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Synthesis and Spectroscopic Characterization of Cobalt(III) and Copper(II) Complexes of Hexadentate and Tetradentate Ligands Containing Pyridyl Arms

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The newly prepared complexes [Co(edampda)]ClO_4 (edampda is *N*,*N*′-bis(2-pyridylmethyl)ethylenediamine-*N*,*N*′-diacetate), [Co(tpa)(H_2O)Cl]$(ClO_4)_2$ (tpa is tris(2-pyridylmethyl)amine), [Co(*uns*-penp)(H_2O)Cl]$(ClO_4)_2$ (*uns*-penp is *N*,*N*-bis(2-pyridylmethyl)ethylenediamine), and [Cu(*uns*-Hpenp)Cl_2]ClO_4 have been synthesized and characterized. In addition, the previously reported complexes [Co(tpen)]$(ClO_4)_3$ (tpen is *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine), [Co(tptn)]$(ClO_4)_3$ (tptn is *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,3-propanediamine), and $\Lambda\Lambda\Delta$-$(-)_{589}$-[Co(tppn)]$(ClO_4)_3$ (tppn is *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-propanediamine) have been synthesized and characterized by high-resolution ^1H nuclear magnetic resonance (NMR) spectroscopy for the first time. Two-dimensional ^1H NMR spectroscopy has been utilized to complete the pyridine hydrogen assignments in the one-dimensional ^1H NMR spectra of the tpen and tptn complexes. The 300-MHz ^1H NMR spectra of all of these complexes show good resolution for all of the hydrogens. The AB patterns of the pyridyl hydrogens and ethylenediamine hydrogens are discussed and correlated to one another. The AB coupling constants of the pyridyl rings are approximately 16 and 20 Hz for the G (in the plane of the ethylenediamine ring) and R (out of the plane of the ethylenediamine ring) chelate rings, respectively; these results are consistent with the well-documented AB coupling constants of (amino polycarboxylato)cobalt complexes. All of the ^1H NMR spectra have been interpreted completely, and the usefulness of using AB coupling constants to assign individual AB patterns to R, G, or E chelate rings in polypyridyl complexes is demonstrated. In addition, the partial resolution of [Co(tpen)]$(ClO_4)_3$ is reported, and the visible spectra of all of the complexes are reported.

Introduction

Complexes of amino polycarboxylate ligands have been thoroughly investigated in recent decades.[3] Extensive studies have been conducted in the areas of synthesis, visible spectroscopy, circular dichroism (CD) spectroscopy, ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and crystallography.

Various polypyridyl analogues of the amino polycarboxylate ligands have also been reported; however, the complexes of the polypyridyl ligands have not been investigated as thoroughly as those of the amino polycarboxylates. The polypyridyl complexes have not been studied by using high-resolution (300 MHz) ^1H NMR spectroscopy and have not been studied by using crystallography to analyze the amount of strain that pyridyl arms induce in the complexes.

In this study, we report the syntheses and high-resolution ^1H NMR spectra of a series of cobalt(III) complexes with tetradentate or hexadentate polypyridyl ligands. The results of the ^1H NMR spectra reported in this work are compared to those of the spectra of analogous cobalt(III) complexes of amino polycarboxylate ligands. Crystal structures of five of the polypyridyl complexes in this study will be reported in a subsequent paper.[4]

In addition to the synthetic, spectroscopic, and structural investigations of interest to a coordination chemist, heavy-metal chelation by polypyridyl ligands is of potential use in biochemical studies. The ligand tpen (*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine) has recently been used as a heavy-metal chelator in studies measuring free cytosolic Ca^{2+} in Ehrlich and Yoshida ascites carcinomas.[5] Also, tpen has recently been used in work investigating the effect of iron-chelating agents on the toxicity of doxorubicin for MCF-7 human breast cancer cells.[6]

The ability of lipid-soluble tpen to cross artificial and natural membranes and preferentially chelate intracellular heavy metals makes it a useful tool for investigating the roles of heavy metals inside cells. High affinities for heavy metals and low affinities for Mg^{2+} and Ca^{2+} also contribute to tpen's value. Studies conclude that further modification of tpen's structure is needed to increase its ability to discriminate between beneficial and toxic heavy metals.[5] Therefore, studies of metal complexes of polypyridyl ligands related to tpen are of potential biochemical significance.

Some work with polypyridyl ligands has been reported. The ligand edampda (*N*,*N*′-bis(2-pyridylmethyl)ethylenediamine-*N*,*N*′-diacetic acid) was synthesized by Martell[7] by a method different from the one used here. Divalent metal ion affinities of edampda were measured.[7]

The ligands tpen and tpa (tris(2-pyridylmethyl)amine) were reported by Anderegg and Wenk, and the ligands' divalent metal ion affinities were measured.[8] Various divalent metal complexes of tpa have been isolated.[8b,9] A recent study investigated the basicity of the aromatic and aliphatic nitrogens of tpa using ^{15}N NMR.[10]

The ligands tpen, tppn (*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-propanediamine), and tptn (*N*,*N*,*N*′*N*′-tetrakis(2-pyridylmethyl)-1,3-propanediamine) and their iron(II) and cobalt(III) complexes were reported by Toftlund and Yde-Andersen.[11] Recently, a binuclear copper(I) complex of tpen was reported,[12] and fast atom bombardment (FAB) mass spectrometry and Mössbauer spectroscopy were used to study divalent metal complexes of tpen.[13]

The ligand *uns*-penp is novel; however, the symmetrical isomer, penp (*N*,*N*′-bis(2-pyridylmethyl)ethylenediamine) and numerous metal complexes have been reported.[14]

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Experimental Section

Compound Preparation. Optical isomers are identified either by (+) or (−), the sign of the longest wavelength CD band, or by the sign of the optical rotation at a specified wavelength, e.g., $(+)_{546}$.

All of the perchlorate salts of the cobalt(III) complexes included in this work were stable for routine synthesis and purification procedures. However, caution should be used because perchlorate salts of metal complexes with organic ligands are potentially explosive.[15]

***N,N,N',N'*-Tetrakis(2-pyridylmethyl)ethylenediamine (tpen).** This ligand was prepared by a method that was a modification of the methods of Anderegg[8a] and Toftlund.[11] Sodium hydroxide (10 M, 19.4 mL) was added slowly to a stirred and heated solution (70 °C) of 2-(chloromethyl)pyridine hydrochloride (Aldrich, 15.9 g, 0.097 mol) and ethylenediamine (1.6 mL, 0.024 mol) in water (85 mL) over a period of 1 h. The solution was cooled and extracted with chloroform. Some solid formed during cooling and was filtered out and dissolved in chloroform, and the solution was added to the extraction mixture. The chloroform layer was evaporated under pressure, and the residue was filtered out and washed with water to give a tan solid. Yield: 2.94 g (29%). 60-MHz NMR spectrum ($CDCl_3$, TMS_{int}): δ 2.75 (s, ethylene CH_2), 3.75 (s, pyridylmethyl CH_2), 6.95–7.7, 8.3–8.5 (m, pyridine H).

***N,N,N',N'*-Tetrakis(2-pyridylmethyl)-1,3-propanediamine (tptn)** was prepared in a manner analogous to that used for the tpen ligand using 1,3-propanediamine dihydrochloride. The chloroform layer from the extraction in the tptn synthesis was evaporated under pressure, and the residue was cooled and stored in an open flask in a fume hood overnight. The next day the sticky solid was filtered out and washed with water to give a tan solid. Yield: 1.70 g (16%). 60-MHz NMR spectrum ($CDCl_3$, TMS_{int}): δ 1.85 (broad s, ethylene CH_2), 2.6 t, ethylene CH_2), 3.8 (s, pyridylmethyl CH_2), 6.9–7.9, 8.3–8.7 (m, pyridine H).

