two resonances for R = Me, Et, *i*-Pr is in accordance with the presence of two isomers (vide supra), and the relative intensities of these resonances correspond very well with the isomer ratio as determined from the $^1$H NMR spectra (see Table I). For R = *i*-Pr, a very small second resonance is observed, and this may correspond to the minor (1%) isomer, but the assignment is uncertain (see Figure 3a). The $^{109}$Ag resonances with the smallest linewidth (8–10 Hz) were observed for the compounds [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)NR]PtAgBr] with R = *p*-tol and for the main isomer with R = Me. These are the compounds in which Ag couples with only one hydrogen atom ($H_B$). Broader lines (15–17 Hz) were observed for the other isomers. This is almost certainly due to the fact that in these isomers Ag couples with different hydrogen atoms ($H_B$ and $H_A$) and that the couplings differ in magnitude. With respect to the above it is worth noting that equal couplings should lead to multiplets with intensity ratios of −1:+1 (one H), −1:0:+1 (two H's), −1:−1:+1:+1 (three H's), etc.[15] For those compounds in which Ag couples with only one (R = *p*-tol, Me) or two (R = *i*-Pr) hydrogen atoms the separation between the two peaks within one doublet corresponds very well with $J(Ag–H_B)$ and sum $J(Ag–H_B) + J(Ag–H_A)$, respectively ($^1$H NMR).

On the basis of the above observations, i.e., linewidth, relative intensity, and $J(^{109}Ag–H)$, assignment of the resonances to the isomers having the *N*-*p*-tolyl group bonded either to Pt (isomer II) or the Ag (isomer I) was possible. From Table II it is clear that the two types of isomers can also be discriminated on the basis of their $^{109}$Ag chemical shifts, i.e., downfield for isomer I and upfield for isomer II. Furthermore, the chemical shifts change systematically as R is changed from Me to Et to *i*-Pr. Finally, the chemical shift of the compound with R = *p*-tolyl falls within the range of isomers II, and this fact is consistent with a structure in which these latter isomers contain a Ag-bonded *N*-*p*-tolyl moiety.

As mentioned above the main $^{109}$Ag doublet resonances show satellite doublets. By integration of the normal INEPT spectrum, which, however, has the disadvantage of losing the information concerning the $J(Ag–H)$ couplings, the satellite resonances become more evident (see Figure 3b). For all the compounds the separation between the two satellites amounts to about 170 Hz (see Table II) and there is no doubt that these satellites are due to coupling between $^{109}$Ag and $^{195}$Pt ($I = {}^1/_2$, 33% natural abundance). Although a coupling pathway through the skeleton of the bridging formamidino ligand cannot be excluded, we propose that this coupling is a one-bond $^{109}Ag–^{195}Pt$ coupling implying the presence of a direct Pt-to-Ag interaction.

Since these are the first Pt–Ag couplings reported, it is difficult to give a rationale for the absolute values found though their magnitude can be compared to that of the $^1J(^{195}Pt–^{195}Pt)$ of 332 Hz found in $[[(Ph_2P)_2CH_2]_2Pt_2Me_3]^+$.[16] The latter complex contains a square-pyramidally coordinated platinum(II) atom with a donor bond to an apically positioned (Pt(2)) atom (Pt(1)–Pt(2) = 2.769 Å). In the present Pt–Ag complexes the platinum(II) center is also expected to be square-pyramidally coordinated as established by X-ray diffraction analysis of a corresponding Pt–Hg complex [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)NR]PtHgBrCl] (see Figure 1).[12] The latter structure shows a square-pyramidal platinum(II) center directly bonded to mercury (Pt–Hg = 2.8331 (7) Å) in the apical position.[11,12] From that work it was concluded that the terdentate ligand system 2,6-$(Me_2NCH_2)_2C_6H_3$, by virtue of its fixed trans-N-donor ligand sites, enhances the nucleophilicity of the platinum center and thus stabilizes a Pt-to-Hg donor interaction. It is therefore apparent that in all these complexes the platinum center is making use of a filled orbital, perpendicular to the basal coordination plane, which is anticipated to have low s character.

## Conclusions

The INEPT $^{109}$Ag NMR spectra of the complexes [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)NR]PtAgBr] support the data obtained from the $^1$H NMR spectra: i.e., the presence of two isomers and their structural assignment, the dependence of the isomer ratio on the alkyl substituent R (Me, Et, *i*-Pr), and the presence of $J(^{107,109}Ag–^1H)$ couplings. Unique information, which could not be obtained from $^{195}$Pt NMR (linewidth 500 Hz), is provided by these INEPT $^{109}$Ag NMR spectra: i.e, observation of a $^1J(^{195}Pt–^{109}Ag)$ (±170 Hz) pointing to the presence of a direct Pt–Ag interaction.

