Ni(methylpyrazine)Cl_2$ complex prepared by Lever, Lewis, and Nyholm.[11] Stoichiometric and spectral data indicate that this complex is a six-coordinate Ni(II) compound with polymeric chloride and 4,4′-bipyridine bridging.

The nitrate bands for $Cu(bipy)(NO_3)_2$ occur at 1420, 1305, 818, 728, and 708 cm^{-1} which are typical of monodentate coordinated nitrate.[9] The visible diffuse reflectance spectrum exhibits a broad band with a maximum at 17,000 cm^{-1}. This spectrum is nearly identical with that of $Cu(py)_2(NO_3)_2$, which is thought to be octahedral with bidentate coordinated nitrate.[12] On the basis of currently available evidence, it is not possible to assign a structure to the $Cu(bipy)(NO_3)_2$ complex.

The reflectance spectrum of $Ni(bipy)_2(NO_3)_2$ is nearly identical with that of $Ni(en)_2(NO_3)_2$ in the visible region,[9] with absorption bands at 13,500, 18,000, and 29,000 cm^{-1}. Symmetrical octahedral nickel(II) complexes normally display three absorption bands in the 8000–30,000-cm^{-1} spectral region, attributed to ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}[F]$), ν_2 ($^3A_{2g} \rightarrow {}^3T_{1g}[F]$), and ν_3 ($^3A_{2g} \rightarrow {}^3T_{1g}[P]$) transitions, respectively. However, Hare and Ballhausen have shown that for octahedral nickel(II)

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[7] P. Krumholz, *J. Am. Chem. Soc.*, **73**, 3487 (1951).

[8] B. M. Gatehouse, S. E. Livingston, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

[9] N. F. Curtis and V. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

[10] R. C. Vranka and E. L. Amma, *ibid.*, **5**, 1024 (1966).

[11] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 4761 (1964).

[12] R. V. Biagetti, W. G. Bottjer, and H. N. Haendler, *Inorg. Chem.*, **5**, 379 (1966).

complexes of the type NiL_4X_2, where L and X are ligands widely separated in the spectrochemical series, tetragonal distortion results in a broadening and splitting of the ν_1 band.[13] The spectra of octahedral complexes such as $Ni(py)_4Cl_2$, $[Ni(en)_2(H_2O)_2]^{2+}$, and $Ni(en)_2(NO_3)_2$ have been explained on the basis of ν_1 splitting due to tetragonal distortion.[9,14] With the instrumentation available in this study, it was impossible to obtain reflectance absorption measurements in the infrared region from 8000 to 10,000 cm^{-1}. For $Ni(bipy)_2(NO_3)_2$, however, the band at 13,500 cm^{-1} is much too high in energy to be attributed to a single ν_1 band (which is $10Dq$ for octahedral nickel(II) complexes), unless 4,4′-bipyridine lies considerably higher than pyridine in the spectrochemical series. Therefore, it is assumed that the 13,500-cm^{-1} band is due to a splitting of ν_1. Infrared absorption bands for $Ni(bipy)_2(NO_3)_2$ are typical of monodentate nitrate coordination, and on the basis of stoichiometry and spectral data, a reasonable structure of the complex may be assigned as consisting of Ni(II) ions surrounded octahedrally by four bridging 4,4′-bipyridine molecules and two monodentate coordinated nitrate ions.

Infrared and visible reflectance spectra for $Co(bipy)_2(NO_3)_2$ and the approximate stoichiometry are consistent with an octahedral structure containing monodentate coordinated nitrate groups. While it is tempting to conclude that the structure is similar to that of $Ni(bipy)_2(NO_3)_2$, the impurity of the product based upon analytical data precludes a valid structural assignment. When the product listed as $Cu(bipy)_2(NO_3)_2$ was dried at 94°, it then analyzed as $Cu(bipy)(NO_3)_2$. However, $Cu(bipy)_2(NO_3)_2$ displayed an absorption maximum at 18,200 cm^{-1} compared to 16,400 cm^{-1} for $Cu(bipy)(NO_3)_2$, and assuming that 4,4′-bipyridine is higher in the spectrochemical series than NO_3^-, CH_3OH, or H_2O, it would seem that the degree of coordination of 4,4′-bipyridine must be higher in the former product than in the latter.

Acknowledgment.—Work was supported by a Colorado State University faculty improvement grant and an American Cancer Society institutional grant.

[13] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).

[14] M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).

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Metal Complexes of *o*-Aminobenzenethiol

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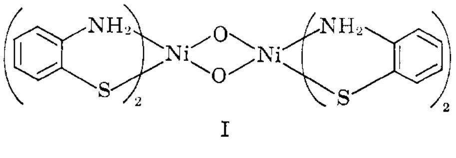
The compounds $Zn(abt)_2$, $Cu(abt)$, $Ni(abt)_2$, $Ni(NHC_6H_4S)_2$, $Co(abt)_2$, $Co(abt)_3$, $Fe(abt)_2$, $Mn(abt)_2$, $Cr(abt)_2$, and $VO(abt)_2$ (abt = *o*-$NH_2C_6H_4S$) have been prepared under anaerobic conditions. They have been characterized where possible by solution and reflectance electronic spectra, infrared spectra, X-ray powder photographs, and magnetic studies down to liquid nitrogen temperatures. The original reports of $Co(abt)_2$ stated that it was a dark blue, low-spin, planar cobalt(II) complex. This dark blue material has been shown to be an oxidation product of the true $Co(abt)_2$ complex, which is orange-brown and high spin with a sulfur-bridged, six-coordinate structure. The dark blue material has physical properties almost identical with those of the cobalt(III) complex $Co(abt)_3$ and is a mixture of it and some hydroxide species. In contrast $Ni(abt)_2$ on oxidation forms the imino complex $Ni(NHC_6H_4S)_2$, previously reported as an oxygen-bridged nickel(IV) complex. Presumably as a result of sulfur-bridged structures, several complexes show magnetic interaction, especially $Fe(abt)_2$ which has a Néel point at 138°K.

There has been considerable recent interest in sulfur ligands, especially those of the dithiol type, which produce series of complexes interrelated by electron-transfer reactions.[1] Some related ligands, including *o*-aminobenzenethiol, have been shown to behave similarly.[2,3] Considerable confusion exists in the literature on the complexes of *o*-aminobenzenethiol, probably owing to their air-sensitive nature. For example, preliminary reports from these[4] and other laboratories[2] showed that the deep blue oxidation product of $Ni(abt)_2$ (abt = *o*-$NH_2C_6H_4S$) does not have the reported[5] oxygen-bridged structure I but has structure II similar to



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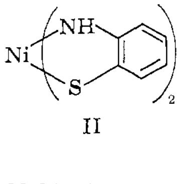

II

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[1] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964); E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 2956 (1966).

[2] A. L. Balch, F. Röhrscheid, and R. H. Holm, *ibid.*, **87**, 2301 (1965); E. I. Steifel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965).

[3] R. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966); A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 5201 (1966); R. H. Holm, A. L. Balch, A. Davison, A. H. Maki, and T. E. Berry, *ibid.*, **89**, 2866 (1967).

[4] L. F. Larkworthy, J. M. Murphy, and D. J. Phillips, *ibid.*, **88**, 1570, (1966). Note, the structural formula cited for $(abt)_2NiOONi(abt)_2$ in this earlier communication contains a typographical error and it should appear as I in this present paper.

[5] W. Hieber and R. Brück, *Z. Anorg. Allgem. Chem.*, **269**, 13 (1952).