***N,N,N',N'*-Tetrakis(2-pyridylmethyl)-1,2-propanediamine (tppn)** was prepared in a manner analogous to that used for the tpen ligand using *l*-1,2-propanediamine dihydrochloride, which was synthesized by using the method of Brennan.[16] The *l*-1,2-propanediamine was recrystallized seven times as the tartrate, and the specific rotation of the dihydrochloride was +4.0°, which agrees with the literature values.[17] Evaporation of the chloroform layer from the extraction in the tppn synthesis yielded a tan solid that was filtered out and washed with water. Yield: 4.30 g (41%). 60-MHz NMR spectrum ($CDCl_3$, TMS_{int}): δ 1.15 (d, CH_3), 2.4–3.3 (m, ethylene CH, ethylene CH_2), 3.8 (s, pyridylmethyl CH_2), 6.9–7.8, 8.45–8.7 (m, pyridine H).

(*N,N,N',N'*-Tetrakis(2-pyridylmethyl)ethylenediamine)cobalt(III) Triperchlorate, $[Co(tpen)](ClO_4)_3$. The ligand tpen (2.37 g, 5.6 mmol) in 95% ethanol (40 mL) was added with stirring to a solution of $CoCl_2 \cdot 6H_2O$ (1.33 g, 5.6 mmol) in water (40 mL). A catalytic amount of activated charcoal was added to the mixture, and a gas dispersion tube was used to bubble air through the mixture overnight. The next day, the solution was filtered to remove the activated charcoal, and 1.0 mL of 6 M $HClO_4$ was added to the solution to precipitate immediately yellow-orange $[Co(tpen)](ClO_4)_3$. The solid was washed with 95% ethanol and ether and air-dried. Yield: 1.62 g (37%).

The complex was recrystallized from hot water three times. A water solution of the recrystallized complex was then chromatographed on a 2.0 × 20 cm column of Dowex 1-X8 (200–400 mesh) anion-exchange resin in the Cl^- form. The eluted band was then rotary-evaporated to a volume of 0.5 mL and desalted by gel filtration using a column (2.0 × 40 cm) of G-10-120 Sephadex (Sigma). The solution was then rechromatographed on a 2.0 × 20 cm column of Dowex 1-X8 (200–400 mesh) anion-exchange resin in the ClO_4^- form and evaporated in an air stream to a solid. The orange solid was again recrystallized from hot water, washed with 95% ethanol and ether, and air-dried. Anal. Calcd for $[Co(tpen)](ClO_4)_3$: C, 39.94; H, 3.61; N, 10.75. Found: C, 39.76; H, 3.81; N, 10.73.

(*N,N,N',N'*-Tetrakis(2-pyridylmethyl)-1,3-propanediamine)cobalt(III) Triperchlorate–0.5-Water, $[Co(tptn)](ClO_4)_3 \cdot 0.5H_2O$. This complex was prepared in a manner analogous to that used for the preparation of the cobalt tpen complex. Anal. Calcd for $[Co(tptn)](ClO_4)_3 \cdot 0.5H_2O$: C, 40.29; H, 3.76; N, 10.44. Found: C, 40.34; H, 4.00; N, 10.13.

ΔΛΔ-$(-)_{589}$-(*N,N,N',N'*-Tetrakis(2-pyridylmethyl)-1,2-propanediamine)cobalt(III) Triperchlorate–Water, ΔΛΔ-(−)-$[Co(tppn)](ClO_4)_3 \cdot H_2O$. This complex was prepared in a manner analogous to that used for the preparation of the cobalt tpen complex. Anal. Calcd for ΔΛΔ-$(-)_{589}$-$[Co(tppn)](ClO_4)_3 \cdot H_2O$: C, 39.85; H, 3.72; N, 10.33. Found: C, 39.89; H, 4.35; N, 10.06.

(*N,N'*-Bis(2-pyridylmethyl)ethylenediamine-*N,N'*-diacetato)cobalt(III)–4.5-Water, $[Co(edampda)]Cl \cdot 4.5H_2O$. A solution of 2-(chloromethyl)pyridine hydrochloride (5 g, 0.030 mol) in water (20 mL) was added with stirring to a mixture of ethylenediaminediacetic acid (2.68 g, 0.015 mol, Aldrich), NaOH (3 mL, 0.03 mol, 10 M), and water (130 mL). After the mixture was stirred for 5 min, 6 mL of NaOH (0.06 mol, 10 M) was added over a period of 5 min, and the solution was stirred and heated (70 °C) for 1 h. A solution of $CoCl_2 \cdot 6H_2O$ (3.57 g, 0.015 mol) in water (20 mL) was added to the reaction mixture, which was then adjusted to a pH of 6 by the addition of concentrated HCl. A catalytic amount of activated charcoal was added, and air was bubbled through the reaction mixture overnight by using a gas dispersion tube. The next day, the solution was filtered to remove the activated charcoal and divided into 50-mL portions. Perchloric acid (5 mL, 6 M) and isopropyl alcohol (800 mL) were added to each portion with vigorous mixing. After 1 min, a pink precipitate formed, which was filtered out by suction.

The precipitate formed red needles when recrystallized three times from hot water. For further purification, the complex was chromatographed on a 3.5 × 30 cm column of SP-C25-120 Sephadex (Sigma) with 0.05 M HCl. One red band was observed, which was eluted and evaporated in a stream of air to a red solid. Yield: 7.1 g (92%). Anal. Calcd for $[Co(edampda)]Cl \cdot 4.5H_2O$: C, 40.65; H, 5.50; N, 10.53; Cl, 6.67. Found: C, 40.61; H, 4.64; N, 10.43; Cl, 7.16.

Tris(2-pyridylmethyl)amine perchlorate, tpa·*n*$HClO_4$, was prepared by a method that was a modification of the method of Anderegg and Wenk.[8a] A 4-mL portion of 2-(aminomethyl)pyridine (0.04 mol) was added to a solution of 2-(chloromethyl)pyridine hydrochloride (12.74 g, 0.08 mol) in water (20 mL). NaOH (15.5 mL, 0.16 mol, 10 M) was added during the following 1 h, and the solution was heated (70 °C) and stirred for another 30 min. The mixture was cooled, and perchloric acid (10 mL, 6 M) was added to precipitate the tan perchlorate salt of the ligand. The solid was filtered out and washed with ethanol and ether. No further purification of the ligand was attempted due to its possible explosive properties.[15] Yield: 13.9 g (52%). 60-MHz NMR spectrum (dmso-d_6, TMS_{int}): δ 4.4 (s, pyridylmethyl CH_2), 7.89–9.1 (m, pyridine H), 9.3 (s, aromatic N–H).

Chloro(tris(2-pyridylmethyl)amine)aquacobalt(III) Diperchlorate–3.5-Water, $[Co(tpa)(H_2O)Cl](ClO_4)_2 \cdot 3.5H_2O$. (a) Preparation of the Nitro Complexes. The above ligand (5.29 g) in water (20 mL) was slowly dropped into a solution of sodium hexanitrocobaltate(III) (3.09 g, 7.7 mmol) in water (20 mL). The mixture turned red-brown, and NO_2 gas was evolved. The solution was heated at 50 °C for 0.5 h and then cooled in an ice bath. Orange nitro complexes precipitated almost immediately. Yield: 3.58 g.

(b) $[Co(tpa)(H_2O)Cl](ClO_4)_2 \cdot 3.5H_2O$. A solution of 2.24 g of the nitro complexes from part a in 1000 mL of water was heated to 80 °C. Concentrated HCl (1 mL) was added, and heating was continued for 0.5 h. Perchloric acid (1.5 mL, 6 M) was added, and, after another 0.5 h of heating, the solution was rotary-evaporated to a purple solid. Yield: 1.28 g.