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**Registry No.** [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)NMe]PtAgBr], isomer I, 80484-86-2; [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)NMe]PtAgBr], isomer II, 80484-95-3; [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)NEt]PtAgBr], isomer I, 80484-87-3; [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)NEt]PtAgBr], isomer II, 80484-96-4; [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)N-*i*-Pr]PtAgBr], isomer I, 80484-88-4; [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)N-*i*-Pr]PtAgBr], isomer II, 80484-97-5; [[2,6-$(Me_2NCH_2)_2C_6H_3$][*p*-tolNC(H)N-*p*-tol]PtAgBr], 80484-89-5.

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# Synthesis and Characterization of Cobalt(III) Nicotinic Acid Complexes

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There has been considerable interest in transition-metal complexes that have aromatic ligands such as nicotinic acid functioning as electron-transfer mediators in oxidation–reduction reactions.[1] Nicotinic acid has two potential ligating groups (Table I), the pyridine nitrogen and the carboxylic acid oxygen. In redox reactions, pyridinecarboxylic acids facilitate electron transfer by bridging two metal ions. Recently, transition-metal complexes of nicotinic acid have again drawn attention because of their potential involvement in biological systems.[2]

To date, relatively little has been reported on the stereochemistry and spectral properties associated with coordinated nicotinic acid. In order to improve our understanding of the coordination chemistry of nicotinic acid, a series of Co(III) complexes of this ligand and related molecules has been synthesized and characterized by visible–UV, IR, and proton NMR spectroscopy. Several of the complexes synthesized in this study have been reported previously but were only partially characterized.

## Experimental Section

**Materials, Measurements, and Analyses.** Reagent grade nicotinic acid and nicotinamide (Sigma), pyridine, isonicotinic acid, and methyl nicotinate (Aldrich) were used.

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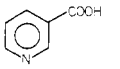
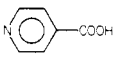
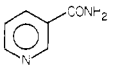
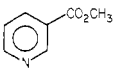
Table I. Ligand Abbreviations and Structure

| ligand | abbrev | structure |
|---|---|---|
| nicotinic acid | nicH[a] |  |
| isonicotinic acid | inicH[a] |  |
| nicotinamide | nica |  |
| methyl nicotinate | mnic |  |

[a] Protonation can also occur at N. The conjugate bases are abbreviated nic and inic.

Thin-layer chromatography was carried out on EM-precoated aluminum-backed TLC plates (VWR) in isopropyl alcohol–triethylammonium bicarbonate buffer (ISTEA).[3]

$^1$H NMR spectra were recorded on a JEOL MH-100 spectrometer (0.3 M in $D_2O$). IR spectra were obtained with a Beckman Acculab 1, with use of KBr pellets or AgCl plates (path length = 0.05 mm, 0.25 M in $D_2O$). So that solubility could be increased, perchlorates were often converted to chlorides by anion exchange.

Chemical analyses were obtained from either Canadian Microanalytical Service, Ltd., Vancouver, B.C., Canada, or Galbraith Laboratories, Inc., Knoxville, TN. Results are reported in Table II.

The majority of the complexes discussed in this study were obtained as perchlorate salts. Although no problems were encountered, caution should be exercised not to evaporate the solutions to dryness while acidic or to filter on sintered glass since perchlorate salts of coordination complexes are potentially explosive.

**Synthesis. $[Co(NH_3)_5X](ClO_4)_3$, Where X = Pyridine, N-Coordinated Nicotinic Acid, Nicotinamide, Methyl Nicotinate, or $H_2O$.** The pentaammine N-coordinated complexes were prepared as previously described by Nordmeyer and Taube[4] from $[Co(NH_3)_5H_2O](ClO_4)_3$.[5] The methyl nicotinate complex was prepared by the above method, but it has not been previously reported. The N-coordinated nicotinic acid complex was prepared as described by Norris and Nordmeyer by hydrolyzing the nicotinamide complex with $NOClO_4$. Nitrosyl perchlorate should be freshly prepared in the quantities needed since it is potentially explosive.[6]

**$[Co(NH_3)_5OAc](ClO_4)_2$.** Although previously prepared by Basolo and Murmann[7] the acetate complex was prepared in the following manner because of improved yields and purity. To 15 mL of glacial acetic acid was slowly added $[Co(NH_3)_5CO_3]NO_3$[8] (5.32 g, 0.02 mol), and the resulting solution was stirred at 60 °C for 1 h. After cooling to room temperature, the orange-red solution was slowly neutralized with 5 M NaOH. The solution was filtered to remove any precipitated salts or unreacted aquo complex, and the filtrate was reduced in volume to approximately 20 mL. At this point product began to precipitate. The orange-red precipitate was washed with 95% ethanol and air-dried and was recrystallized from a minimal amount of water at room temperature by adding a few drops of 70% $HClO_4$. After it was filtered, it was washed with absolute ethanol and ether and air-dried; yield 3.5 g (45%). Additional product can be isolated from the initial filtrate by chromatography on Sephadex G-10.

