

Pyrazole Ligation to Cobalt(III) Centers: Syntheses, Structures, and Properties of Cobalt(III) Complexes of *N,N'*-Bis[2-(1-pyrazolyl)ethyl]pyridine-2,6-dicarboxamide

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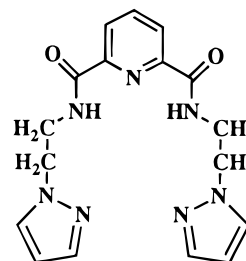
Three cobalt(III) complexes of the ligand PyPz_2PH_2 (**1**, $\text{PyPz}_2\text{PH}_2 = N,N'$ -bis[2-(1-pyrazolyl)ethyl]pyridine-2,6-dicarboxamide; Hs are the dissociable amide Hs), a ligand containing two peptide groups, one pyridine and two pyrazole rings, have been synthesized. They are $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]\text{X}$ ($\text{X} = \text{NO}_3^-$, **2a**; $(\text{H}_3\text{O})(\text{PF}_6)_2^-$, **2b**), $[\text{Co}(\text{PyPz}_2\text{P})(\text{OH})]$ (**3**), and $\text{X}[\text{Co}(\text{PyPz}_2\text{P})_2]$ ($\text{X} = \text{Na}^+$, **4a**; $0.5[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, **4b**). Complex **2b** crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.842(2)$ Å, $b = 11.920(3)$ Å, $c = 12.755(2)$ Å, $\alpha = 111.21(2)^\circ$, $\beta = 103.866(13)^\circ$, $\gamma = 106.992(13)^\circ$, $V = 1479.9(5)$ Å³, and $Z = 2$. The structure of complex **3** has been refined to $R = 6.06\%$ on the basis of 5417 $I > 2\sigma(I)$ data. Complex **4b** crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.471(3)$ Å, $b = 14.070(3)$ Å, $c = 14.171(5)$ Å, $\alpha = 71.58(2)^\circ$, $\beta = 68.08(2)^\circ$, $\gamma = 71.74(2)^\circ$, $V = 2134.0(10)$ Å³, and $Z = 2$. The structure of complex **4b** has been refined to $R = 5.86\%$ on the basis of 6679 $I > 2\sigma(I)$ reflections. In complexes **2a,b** and **3**, the doubly deprotonated $\text{PyPz}_2\text{P}^{2-}$ ligand binds one cobalt(III) center in a pentadentate fashion with five nitrogens of the two deprotonated amido nitrogens, two 2-pyrazole nitrogens, and one pyridine nitrogen. The octahedral coordination is completed by either a water molecule (complexes **2a** and **2b**) or a hydroxo group (complex **3**) at the sixth site. Complex **2b** is the first example of a structurally characterized cobalt(III) complex in which cobalt is bonded to 2-pyrazole nitrogens. In complexes **4a** and **4b**, two $\text{PyPz}_2\text{P}^{2-}$ ligands are bonded to one cobalt(III) center to form a pseudooctahedral bis complex with two pyridine nitrogens and four deprotonated amido nitrogens serving as the donors. Addition of base to the aqua complex **2a** (or **2b**) affords the hydroxo complex **3**. This transformation is reversible, and the pK_a of the coordinated water is 7. Addition of 1 equiv of $\text{Na}_2\text{PyPz}_2\text{P}$, the disodium salt of PyPz_2PH_2 , to $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]^+$ in methanol followed by warming results in quantitative formation of $[\text{Co}(\text{PyPz}_2\text{P})_2]$. Large crystal field stabilization from the four coordinated amido nitrogens makes $[\text{Co}(\text{PyPz}_2\text{P})_2]^-$ thermodynamically more stable than $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]^+$.

Introduction

Pyrazoles have been extensively used as N-donor ligands to metals.¹ Their use in bioinorganic chemistry is prompted by the fact that pyrazoles are potential imidazole mimics and hence can serve in the development of ligand systems that resemble active sites of metalloenzymes.² During the past 20 years, numerous complexes in which transition metal ions in different oxidation states are bonded to 2-pyrazole nitrogen(s) have been isolated and structurally characterized. A close scrutiny of this literature reveals that several Co(II) complexes with ligated 2-pyrazoles have been reported and most of these complexes have been characterized by X-ray crystallography.^{1,3} Quite in contrast, only a few cases are known in which coordination of

a 2-pyrazole nitrogen to Co(III) centers has been implicated, and surprisingly, none of these complexes has been characterized by crystallographic techniques.⁴ Clearly, the utility of the 2-pyrazole nitrogen as a donor to a Co(III) center is not well-documented, and structural parameters for such species are missing.