The complex was purified by eluting it on a 3.5 × 60 cm chromatography column of SP-C25-120 Sephadex (Sigma) with 0.05 M HCl. One purple band was observed, which was eluted and evaporated to a purple oil. The oil was dissolved in water, and the solution was eluted on a 2.0 × 20 cm column of Dowex 1-X8 (200–400 mesh) anion-exchange resin in the ClO_4^- form and evaporated in an air stream to a purple solid. Anal. Calcd for $[Co(tpa)(H_2O)Cl]ClO_4 \cdot 3.5H_2O$: C, 32.52; H, 4.09; N, 8.43. Found: C, 32.43; H, 3.78; N, 8.07.

Dichloro[(2-(bis(2-pyridylmethyl)amino)ethyl)ammonium]copper(II) Perchlorate–8.5-Water, [Cu(*uns*-Hpenp)Cl_2]$ClO_4 \cdot 8.5H_2O$. (a) Preparation of *N,N*-Bis(2-pyridylmethyl)ethylenediamine Hydrochloride, *uns*-penp·*n*HCl. *N*-Acetylethylenediamine (5 g, 0.05 mol) in water (10 mL) was added to a solution of 2-(chloromethyl)pyridine hydrochloride (16 g, 0.1 mol) in water (50 mL). Sodium hydroxide (19.6 mL, 10 M, 0.2 mol) was added slowly into this solution over a period of 1.5 h at 50 °C. The cooled reaction mixture was extracted with chloroform. The chloroform layer was evaporated under reduced pressure, and excess concentrated HCl (100 mL) was added to the residue of brown oil. This mixture was heated at reflux temperatures for 2 h to hydrolyze the acetyl group. The solution was cooled, and the hydrochloric acid was removed via rotary evaporation, yielding a viscous, brown oil.

(b) [Cu(*uns*-Hpenp)Cl_2]$ClO_4 \cdot 8.5H_2O$. A solution of the ligand (2.3 g) from part a in water (20 mL) was added to anhydrous copper(II) chloride (0.8 g) in water (20 mL). The mixture turned deep blue, and $NaClO_4$ (1.5 g) in water (10 mL) was added with stirring. Ethanol (95%, 50 mL) was added, and the reaction mixture was stored in a refrigerator overnight. The next day, blue, diamond-shaped crystals had formed in the beaker. A determination of the crystal structure was

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obtained.[4] This crystal structure determination shows the complex has an unbonded protonated ethylenediamine arm.

Confirmation of the ligand synthesis was obtained by removing *uns*-Hpenp from the copper complex. Copper was precipitated as CuS. The filtrate was made basic with NaOH and extracted into chloroform. Removal of the chloroform layer via rotary evaporation yielded a light brown oil. 60-MHz NMR spectrum ($CDCl_3$, TMS_{int}): δ 2.1 (broad s, NH), 2.8 (broad s, ethylene CH_2), 4.0 (s, pyridylmethyl CH_2), 7.1–8.0, 8.6–8.9 (m, pyridine H).

The copper complex was purified by gel filtration. A water solution of the complex was chromatographed on a 2.0 × 10 cm column of Dowex 1-X8 (200–400 mesh) anion-exchange resin in the Cl^- form and rotary-evaporated to a volume of 0.5 mL. This solution was then desalted by gel filtration using a column (2.0 × 40 cm) of G-10-120 Sephadex (Sigma). The solution was then rechromatographed on a 2.0 × 20 cm column of Dowex 1-X8 (200–400 mesh) anion-exchange resin in the ClO_4^- form and evaporated in a stream of air to a blue oil that solidified after 2 h in a fume hood. Anal. Calcd for [Cu(*uns*-Hpenp)Cl_2]ClO_4·8.5H_2O: C, 26.68; H, 5.76; N, 8.89. Found: C, 26.66; H, 3.81; N, 8.86.

Chloro(*N*,*N*-bis(2-pyridylmethyl)ethylenediamine)aquacobalt(III) Diperchlorate–Water, [Co(*uns*-penp)(H_2O)Cl](ClO_4)$_2$·H_2O. (a) Preparation of the Nitro Complexes. A solution of the hydrochloride of *uns*-penp (2.9 g) in water (20 mL) was added slowly to a solution of sodium hexanitrocobaltate(III) (3.0 g) in water (20 mL). The mixture turned red-brown, and NO_2 gas was evolved while the mixture was heated at 50 °C for 0.5 h. Sodium perchlorate (1.8 g) in water (10 mL) was added to the reaction mixture, which was then cooled in an ice bath. Orange nitro complexes precipitated almost immediately. Yield: 2.2 g.

(b) [Co(*uns*-penp)(H_2O)Cl](ClO_4)$_2$·H_2O. A solution of 1.0 g of the nitro complexes from part a in 50 mL of concentrated HCl was heated (80 °C) and stirred for 0.5 h. The solution was cooled and rotary-evaporated to a sticky purple solid.

The complex was purified by elution on a 3.5 × 60 cm chromatography column of SP-C25-120 Sephadex (Sigma) with 0.05 M HCl. Two bands formed on the column. The first band to elute was a dark purple minor component; a poorly resolved 300-MHz NMR spectrum indicated that this band was the dichloro complex. The second band was the magenta major component. This band was collected and evaporated in an air stream to a magenta oil. The oil was dissolved in water, and the solution was eluted on a 2.0 × 20 cm column of Dowex 1-X8 (200–400 mesh) anion-exchange resin in the ClO_4^- form and evaporated in an air stream to a magenta solid. Anal. Calcd for [Co(*uns*-penp)(H_2O)Cl](ClO_4)$_2$·H_2O: C, 29.42; H, 3.88; N, 9.80. Found: C, 29.49; H, 3.92; N, 9.38.

Partial Resolution of [Co(tpen)](ClO_4)$_3$. A sample of [Co(tpen)](ClO_4)$_3$ (5.05 g, 6.5 mmol) was converted to the chloride form by using a 2.0 × 20 cm column of Dowex 1-X8 (200–400 mesh) anion-exchange resin. The resulting aqueous solution of [Co(tpen)]Cl_3 was evaporated to a volume of 30 mL, heated, and added to a solution of 1.88 g (2.5 mmol) of K_3-(+)-[Co(*l*-cysu)$_3$] (cysu = cysteinesulfinato(2−)-*S*,*N*).[18] The solution was cooled in an ice bath, and a yellow precipitate of the less soluble diastereoisomer formed. This yellow precipitate was recrystallized five times from hot water and was converted to the perchlorate salt by using a 2.0 × 20 cm column of Dowex 1-X8 (200–400 mesh) anion-exchange resin. The solution was evaporated overnight in a fume hood; orange single crystals of (+)-[Co(tpen)](ClO_4)$_3$ formed.

Physical Measurements. Visible Spectra. Visible absorption spectra were obtained on a Hewlett-Packard Model 8540A diode-array spectrophotometer. All samples were prepared volumetrically as analytical standards, and molar absorptivities were calculated.

Circular Dichroism Spectra. The circular dichroism spectra were obtained on a Cary 61 optical rotary spectrophotometer. All samples were prepared volumetrically as analytical standards, and $\Delta\epsilon$ values were calculated.

Elemental Analyses. All of the elemental analyses were carried out by Galbraith Analytical Laboratories, Knoxville, TN. The [Co(*uns*-penp)(H_2O)Cl](ClO_4)$_2$·H_2O sample was dried in an oven at 60 °C for 6 h.

Nuclear Magnetic Resonance Spectroscopy. All 60-MHz NMR spectra were recorded on a Varian Anaspect EM360 nuclear magnetic resonance spectrometer with tetramethylsilane (TMS) as the internal standard.