**$[Co(NH_3)_5X](ClO_4)_2$, Where X = O-Coordinated Nicotinic or Isonicotinic Acid.** Although these complexes were previously reported by Gould and Taube,[1] a more direct synthesis has been developed that avoids excess ligand coprecipitation with the final product.

Nitrogen was bubbled through the reaction mixture until the heating step to facilitate removal of $CO_2$. To a suspension of $[Co(NH_3)_5CO_3]NO_3$ (5.32 g, 0.02 mol) in 15 mL of water was added nicotinic or isonicotinic acid (12.31 g, 0.1 mol) at such a rate as to control effervescence. The final pH should be below 1 to assure complete $CO_2$ removal, and it was adjusted as needed with 5 M HCl. After the reaction mixture was stirred for 30 min, the pH was readjusted to 7 with 3 g of NaOH and 5 M NaOH as needed, and the solution was placed in a 60 °C water bath for 60 min. After the solution cooled to room temperature, excess nicotinic acid was precipitated by adjusting the pH to 3.5 with 10 M HCl. The filtrates were combined and reduced in volume, and the precipitation step was repeated until no further nicotinic acid could be obtained. The pH was then adjusted to 7, and the solution was reduced in volume to 10 mL and loaded onto a Sephadex G-10 column (5 × 75 cm). When the column was eluted with distilled water at a flow rate of 1 mL/min, two orange bands cleanly separated. The second band was collected, reduced in volume, crystallized by adding 70% $HClO_4$, and filtered. The orange-red product was recrystallized twice, washed with absolute ethanol, and air-dried; yield 4.1 g (44% nicotinic acid) and 3.9 g (42% isonicotinic acid).

***trans*-$[Co(NH_3)_4(nicH\text{-}O)_2](ClO_4)_3$.** The trans-O complex was prepared by stirring $[Co(NH_3)_4CO_3]NO_3 \cdot {}^1/_2H_2O$[8] (5.16 g, 0.02 mol), nicotinic acid (6.16 g, 0.05 mol), and 0.25 g of coconut charcoal in 50 mL of diethylene glycol at 65–70 °C for 1 h. After the mixture cooled to room temperature, the charcoal was removed by filtration and washed with 10 mL of water. The filtrates were combined, and 10 mL of 70% $HClO_4$ was added. When the solution was cooled overnight at −5 °C, small purple crystals slowly precipitated. The product was filtered, washed with 95% ethanol, and air-dried. The complex was recrystallized twice from hot water by adding a few drops of 70% $HClO_4$; yield 1.9 g (14%).

***cis*-$[Co(NH_3)_4(nic\text{-}O)_2]Cl$.** The cis-O isomer was prepared by slowly adding $[Co(NH_3)_4CO_3]NO_3 \cdot {}^1/_2H_2O$ (5.16 g, 0.02 mol) to 10 mL of 5 M $H_2SO_4$, into which $N_2$ was slowly bubbled (the stream of $N_2$ was continued throughout the reaction), while the solution stirred for 30 min. The solution was then placed in an ice bath, and 3 g of NaOH was added. The solution was removed from the ice bath, and nicotinic acid (12.31 g, 0.1 mol) and NaOH (4.0 g, 0.1 mol) were added. The final pH was adjusted to 6, 0.5 g of coconut charcoal was added, and the stirred solution was placed in a 60 °C bath for 60 min. After the solution cooled to room temperature, the charcoal was removed by filtration and was washed with a small amount of water. Excess nicotinic acid was precipitated by adjusting the pH to 3.5 with 10 M HCl and filtering. This step was repeated several times, with intermediate evaporation, to remove most of the excess nicotinic acid. The desired complex was slowly precipitated from solution as it evaporated under an air stream at pH 7.5. The orange-red powder was filtered, washed with 95% ethanol, and air-dried. It was repeatedly recrystallized from water, pH 7.5, until shown pure by TLC; yield 2.1 g (26%).

***cis*- and *trans*-$[Co(en)_2(nicH\text{-}O)_2](ClO_4)_3$.** The method used to synthesize these complexes was identical with that used for the cis-O-tetraamine complex up to the crystallization step, except that $[Co(en)_2CO_3]Cl$[9] (5.49 g, 0.02 mol) was substituted for the ammine carbonate.

After excess nicotinic acid was removed with 10 M $HClO_4$, a half-volume of $HClO_4$ was added to the solution. When the solution was cooled overnight in an ice bath, a small quantity of the red-purple trans-O isomer precipitated. This isomer was removed by filtration and the filtrate (Fl) set aside to obtain the cis-O isomer. The trans-O complex was washed with 95% ethanol, air-dried, and recrystallized from water at room temperature, at pH 7.5. The precipitate was washed with absolute ethanol and ether and air-dried; yield 0.1 g (0.7%).

The cis-O isomer was obtained by slowly evaporating the filtrate (Fl) under an air stream after the pH had been readjusted to 7.5 with 5 M NaOH, filtering, and washing with absolute ethanol and ether. It was repeatedly recrystallized from water, pH 7.5, until shown pure by TLC; yield 2.5 g (19%).

## Results and Discussion

**Synthesis and Purification of Complexes.** The syntheses of several of the pentaammine complexes prepared for this study have been reported previously. Gould and Taube[1] encountered a serious contamination problem with unreacted nicotinic and isonicotinic acid. This difficulty was circumvented through precipitation of the unreacted ligands in acid solution and by Sephadex G-10 gel chromatography.

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**Table II.** Elemental Analyses and $R_f$ Values

| complex | % C | | % H | | % N | | $R_f$[a] |
|---|---|---|---|---|---|---|---|
| | calcd | found | calcd | found | calcd | found | |
| $[Co(NH_3)_5OAc](ClO_4)_2$ | 4.79 | 4.83 | 3.63 | 3.58 | 13.97 | 13.89 | 0.11 |
| $[Co(NH_3)_5(nicH\text{-}O)](ClO_4)_3$ | 12.74 | 12.80 | 3.57 | 3.76 | 14.86 | 14.75 | |
| $[Co(NH_3)_5(inicH\text{-}O)](ClO_4)_3 \cdot {}^3/_2H_2O$ | 12.16 | 12.16 | 3.92 | 4.06 | 14.19 | 14.27 | |
| $[Co(NH_3)_5(mnic)](ClO_4)_3 \cdot H_2O$ | 14.07 | 14.12 | 4.02 | 4.61 | 14.07 | 14.20 | 0.05 |
| $[Co(NH_3)_5(nica)](ClO_4)_3 \cdot {}^3/_2H_2O$ | 12.18 | 12.18 | 4.10 | 3.92 | 16.58 | 16.49 | 0.05 |
| *cis*-$[Co(NH_3)_4(nic\text{-}O)_2](ClO_4)$ | 30.48 | 30.33 | 4.27 | 4.31 | 17.78 | 17.68 | 0.58 |
| *trans*-$[Co(NH_3)_4(nicH\text{-}O)_2](ClO_4)_3 \cdot {}^1/_2H_2O$ | 21.17 | 21.16 | 3.41 | 3.61 | 12.35 | 12.26 | 0.64 |
| *cis*-$[Co(en)_2(nic\text{-}O)_2](ClO_4)_3 \cdot {}^5/_2H_2O$ | 25.00 | 25.01 | 3.81 | 3.23 | 10.94 | 10.73 | 0.69 |
| *trans*-$[Co(en)_2(nic\text{-}O)_2](ClO_4)_3 \cdot H_2O$ | 25.91 | 26.02 | 3.78 | 3.81 | 11.33 | 11.30 | 0.45 |

[a] Pentaammine complexes are 70/30 ISTEA, others are 50/50; see Experimental Section.

**Table III.** Spectral Data

| complex | band position[a] | | $Dt'$,[b] $cm^{-1}$ | $Dq'$, $cm^{-1}$ |
|---|---|---|---|---|
| | I | II | | |
| $Co(NH_3)_6^{3+}$ [12] | 2.105[b] (56) | 2.950 (47) | | 2490 ($NH_3$) |
| $Co(NH_3)_5H_2O^{3+}$ [12] | 2.039 (47) | 3.030 (44) | 172 | 1888 ($H_2O$) |
| $Co(NH_3)_5OAc^{2+}$ | 1.992 (74) | 2.849 (59) | 132 | 2028 (OAc) |
| $Co(NH_3)_5(nic\text{-}O)^{2+}$ | 1.992 (67) | 2.849 (56) | 132 | 2028 (nic-*O*) |
| $Co(NH_3)_5(inic\text{-}O)^{2+}$ | 1.992 (84) | 2.740 (95) | 132 | 2028 (inic-*O*) |
| $Co(NH_3)_5py^{3+}$ | 2.105 (61) | 2.933 (58) | | 2490 (py) |
| $Co(NH_3)_5(nic\text{-}N)^{3+}$ | 2.096 (62) | 2.948 (55) | 13 | 2444 (nic-*N*) |
| $Co(NH_3)_5nica^{3+}$ | 2.105 (62) | 2.954 (54) | | 2490 (nica) |
| $Co(NH_3)_5mnic^{3+}$ | 2.105 (68) | 2.959 (54) | | 2490 (mnic) |
| *cis*-$Co(NH_3)_4(nic\text{-}O)_2^+$ | 1.988 (91) | 2.841 (68) | | |
| *trans*-$Co(NH_3)_4(nic\text{-}O)_2^+$ | 1.818 (74), 2.110 (sh) | 2.817 (79) | 331 | 1911 (nic-*O*) |
| $Co(en)_3^{3+}$ [12] | 2.147 (98) | 2.950 (87) | | 2530 (en) |
| *cis*-$Co(en)_2(nic\text{-}O)_2^+$ | 1.995 (146) | 2.760 (107) | | |
| *trans*-$Co(en)_2(nic\text{-}O)_2^+$ | 1.848 (81), 2.151 (sh) | 2.825 (91) | 321 | 1969 (nic-*O*) |