All one-dimensional 300-MHz NMR spectra were recorded on a Bruker WH300 Fourier-transform nuclear magnetic resonance spectrometer. The solvent used for all samples was dimethyl-d_6 sulfoxide. The internal standard was tetramethylsilane (TMS). Spin-tickling of AB patterns caused by pyridyl protons required about 0.002 W of power.

All two-dimensional 300-MHz NMR spectra were recorded on a Bruker/IBM AF-300 Fourier-transform nuclear magnetic resonance spectrometer. The solvent used for all samples was dimethyl-d_6 sulfoxide. The internal standard was TMS. A program was used to suppress the water-of-crystallization peak to obtain the two-dimensional NMR spectra. Two-dimensional NMR spectra of [Co(edampda)]ClO_4 and [Co(*uns*-penp)(H_2O)Cl](ClO_4)$_2$ could not be measured due to the large water-of-crystallization peak in the NMR spectra of these compounds.

Table I. Visible Absorption Spectral Data for the Complexes Studied

complex	λ, nm	ϵ, L mol^{-1} cm^{-1}
[Co(edampda)]ClO_4	464	71
	356	69
[Co(tpen)](ClO_4)$_3$	468	283
[Co(tptn)](ClO_4)$_3$	464	110
[Co(tppn)](ClO_4)$_3$	470	300
[Co(tpa)(H_2O)Cl](ClO_4)$_2$	528	139
	383	161
[Co(*uns*-penp)(H_2O)Cl](ClO_4)$_2$	534	144
	374	150
[Cu(*uns*-Hpenp)Cl_2]ClO_4	~800	58

Results and Discussion

Visible Spectra. The visible absorption spectral data are listed in Table I. The low energy d → d transition (464 nm) of the edampda complex has a distinct shoulder that is characteristic of a trans(*O*)-coordinated complex.[19] The data for the tpen, tptn, and tppn complexes agree with previously published results.[11] The second d → d transition in the tpen, tptn, and tppn complexes is covered by the charge-transfer band. This overlap of bands is probably due to $\pi \rightarrow \pi^*$ transitions of the pyridine rings, which occur in the near-ultraviolet region. These transitions increase the intensity and bandwidth of the charge-transfer band. Similar obscuration of the second d → d transition has been observed in cobalt(III) complexes of bipyridine and phenanthroline.[20] The extinction coefficients of many of the complexes are higher than the usual range expected for vibronically allowed but symmetry-forbidden transitions. The increase in rotational strength of these transitions is probably due to either gain in electric dipole intensity with $\pi \rightarrow \pi^*$ transitions of similar symmetry or increase in strain in the chelate ring systems, increasing the intensity of the visible absorption bands.

Resolutions. Attempts to resolve the enantiomers of the [Co(edampda)]$^+$ cation have been unsuccessful. The resolving agents used were tartrate, dibenzoyl tartrate, bromocamphorsulfonate, [Co(edta)]$^-$, and [Cr(ox)$_2$(phen)]$^-$.[21] Because of the high solubility of most [Co(edampda)]$^+$ salts, either extensive evaporation or addition of large amounts of ethanol was required to isolate solids. Recrystallization was carried out by using ethanol/water mixtures. None of the solids obtained showed any optical activity. Similar resolution difficulties have been reported for various cobalt complexes of pyridyl-containing ligands.[22]

The resolving agent K_3-(+)-[Co(*l*-cysu)$_3$] has been successfully used to separate previously unresolvable enantiomers of trivalent cobalt complexes of pyridyl-containing ligands.[18] The use of this resolving agent with [Co(tpen)]$^{3+}$ produced a separation of enantiomers. The maximum $\Delta\epsilon$ values of +0.31, +2.78, and +0.83 L mol^{-1} cm^{-1} at 381, 450, and 500 nm, respectively, indicate the enantiomer was ΛΔΛ-[Co(tpen)](ClO_4)$_3$. These $\Delta\epsilon$ values for the tpen complex are of the same order of magnitude as the $\Delta\epsilon$ values of ΔΛΔ-(−)$_{589}$-[Co(tppn)](ClO_4)$_3$, which were measured in this study. The maximum $\Delta\epsilon$ values obtained in this study of the tppn complex are −0.17, −2.41, and −0.76 L mol^{-1} cm^{-1} at 381, 450, and 500 nm, respectively. The tppn complex in this study was synthesized via a chiral route from a resolved ligand and should be fully resolved. Unfortunately, the $\Delta\epsilon$ values of the tppn complex measured in this study are less than previously reported

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(19) (a) Matsuoka, N.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1868. (b) Yamatera, H. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 95.

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Table II. ^{1}H NMR Data for the Complexes Studied[a]

complex	protons	pattern	δ, ppm	Δ, ppm	J Hz
K[Co(edta)][b]	R	AB	3.91	0.12	18.4
	G	AB	3.74	0.34	15.8
	E	AB	3.60	0.36	9.8
[Co(edampda)]ClO_4	R	AB	3.76	0.45	18.1
	G	AB	4.53	0.36	15.4
	E	AB	3.73	0.38	9.4
[Co(tpen)]$(ClO_4)_3$	R	AB	5.20	0.44	19.7
	G	AB	4.50	0.28	16.6
	E	AB	3.97	0.31	9.8
[Co(tptn)]$(ClO_4)_3$	R	AB	5.09	0.66	19.8
	G	AB	4.71	0.18	16.9
$(-)_{589}$-[Co(tppn)]$(ClO_4)_3$	R_1	AB	5.05	0.98	20.3
	R_2	AB	5.19	0.56	20.4
	G_1	AB	4.52	0.31	16.4
	G_2	AB	4.47	0.38	16.5
[Co(tpa)(H_2O)Cl]$(ClO_4)_2$	P_1	singlet	5.27	0	
	P_2	AB	5.09	0.42	15.8
[Co(*uns*-penp)(H_2O)Cl]$(ClO_4)_2$	R	AB	4.85	0.41	16.7
trans-(*O*)-[Co(*uns*-edda)$(NH_3)_2$]Cl[c]	R	AB	4.26	0.51	16.4

[a] Δ is the spread between the average chemical shifts of the AB patterns. The spectra of K[Co(edta)] and [Co(*uns*-edda)$(NH_3)_2$]Cl were measured in D_2O. All of the other spectra were measured in dmso-d_6. [b] Reference 28. [c] Reference 30.

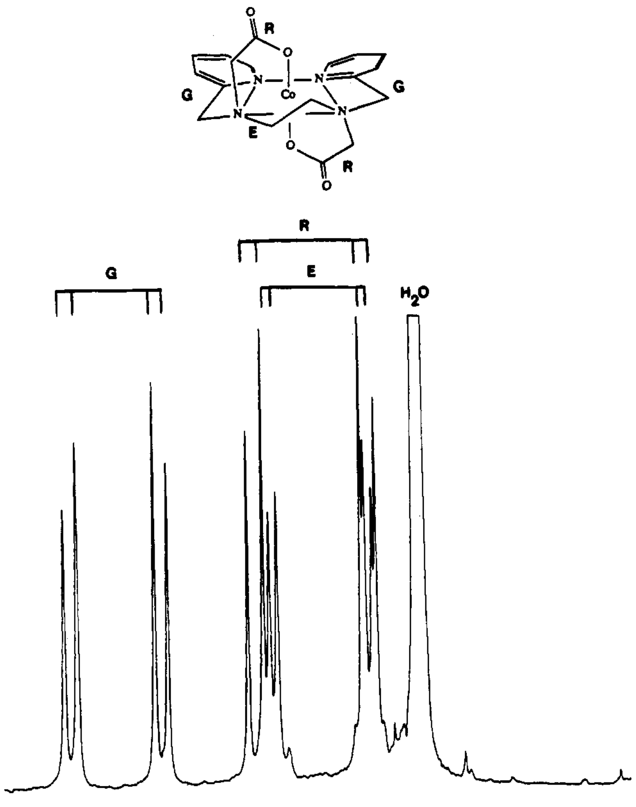

Figure 1. 300-MHz ^{1}H NMR spectrum of [Co(edampda)]ClO_4.

values.[11] This indicates possible partial resolution of the tppn and tpen complexes. Single crystals obtained from solutions of the resolved complexes were optically resolved for [Co(tppn)]$(ClO_4)_3$ ($P2_12_12_1$) but not for [Co(tpen)]$(ClO_4)_3$ ($P2_1/c$).

^{1}H NMR Spectra. The ^{1}H nuclear magnetic resonance spectral parameters of [Co(edampda)]ClO_4, [Co(tpen)]$(ClO_4)_3$, [Co(tptn)]$(ClO_4)_3$, [Co(tppn)]$(ClO_4)_3$, [Co(tpa)(H_2O)Cl]$(ClO_4)_2$, and [Co(*uns*-penp)(H_2O)Cl]$(ClO_4)_2$ are listed in Table II along with those of K[Co(edta)] and [Co(*uns*-edda)$(NH_3)_2$]Cl. The edta and *uns*-edda complexes are included since these complexes are acetate analogues of the pyridyl complexes. The ^{1}H NMR spectra were obtained by using a 300-MHz superconducting magnet, which provided excellent resolution. The AB patterns of the pyridyl ring protons are well resolved in all cases.

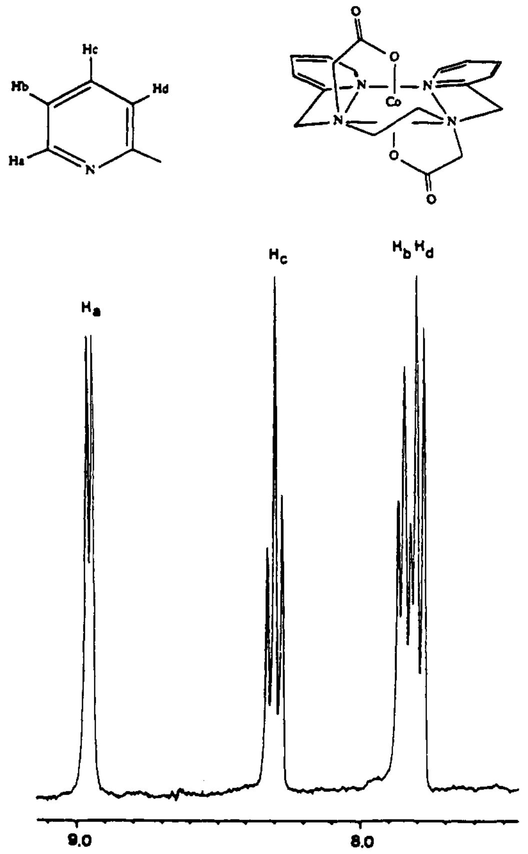

Figure 2. 300-MHz ^{1}H NMR spectrum of [Co(edampda)]ClO_4.

Figure 1 shows the ^{1}H NMR spectrum of the pyridyl and ethylenediamine hydrogens of [Co(edampda)]ClO_4, and Figure 2 shows the ^{1}H NMR spectrum of the pyridine hydrogens of [Co(edampda)]ClO_4. Both spectra are representative of the results obtained for the aliphatic and aromatic hydrogens of the cobalt complexes of both the hexadentate and tetradentate ligands. The edampda, tpen, and tptn complexes have C_2 symmetry with the C_2 axis bisecting the ethylenediamine, or propanediamine, ring and the central cobalt atom. This C_2 axis simplifies interpretation of the ^{1}H NMR spectra and produces similarities in the spectra of the complexes containing this symmetry element.

The ^{1}H NMR spectrum of [Co(edampda)]ClO_4 shown in Figures 1 and 2 contains two AB patterns centered at 3.76 and 4.53 ppm with coupling constants of 18.1 and 15.4 Hz, respectively. It is well documented that the methylene protons of trans-coordinated acetate arms produce an AB pattern with a coupling constant of about 18 Hz.[23] Therefore, the upfield AB pattern with a coupling constant of 18.1 Hz arises from the methylene hydrogens of the two symmetry-equivalent R (out of the plane of the ethylenediamine ring) acetate arms, and the downfield AB pattern with a coupling constant of 15.4 Hz arises from the methylene hydrogens of the two symmetry-equivalent G (in the plane of the ethylenediamine ring) pyridyl arms.

The AB pattern centered at 3.73 ppm with a coupling constant of 9.4 Hz arises from the two symmetry-equivalent axial hydrogens of the ethylenediamine ring and the two symmetry-equivalent equatorial hydrogens of the ethylenediamine ring.

Four types of pyridine hydrogens appear in the range 7.7–9.0 ppm. These four types of hydrogens represent two symmetry-equivalent sets of four G ring pyridine hydrogens. Two doublets and two triplets are formed by the splitting of each pyridine hydrogen by its adjacent hydrogen(s). The splitting scheme is shown in Figure 2. H_a is split into a doublet by H_b ($J = 5$ Hz), and H_d is split into a doublet by H_c ($J = 7$ Hz). H_a is assigned

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[23] (a) Sudmeier, J. L.; Senzel, A. J.; Blackmer, G. L. *Inorg. Chem.* **1971**, *10*, 90. (b) Blackmer, G. L.; Sudmeier, J. L. *Inorg. Chem.* **1971**, *10*, 2019.

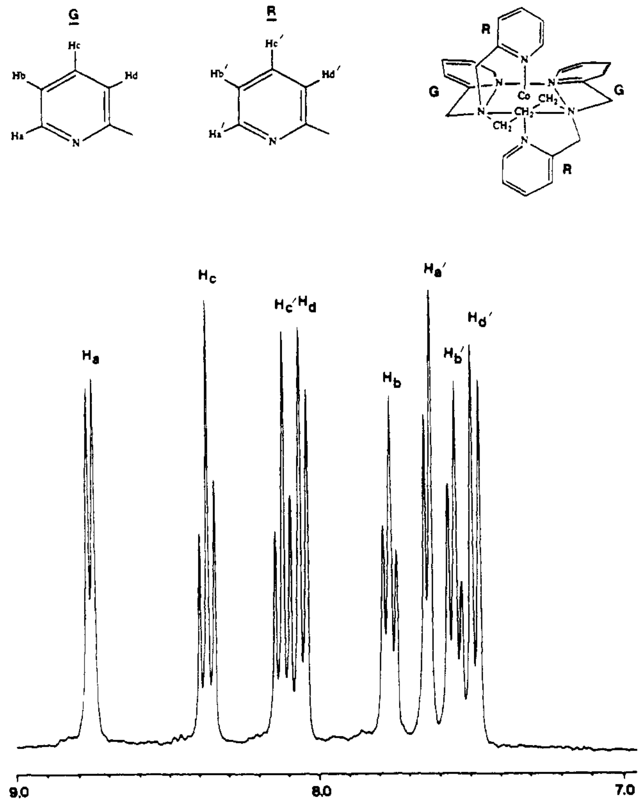

Figure 3. 300-MHz ^{1}H NMR spectrum of [Co(tptn)](ClO$_4$)$_3$. (Hydrogen atom assignments apply to both [Co(tptn)]$^{3+}$ and [Co(tpen)]$^{3+}$.)