[a] In $cm^{-1} \times 10^{-4}$, with $\epsilon$ in parentheses. [b] The Racah parameter $C$ was taken to be 3825 and 3835 $cm^{-1}$ for ammonia and ethylenediamine, respectively.[12]

Since only partial chemical analyses for a number of the complexes studied have been reported previously, analyses were obtained and are given in Table II. Differences in the visible absorption spectra were noted in both band position and intensity for several complexes, and so their analyses are also included. Chromatographic methods have evolved significantly since some of these complexes were initially prepared and have simplified their purification. In particular the analytical and preparative TLC[3] and HPLC[10] methods have been very useful in isolating pure complexes ($R_f$ values are given in Table II).

When linkage isomerism is possible (N- or O-coordination of nicotinic and isonicotinic acid), oxygen coordination is favored for $Co^{III}N_4X_2$ and $Co^{III}N_5X$ complexes. For nitrogen coordination, the nicotinamide complex has to be prepared followed by hydrolysis of the amide with $NOClO_4$. It is difficult to prepare an N-coordinated species, as evidenced by low yields in the pyridine series of complexes, and thus far, it has been impossible to isolate a tetraammine N-coordinated nicotinamide complex. Resistance to N-coordination has also been noted in the formation of $Co(NH_3)_6^{3+}$. Activated charcoal is required to coordinate the last ammonia of $[Co(NH_3)_6]Cl_3$.[11] In this study reactions with charcoal thus far have led to disproportionation and decomposition in the tetraammine series of complexes.

The tetraammine and ethylenediamine series of complexes favor the formation of the cis geometrical isomers. A stacking interaction between the two aromatic rings, which is clearly evidenced by molecular models, may occur in the cis isomers that could explain the preference for the cis geometry. Only small quantities of the trans isomer have been found in this series of complexes.

**Electronic Absorption Spectra.** The band positions and molar absorptivities for this series of complexes are presented in Table III. The crystal field model developed by Wentworth and Piper[12] was used to calculate $Dt'$ and $Dq'$ values for the ligands. Substitution on the pyridine ring appears to have little effect on the ligand strength of the nitrogen as evidenced by values calculated for pyridine, nicotinic acid, nicotinamide, and methyl nicotinate. These values are also identical with that of ammonia. The $Dq'$(acetate) values for nicotinic and isonicotinic acid are in good agreement with those for acetate itself and related acetate ligand complexes, which have a calculated $Dq'$ value in the range 1900–2000 $cm^{-1}$.

The isomers of *cis*- and *trans*-$[Co(NH_3)_4(nic\text{-}O)_2]^+$ and -$[Co(en)_2(nic\text{-}O)_2]^+$ were assigned on the basis of their spectral characteristics. Consistent with ligand field theory,[13] partial splitting was evident in band I of the trans complexes. The low-intensity shoulder (band $I_B$) in each complex has an energy comparable to that of band I in the parent complexes, $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$, respectively (Table II). As predicted by ligand field theory, the first absorption bands in the cis isomers do not split but have increased molar absorptivities due to lowered symmetry of the cis isomers.

**Determination of Coordination Mode of Nicotinic Acid. Infrared Analysis.** Infrared spectroscopy provides a means of distinguishing the mode of coordination of nicotinic and isonicotinic acid that is independent of other ligands present in the coordination sphere. Sievers and Bailar[14] and recently Deacon and Phillips[15] have noted the effects of metal ion

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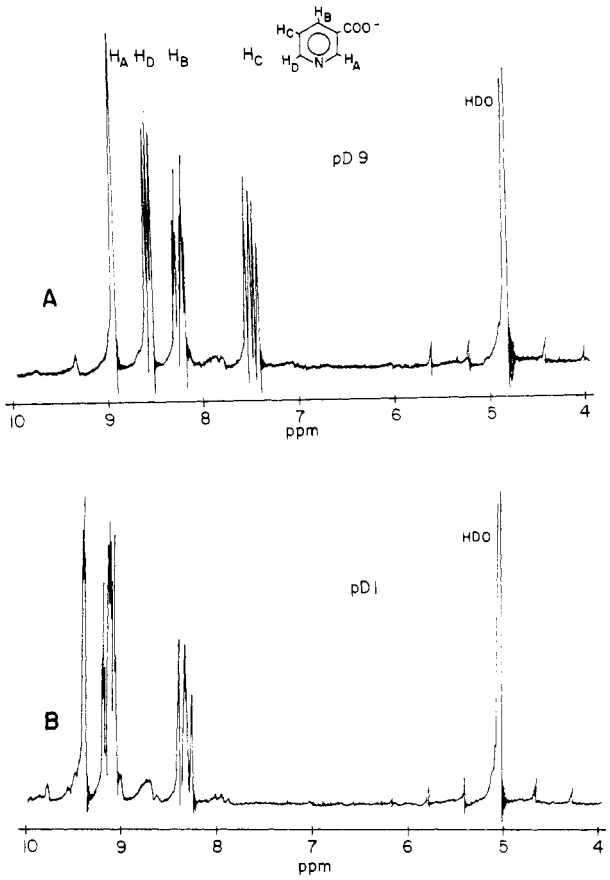