to the downfield doublet, and H_d is assigned to the upfield doublet. The assignments of H_a and H_d are based on induction, increased shielding in the space between the two pyridine rings, and previous assignments of pyridine hydrogens in [(NH$_3$)$_5$Ru(py)]$^{2+}$ and [(NH$_3$)$_5$Co(py)]$^{3+}$.[12,24] H_b is split by both H_a (J = 7 Hz) and H_c (J = 7 Hz) to form a triplet, and H_c is split by both H_b (J = 7 Hz) and H_d (J = 7 Hz) to form a triplet. H_c is assigned to the downfield triplet, and H_b is assigned to the upfield triplet. The assignments of H_c and H_b are based on greater stabilization of electron withdrawal in a para position, compared to a meta position, and previous assignments of pyridine hydrogens in [(NH$_3$)$_5$Ru(py)]$^{2+}$ and [(NH$_3$)$_5$Co(py)]$^{3+}$.[12,24]

The ^{1}H NMR spectrum of [Co(tpen)](ClO$_4$)$_3$ (C_2 symmetry) shows three AB patterns at 5.20, 4.50, and 3.97 ppm with coupling constants of 19.7, 16.6, and 9.8 Hz, respectively. These AB patterns are assigned to the R, G, and E rings, respectively. The assignments of these AB patterns are based on the considerations used to assign the AB patterns in [Co(edampda)]$^+$.

The aromatic region of [Co(tpen)](ClO$_4$)$_3$ shows eight types of pyridine hydrogens in the range of 7.1–9.0 ppm. These eight types of hydrogens represent two symmetry-equivalent sets of four G ring pyridine protons and two symmetry-equivalent sets of four R ring pyridine protons. Four doublets and four triplets appear, agreeing with the splitting scheme described for [Co(edampda)]$^+$.

This sequence of doublets and triplets in the aromatic region of [Co(tpen)](ClO$_4$)$_3$ is *identical* with the sequence of doublets and triplets in the aromatic region of [Co(tptn)](ClO$_4$)$_3$. The pyridine hydrogens in both complexes represent two isolated, well-resolved spin systems; therefore, two-dimensional ^{1}H NMR spectra[25] of [Co(tptn)](ClO$_4$)$_3$ were used to assign each pair of symmetry-equivalent pyridine hydrogen atoms in [Co(tpen)](ClO$_4$)$_3$ to its unique doublet or triplet. The NMR assignments for these eight types of hydrogen atoms are shown in Figure 3. The reasoning for these assignments will be presented in the section discussing the ^{1}H NMR spectra of [Co(tptn)](ClO$_4$)$_3$.

The ^{1}H NMR spectrum of [Co(tptn)](ClO$_4$)$_3$ (C_2 symmetry) shows two AB patterns at 5.09 (J = 19.8 Hz) and 4.71 ppm (J = 16.9 Hz), which are assigned to the R and G rings, respectively. The existence of two AB patterns, instead of four, confirms the existence of a C_2 symmetry axis. The propanediamine ring must have a conformation identical with that of the propanediamine ring of [Co(trdta)]$^-$ (trdta = trimethylenediaminetetraacetate).[26] The central cobalt(III) ion, the two aliphatic nitrogen atoms, and the central carbon of the propanediamine backbone lie in the same plane. One remaining carbon of the propanediamine backbone is above the plane, and the other remaining carbon of the propanediamine backbone is below the plane. The hydrogens of these two out-of-plane carbon atoms are symmetrically equivalent and form a poorly resolved AB pattern (dmso interferes) centered at 2.81 ppm (J = 11.6 Hz). Spin-tickling experiments were used to confirm all of the AB patterns in the [Co(tptn)](ClO$_4$)$_3$ ^{1}H NMR spectrum.

The central carbon of the propanediamine backbone produces a broad singlet at 2.8 ppm, and the pyridine hydrogens of [Co(tptn)](ClO$_4$)$_3$ produce the expected eight types of pyridine hydrogens (four doublets, four triplets) in the range 7.4–8.9 ppm.

The pyridine hydrogens in [Co(tptn)](ClO$_4$)$_3$ represent two isolated, well-resolved spin systems; therefore, two-dimensional ^{1}H NMR spectroscopy[25] was used to assign each pair of symmetry-equivalent pyridine hydrogen atoms in [Co(tptn)](ClO$_4$)$_3$ to its unique doublet or triplet. The NMR assignments for these eight types of hydrogen atoms are shown in Figure 3.

The two-dimensional (2D) NMR spectrum of [Co(tptn)](ClO$_4$)$_3$ was measured twice. The first spectrum showed poor resolution and first-order coupling; the second spectrum showed good resolution and both first- and second-order coupling. Both spectra yielded the same sets of hydrogen atom assignments.

The lowest field resonance in Figure 3 is assigned to H_a (G pyridine ring) by comparison to the [Co(edampda)]$^+$ NMR spectrum. (This resonance could *not* be $H_{a'}$ (R pyridine ring); $H_{a'}$ is directed toward the π-electron cloud of a G pyridine ring and is shifted upfield.) The 2D NMR spectrum shows that doublet H_a is a member of an aromatic ring system that also contains two triplets and another doublet. The hydrogen atom assignments of these two doublets and two triplets, shown in Figure 3, are based on the considerations used to assign the pyridine hydrogen atoms in the [Co(edampda)]$^+$ NMR spectrum.

The 2D NMR spectrum shows that the remaining two doublets and two triplets are all members of another aromatic ring system. These resonances are all assigned to R pyridine hydrogens (Figure 3). The assignments of $H_{b'}$ and $H_{c'}$ to the upfield and downfield triplets, respectively, are based on the considerations used to assign analogous pyridine hydrogen atoms in the [Co(edampda)]$^+$ NMR spectrum. Unfortunately, $H_{a'}$ in these complexes is directed toward the π-electron cloud of a G pyridine ring and is shifted upfield; this makes assignment of $H_{a'}$ and $H_{d'}$ difficult. $H_{a'}$ is assigned to the downfield doublet, and $H_{d'}$ is assigned to the upfield doublet for three reasons. First, the poorly resolved 2D NMR spectrum that showed only first-order coupling indicated these assignments. Second, the upfield peak of doublet $H_{a'}$ is larger than the downfield peak of doublet $H_{a'}$, and the downfield peak of triplet $H_{b'}$ is larger than the upfield peak of triplet $H_{b'}$. These symmetry distortions indicate that this doublet–triplet pair is coupled. The triplet can be logically assigned to $H_{b'}$, as was previously explained; therefore, the doublet that is related to $H_{b'}$ by symmetry distortions must be $H_{a'}$. Third, the [Co(edampda)]$^+$ spectrum indicated that J_{ab} was slightly smaller than J_{dc} (5 vs 7 Hz). This indicates that the doublet with the smaller coupling constant ($H_{a'}$) should be coupled to the triplet that has the smaller total (left peak to right peak) coupling constant ($H_{b'}$). The assignments indicated in Figure 3 agree with these predictions.

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(24) (a) Lavallee, D. K.; Baughman, M. D.; Phillips, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 718. (b) Lavallee, D. K.; Fleischer, E. B. *J. Am. Chem. Soc.* **1972**, *94*, 2583. (c) Hoq, M. F. M.S. Thesis, University of Pittsburgh, 1983.

(25) (a) Nagayama, K.; Kumar, A.; Wütrich, K.; Ernst, R. R. *J. Magn. Reson.* **1980**, *40*, 321. (b) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.

(26) Ogino, H.; Takahashi, M.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 424.

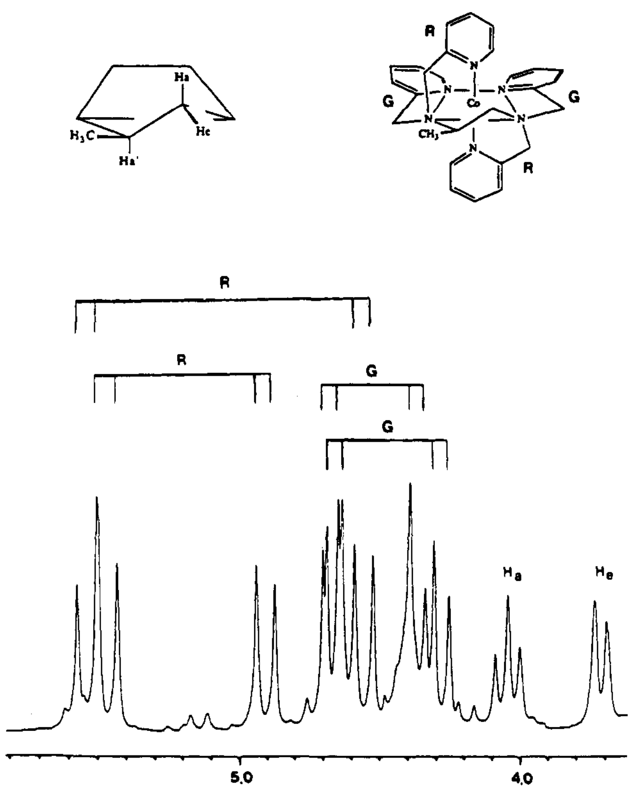

Figure 4. 300-MHz ^{1}H NMR spectrum of $[Co(tppn)](ClO_4)_3$.

The ^{1}H NMR spectrum of $(-)_{589}$-$[Co(tppn)](ClO_4)_3$ (Figure 4) is more complicated than the other spectra since this complex contains no symmetry elements. Four AB patterns are listed in Table II. The coupling constants of 20.3, 20.4, 16.4, and 16.5 Hz correspond to two R pyridyl arms and two G pyridyl arms, respectively. With reference to the labeling shown in Figure 4, axial proton H_a of the 1,2-propanediamine backbone is split by geminal proton H_e (J_{ae} = 13 Hz) and then by vicinal proton $H_{a'}$ ($J_{aa'}$ = 13 Hz) to form a triplet centered at 4.0 ppm. Equatorial proton H_e is split by geminal proton H_a (J_{ea} = 12 Hz) into a doublet centered at 3.7 ppm. Coupling between H_e and vicinal $H_{a'}$ is too small to be observed in this ^{1}H NMR spectrum. Previously observed values for $J_{ea'}$ are about 4 Hz.[27] Axial proton $H_{a'}$ should form a multiplet from coupling with the geminal methyl group and vicinal proton H_a; however, the multiplet appears overlapped by the AB patterns at about 4.4 ppm. The methyl group is split by $H_{a'}$ (J = 6 Hz) into a doublet centered at 1.5 ppm. These coupling constants and spectral patterns are consistent with previously reported values for 1,2-propanediamine backbones.[27a] Spin-tickling experiments were used to confirm all of the AB patterns in the $(-)_{589}$-$[Co(tppn)](ClO_4)_3$ spectrum.

The ^{1}H NMR aromatic region of the tppn complex clearly shows the lack of symmetry in this complex. The triplets and doublets formed by the pyridine hydrogens are no longer clearly resolved in all cases, but the pyridine pattern from 7.0 to 9.0 ppm integrates to the expected 16 hydrogens.

The upfield and downfield peaks in the AB patterns of the $[Co(edampda)]^+$, $[Co(tpen)]^{3+}$, $[Co(tptn)]^{3+}$, and $[Co(tppn)]^{3+}$ complexes can be assigned to different pairs of symmetry-equivalent methylene hydrogen atoms by comparison to similar assignments in cobalt(III) complexes of amino polycarboxylate ligands. The pairs of symmetry-equivalent methylene hydrogen atoms are shown in Figure 5.

First, the downfield peaks of the E ring AB patterns are assigned to the axial hydrogens, and the upfield peaks of the E ring AB patterns are assigned to the equatorial hydrogens. These E ring assignments are based on the observation that equatorial E ring hydrogens appear upfield of axial E ring hydrogens in cobalt(III) amino polycarboxylate complexes.[27b,28] This assignment is also supported by the E ring assignments in the $[Co(tppn)]^{3+}$ NMR spectrum.

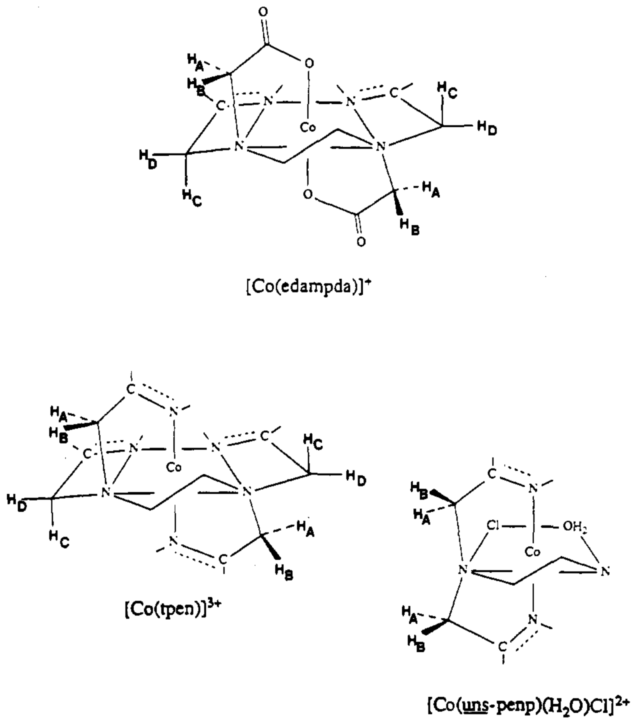

Figure 5. Designations for the hydrogen atoms of pyridyl and glycinate chelate arms.

Second, the upfield peaks of the R pyridyl and R glycinate AB patterns are assigned to H_A (Figure 5), and the downfield peaks of the R pyridyl and R glycinate AB patterns are assigned to H_B (Figure 5). These pyridyl and glycinate assignments are based on NMR assignments of analogous hydrogens in $[Co(edta)]^-$. The $[Co(edta)]^-$ assignments were confirmed by stereospecific deuteriations.[23a,29]

Finally, the upfield and downfield portions of the G pyridyl AB patterns cannot be assigned with certainty. The analogous NMR assignments in $[Co(edta)]^{-}$[23a,29] indicate that the upfield peaks are due to H_D (Figure 5) and that the downfield peaks are due to H_C (Figure 5). However, H_C is directed toward the π-electron cloud of a R pyridine ring; this will shift H_C upfield. Due to this effect, assignments of H_C and H_D cannot be made with certainty.

The ^{1}H NMR spectrum of $[Co(tpa)(H_2O)Cl](ClO_4)_2$ contains an AB pattern centered at 5.09 ppm with a coupling constant of 15.8 Hz and an overlapping singlet at 5.27 ppm. The AB pattern integrates to four hydrogens, and the singlet integrates to two hydrogens. Since this complex contains a mirror plane of symmetry including the cobalt(III) ion, the aliphatic nitrogen, the chloride ion, and the water ligand, the AB pattern is assigned to the methylene hydrogens of the two out-of-mirror-plane pyridyl arms (P_2), and the singlet is assigned to the methylene hydrogens of the pyridyl arm in the mirror plane (P_1). The corrdinated water molecule appears as a singlet at 7.3 ppm (solvent dmso-d_6) overlapping a doublet from the P_1 pyridine ring. The pyridine pattern from 7.3 to 9.2 ppm clearly shows two symmetry-equivalent pyridine rings (two doublets and two triplets; integration of eight hydrogens) and a unique pyridine ring (two doublets and two triplets, all with half of the previous intensity; integration of four hydrogens). This NMR spectrum was obtained within minutes of preparing the sample. The NMR spectrum of a sample that was prepared 2–3 days earlier was altered compared to a

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(27) (a) Maricondi, C. W.; Maricondi, C. *Inorg. Chem.* **1974**, *13*, 1110. (b) Rohly, K. E.; Douglas, B. E.; Maricondi, C. *Inorg. Chem.* **1986**, *25*, 4119.