**Figure 1.** $^1$H NMR spectrum of nicotinic acid: (A) pD 9; (B) pD 1.

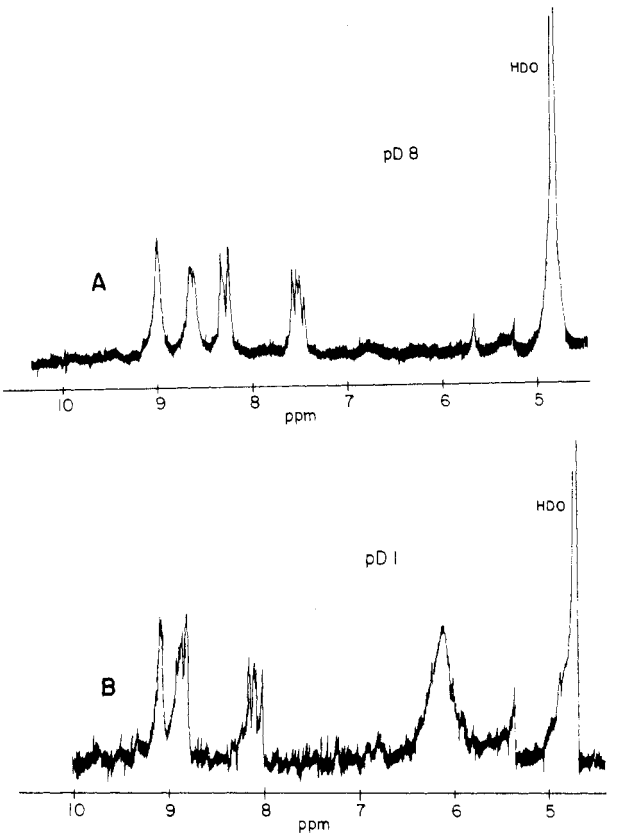


**Figure 2.** $^1$H NMR spectrum of *trans*-$[Co(en)_2(nic\text{-}O)_2]^+$ in the aromatic region: (A) pD 8; (B) pD 1.

coordination on the carbonyl asymmetric stretching frequency of carboxylic acids. Coordinated carboxylic acids absorb between 1600 and 1650 $cm^{-1}$ with frequencies dependent on the metal ion. Cobalt(III) carboxylic acid complexes absorb at approximately 1640 $cm^{-1}$. When a carboxylic acid is protonated, the stretching frequency shifts to 1700 $cm^{-1}$ and when deprotonated shifts below 1600 $cm^{-1}$. A simple $D_2O$ titration can then be used to establish the mode of nicotinic acid coordination; if the carboxylate can be titrated, as evidenced by the shift in the carboxylate asymmetric stretching frequency, nicotinic acid has to be nitrogen coordinated.

For N-coordinated $[Co(NH_3)_5(nic)]^{2+}$ a band at 1705 $cm^{-1}$ (pD 1, protonated) shifts to 1600 $cm^{-1}$ with increasing pD (pD 8, deprotonated). For O-coordinated $[Co(NH_3)_5(nic)]^{2+}$ a band at 1645 $cm^{-1}$ is invariant with pD. The other nicotinic acid complexes exhibited the same invariance in the carbonyl stretching frequency indicating O-coordination. $^1$H NMR spectroscopy confirmed these assignments.

**Proton Magnetic Resonance.** The aromatic region of the $^1$H NMR spectrum is sensitive to nitrogen substitution by both metal ions and protons (deuterium). The $^1$H NMR spectrum of nicotinic acid is presented in Figure 1A. The proton assignments are in agreement with those made by Zanger and Simons.[16] When the solution is acidified, the pyridine nitrogen is deuterated, which will perturb the aromatic system by removing electron density from the nitrogen and effectively the entire $\pi$ system. The ring protons, thus, are shifted downfield as shown in Figure 1B, but now $H_B$ and $H_D$ overlap, giving three rather than four individual sets of resonances.

A similar effect is also observed on Co(III) coordination. A simple pD titration will then determine N- or O-coordination. When nicotinic acid is O-coordinated, protons $H_B$ and $H_D$ will overlap at low pD and split as the pD is raised. Conversely, when nicotinic acid is N-coordinated, protons $H_B$ and $H_D$ will overlap at all pDs. A $D_2O$ titration is shown in Figure 2 for trans-$[Co(en)_2(nic\text{-}O)_2]^+$. The aromatic region of the spectrum of the O-coordinated species varies with pD in a manner similar to that observed for free nicotinic acid (Figure 2). The broad line centered at 6.1 ppm in the pD 1 spectrum is due to the N–H resonances that appear due to slow exchange in acidic solutions. On the other hand, the NMR spectrum of $[Co(NH_3)_5(nic\text{-}N)]^{2+}$ shows three sets of resonances in the aromatic region that are invariant with pD consistent with N-coordinated nicotinic acid.

$^1$H NMR can also be used to confirm the assignment of the *cis*- and *trans*-$[Co(en)_2(nic\text{-}O)_2]^+$ geometrical isomers. In practice, the chemical shifts and coupling constants of chelated ethylenediamine are too small to resolve and only a broad envelope is found at 2.8 ppm.[17] From molecular models it is readily evident that in the cis isomer the carbonyl of the coordinated carboxylate points directly at a methylene group in the chelated ethylenediamine ring, placing it in a deshielding region. The result is that the ethylene resonances are separated into two distinct sets in the cis isomer but not the trans isomer. The downfield set of resonances in the cis isomer is about 0.3 ppm below comparable sets of resonances in other ethylenediamine complexes previously reported.[17]

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**Registry No.** $[Co(NH_3)_5OAc](ClO_4)_2$, 14523-28-5; *trans*-$[Co(NH_3)_4(nicH\text{-}O)_2](ClO_4)_3$, 81554-36-1; *cis*-$[Co(NH_3)_4(nic\text{-}O)_2]ClO_4$,

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81600-73-9; *cis*-$[Co(en)_2(nicH\text{-}O)_2](ClO_4)_3$, 81554-39-4; *trans*-$[Co(en)_2(nicH\text{-}O)_2](ClO_4)_3$, 81600-76-2; $[Co(NH_3)_5py](ClO_4)_3$, 15351-76-5; $[Co(NH_3)_5(nic\text{-}N)](ClO_4)_3$, 81554-40-7; $[Co(NH_3)_5nica](ClO_4)_3$, 15675-82-8; $[Co(NH_3)_5mnic](ClO_4)_3$, 38686-26-9; $[Co(NH_3)_5CO_3]NO_3$, 15244-74-3; $[Co(en)_2CO_3]Cl$, 15842-50-9; $[Co(NH_3)_5(nicH\text{-}O)](ClO_4)_3$, 81554-26-9; $[Co(NH_3)_5(inicH\text{-}O)](ClO_4)_3$, 81554-27-0.

**Supplementary Material Available:** Figures showing the pD IR titration spectra of $[Co(NH_3)_5(nic\text{-}N)]^{2+}$ and $[Co(NH_3)_5(nic\text{-}O)]^{2+}$ and the $^1H$ NMR spectra of *cis*- and *trans*-$[Co(en)_2(nic\text{-}O)_2]^+$ in the alkyl region (4 pages). Ordering information is given on any current masthead page.

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# Concentration- and Solvent-Dependent Electron Paramagnetic Resonance Signals from μ-Nitrido-bis[(5,10,15,20-tetraphenylporphinato)iron]. Solute–Solvent and Solute–Solute Interactions

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We have been investigating the magnetic properties[1] of the nitrogen-bridged iron porphyrin μ-nitrido-bis[(5,10,15,20-tetraphenylporphinato)iron][2-4] [((TPP)Fe)$_2$N]. Unlike the analogous oxygen-bridged porphyrin, which is diamagnetic at low temperatures due to the antiferromagnetic exchange interaction between the two iron ions,[5] ((TPP)Fe)$_2$N has a net spin $S = {}^1/_2$ over the temperature range 4–295 K.[1,2] The EPR spectrum of the complex is characteristic of an axially symmetric system with $g_\perp = 2.15$ and $g_\parallel = 2.01$.[1,2] An early EPR study of a solid sample of ((TPP)Fe)$_2$N failed to reveal any nuclear hyperfine structure on either of the two EPR signals.[2] We recently reexamined the EPR spectrum of the complex in a frozen carbon disulfide solution and observed well-resolved $^{14}N$ nuclear hyperfine splittings on the $g_\perp$ component.[1] We attributed the hyperfine structure to the interaction of the unpaired electron with the nucleus of the bridging nitrogen atom. The frozen-solution EPR spectra also exhibited, however, several signals which were not observed in the spectrum of the solid sample. We were unable to explain the origin of the additional signals at that time.