(28) Marcondi, C.; Utsuno, S.; Radanović, D. J.; Trifunović, S. R.; Abola, J. E.; Douglas, B. *Inorg. Chim. Acta* **1988**, *142*, 135.

(29) (a) Sudmeier, J. L.; Occupati, G. *Inorg. Chem.* **1968**, *7*, 2524. (b) Terrill, J. B.; Reilley, C. N. *Inorg. Chem.* **1966**, *5*, 1988.

spectrum of a freshly prepared sample. In this altered spectrum, the symmetry of the pyridine pattern was broken by the appearance of additional overlapping doublets and triplets. An additional AB pattern also appeared in the altered spectrum. These alterations indicate aquation of a pyridyl arm occurs within 2–3 days.

The ^{1}H NMR spectrum of [Co(*uns*-penp)(H_2O)Cl](ClO_4)$_2$ contains an AB pattern (integration of four hydrogens) centered at 4.85 ppm with a coupling constant of 16.7 Hz. The appearance of one AB pattern indicates the isolated isomer has trans-coordinated pyridyl arms that would be equivalent via a mirror plane containing the cobalt(III) ion, the two aliphatic nitrogens, the chloride ion, and the coordinated water molecule. The coupling constant of 16.7 Hz for the R pyridyl rings originating from a common nitrogen in the *uns*-penp complex matches the coupling constant for the R acetate rings originating from a common nitrogen in *trans*(*O*)-[Co(*uns*-edda)(NH_3)$_2$]Cl.[30] The downfield peaks of the AB pattern are assigned to H_A (Figure 5), and the upfield peaks of the AB pattern are assigned to H_B (Figure 5). H_B is shifted upfield, relative to H_A, because it is shielded by the magnetic anisotropy of the C–N bond of the ethylenediamine backbone.[31]

The NH_2 hydrogens in [Co(*uns*-penp)(H_2O)Cl](ClO_4)$_2$ appear as a broad singlet at 5.6 ppm, and the ethylenediamine methylene hydrogens appear as broad singlets at 1.8 and 3.1 ppm. The broad singlet at 3.1 ppm is assigned to the methylene group adjacent to the tertiary nitrogen, and the broad singlet at 1.8 ppm is assigned to the methylene group adjacent to the primary nitrogen. These ethylenediamine methylene assignments are based on similar assignments in [Co(*uns*-edda)(NH_3)$_2$]Cl.[30] The coordinated water molecule appears as a singlet, integrating to two hydrogens, at 6.8 ppm (solvent dmso-d_6). The two symmetry-equivalent pyridine rings form the expected two doublets and two triplets between 7.7 and 9.2 ppm.

Overall, the AB patterns of the cobalt pyridyl complexes in this study appear slightly downfield (δ 4.4–5.3, solvent dmso-d_6) of the region where the AB patterns of the cobalt amino polycarboxylate complexes generally appear (δ 3.6–4.2, solvent D_2O). This downfield region of pyridyl AB patterns necessitated the use of dmso-d_6 as the solvent of choice for the NMR spectra. If D_2O was used as the solvent for the NMR spectra, the large water-of-crystallization peak overlapped sections of the pyridyl AB patterns. This downfield shift of pyridyl AB patterns, compared to glycinate AB patterns, is expected due to the proximity of the pyridyl CH_2 group to the aromatic ring current of the pyridine ring.

In general, the coupling constants for the R and G pyridyl rings of the cobalt pyridyl complexes are reasonably consistent with the well-established coupling constants of the analogous glycinate rings of the amino polycarboxylate complexes. All previously reported results for glycinate arms show coupling constants of 18 Hz for R glycinate rings and 16 Hz for G glycinate rings.[23] For comparison, the coupling constants in the pyridyl arms in this study are approximately 20 Hz for R pyridyl rings and 16 Hz for G pyridyl rings.

These glycinate and pyridyl coupling constants arise from withdrawal of electrons from the antisymmetric bonding orbital of the CH_2 group by the π-electron system of either the carbonyl or pyridyl group, respectively. The molecular orbital theory of geminal coupling predicts the maximum coupling occurs when the H–H internuclear axis is perpendicular to the nodal plane of the π system. Maximum coupling in a complex should then occur for the more planar and less strained chelate arm.

The coupling constant for the G pyridyl arms of the edampda complex (15.4 Hz) is slightly less than the coupling constants of the G pyridyl arms in the tpen, tptn, and tppn complexes (average 16.6 Hz). Ring angle sums from crystallographic data indicate the total degree of strain in the G pyridyl edampda arms is approximately equal to the total degree of strain in the G pyridyl tpen and tppn arms.[4] Therefore, the slightly lowered coupling constant of the edampda complex G pyridyl arm is not due to an increase in strain in these arms but to a slightly different bonding geometry in the cobalt octahedron due to the presence of two acetate arms. Indeed, crystallographic data show that the edampda ligand strains and distorts the octahedral angles in a cobalt complex in a fashion different from that of the tpen and tppn ligands.

Comparison of the magnitude of a pyridyl coupling constant to the magnitude of a glycinate coupling constant to compare the degrees of strain in these different chelate rings is not valid. The hybridizations of the ligating pyridine nitrogen and ligating acetate oxygen are different, producing different chelate arm geometries. In addition, the pyridine ring induces planarity in part of the pyridyl arm; this planarity does not exist in the glycinate arm. These differing chelate arm geometries, in addition to the differing electronegativities of the carbonyl and pyridine groups, create coupling constant differences. The best method to compare strain in chemically different chelate rings is X-ray crystallography.

To summarize, the magnitudes of the coupling constants of the AB patterns of methylene hydrogens of polypyridyl complexes can be used readily to assign AB patterns to either R or G chelate arms in polypyridyl cobalt complexes. In addition, the ^{1}H NMR data in this study can be used in the identification and analysis of other polypyridyl cobalt complexes via ^{1}H NMR spectroscopy.

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Registry No. tpen, 16858-02-9; tptn, 80384-94-7; tppn, 80384-93-6; tpa·*n*$HClO_4$, 115482-73-0; *uns*-penp·*n*HCl, 115482-74-1; [Co(edampda)]ClO_4, 115463-80-4; [Co(tpen)](ClO_4)$_3$, 80390-04-1; [Co(tptn)](ClO_4)$_3$, 80390-06-3; $\Delta\Lambda\Delta$-(−)$_{589}$-[Co(tppn)](ClO_4)$_3$, 80390-08-5; [Co(tpa)(H_2O)Cl](ClO_4)$_2$, 115512-30-6; [Co(*uns*-penp)(H_2O)Cl](ClO_4)$_3$, 115512-32-8; [Cu(*uns*-Hpenp)Cl_2]ClO_4, 115512-34-0; K_3-(+)-[Co(*l*-cysu)$_3$], 41553-06-4; 2-(chloromethyl)pyridine hydrochloride, 6959-47-3; ethylenediamine, 107-15-3; 1,3-propanediamine dihydrochloride, 10517-44-9; *l*-1,2-propanediamine dihydrochloride, 19777-67-4; ethylenediaminediacetic acid, 5657-17-0; 2-(aminomethyl)pyridine, 3731-51-9; sodium hexanitrocobaltate(III), 13600-98-1; *N*-acetylethylenediamine, 1001-53-2.

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