The appearance of the additional signals in the EPR spectrum of ((TPP)Fe)$_2$N in carbon disulfide suggests that the solvent or solution environment may significantly influence the magnetic properties of the complex. So that the effects of these factors on the EPR signals could be better assessed, the spectrum of the complex has been obtained in various solvents as a function of concentration.

## Experimental Section

The ((TPP)Fe)$_2$N complex was prepared and purified as described in ref 2. The identity of the molecule was confirmed by UV–visible and infrared spectroscopy.

The EPR spectra were recorded from frozen solutions or "thin films" at 110 K with a Bruker ER200D X-band spectrometer with a 12-in. magnet. The temperature was controlled with a Bruker ER4111VT liquid-nitrogen variable-temperature system.

The solvents used for the EPR studies (benzene, ethanol, and carbon disulfide) were all spectral grade and displayed no adventitious EPR signals. Thin films of ((TPP)Fe)$_2$N were made by warming the top of an EPR tube containing the complex in a $6.7 \times 10^{-3}$ M carbon disulfide solution and then inverting and righting the tube, allowing the solvent to run down the warm tube and partially evaporate, leaving a film of ((TPP)Fe)$_2$N. The tube was placed in the EPR cavity such that only the thin-film region was in the microwave field.

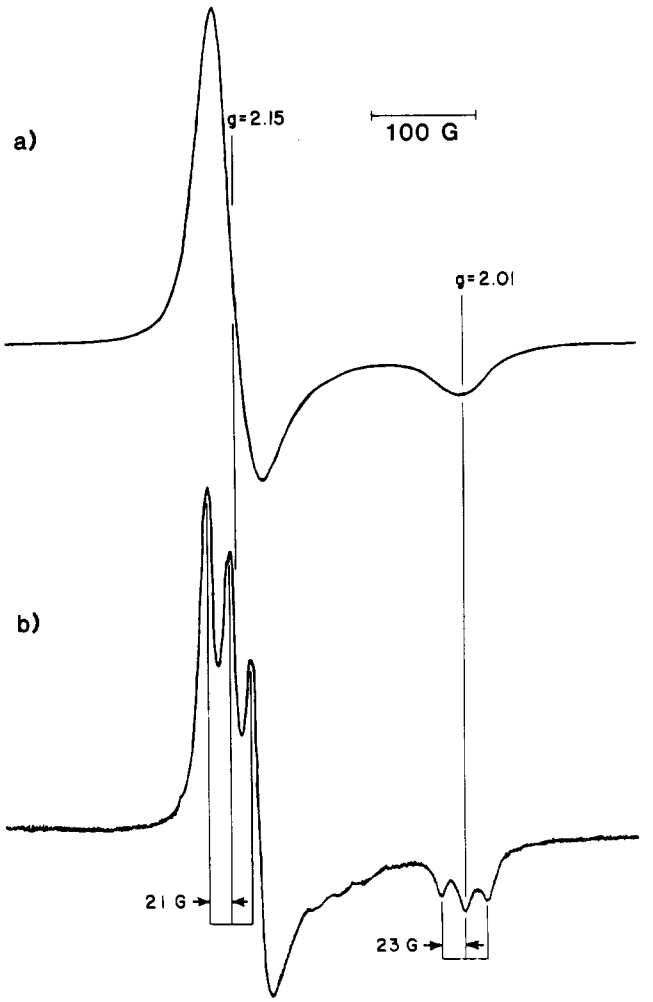


**Figure 1.** EPR spectrum of ((TPP)Fe)$_2$N in carbon disulfide at 110 K (concentration $6.7 \times 10^{-3}$ M): (a) broad-line signal obtained from the bulk solution; (b) signal obtained from a "thin film" (see text) of the same solution (modulation amplitude 4 G; microwave power 1.99 mW (a) and 15.7 mW (b)).

## Results and Discussion

The EPR spectrum of $6.7 \times 10^{-3}$ M ((TPP)Fe)$_2$N in carbon disulfide at 110 K is shown in Figure 1a. The spectrum of the complex at lower concentrations in carbon disulfide and in benzene is similar. The EPR spectrum is characteristic of an axially symmetric system with $g_\parallel = 2.01$ and $g_\perp = 2.15$. The signals exhibit no resolved $^{14}N$ nuclear hyperfine structure[1] and are similar to those observed for solid ((TPP)Fe)$_2$N.[2] The EPR signals narrow only slightly as the concentration is reduced, and no nuclear hyperfine structure can be resolved at 110 K, even at concentrations where the signal intensity limits the acquisition of the spectrum ($\sim 10^{-5}$ M). The lack of resolved $^{14}N$ nuclear hyperfine structure in the spectrum obtained at 110 K is in contrast to the well-resolved structure observed at 50 K.[1]

In order to investigate the possibility that the hyperfine structure in the solutions of carbon disulfide and benzene at 110 K is rendered unobservable by sample aggregation and

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