In this report, we describe the syntheses and properties of three Co(III) complexes of a potentially pentadentate ligand PyPz_2PH_2 (**1**, $\text{PyPz}_2\text{PH}_2 = N,N'$ -bis[2-(1-pyrazolyl)ethyl]pyridine-2,6-dicarboxamide; Hs are the dissociable amide Hs). PyPz_2PH_2 employs the pyridine nitrogen, two deprotonated amido nitrogens, and two 2-pyrazole nitrogens to bind copper in $[\text{Cu}(\text{PyPz}_2\text{P})]$.⁵ The Co(III) complexes of PyPz_2PH_2 , namely,



PyPz_2PH_2 (**1**)
 $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]\text{X}$ ($\text{X} = \text{NO}_3^-$, **2a**; $(\text{H}_3\text{O})(\text{PF}_6)_2^-$, **2b**),

- (4) (a) Schubert, D. M.; Knobler, C. B.; Trofimenko, S.; Hawthorne, M. F. *Inorg. Chem.* **1990**, 29, 2364. (b) Johnson, C. R.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1984**, 23, 2754.
 (5) Chavez, F. A.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chim. Acta*, in press.

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- (1) (a) Trofimenko, S. *Chem. Rev.* **1993**, 93, 943. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, 34, 115. (c) Trofimenko, S. *Chem. Rev.* **1972**, 72, 497.
 (2) (a) Sorrell, T. N. *Tetrahedron* **1989**, 45, 3. (b) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, 35, 219. (c) *Copper Coordination Chemistry; Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983.
 (3) Recent examples include: (a) Driessen, W. L.; Wiesmeijer, W. G. R.; Schipper-Zablotskaja, M.; De Graaff, R. A. G.; Reedijk, J. *Inorg. Chim. Acta* **1989**, 162, 233. (b) Haanstra, W. G.; Driessen, W. L.; Reedijk, J.; Frohlich, R. Krebs, B. *Inorg. Chim. Acta* **1991**, 185, 175. (c) Dowling, C.; Murphy, V. J.; Parkin, G. *Inorg. Chem.* **1996**, 35, 2415. (d) van Berkel, P. M.; Driessen, W. L.; Hamalainen, R.; Reedijk, J.; Turpeinen, U. *Inorg. Chem.* **1994**, 33, 5920. (e) Driessen, W. L.; de Graaff, R. A. G.; Parlevliet, F. J.; Reedijk, P. J.; de Vos, R. M. *Inorg. Chim. Acta* **1994**, 216, 43.

[Co(Py₃Pz₂P)(OH)] (**3**), and X[Co(PyPz₂P)₂] (X = Na⁺, **4a**; 0.5-[Co(H₂O)₆]²⁺, **4b**), however, demonstrate that, in addition to the pentadentate mode of binding, PyPz₂PH₂ can bind Co(III) in a tridentate fashion in which the two 2-pyrazole nitrogens are not ligated to the metal center. Thus, in complexes, **2a,b** and **3**, the doubly deprotonated PyPz₂P²⁻ ligand binds one cobalt(III) center in a pentadentate fashion with the nitrogens of two deprotonated amido groups, one pyridine, and two 2-pyrazole rings, while in complexes **4a,b**, two PyPz₂P²⁻ ligands are bonded to one cobalt(III) center to form a pseudooctahedral anionic complex with two pyridine nitrogens and four deprotonated amido nitrogens serving as donors. The reactivities of these Co(III) complexes indicate that the species with the tridentate PyPz₂P²⁻ ligand (with two 2-pyrazole nitrogens not coordinated) is thermodynamically more stable. Complex **2b** is the first example of a Co(III) complex with 2-pyrazole nitrogens as donors for which the molecular structure is known.

Experimental Section

Materials. Ammonium hexafluorophosphate, fluoroboric acid (48 wt %) and tetramethylammonium hydroxide pentahydrate were procured from Aldrich Chemical Co. and used without further purification. Cobalt acetate tetrahydrate and cobalt nitrate hexahydrate were obtained from Alfa Products. Hydrogen peroxide (30%) and sodium nitrate were purchased from Fisher Scientific Co. The ligand PyPz₂PH₂ was synthesized by following the published procedure.⁵ The solvents were dried and distilled before use. Satisfactory elemental analyses were obtained for all of the metal complexes.

Preparation of Compounds. [Co(PyPz₂P)(H₂O)]NO₃ (**2a**). To a solution of 1.00 g (2.83 mmol) of **1** in 30 mL of methanol was added dropwise a solution of 705 mg (2.83 mmol) of cobalt acetate tetrahydrate in 20 mL of water. After 5 min of stirring, 3.0 mL of 30% H₂O₂ was added followed by 226 mg (5.66 mmol) of NaOH in 10 mL of water. The deep brown solution was stirred for 14 h, and then the methanol was removed under vacuum. The pH of the mostly aqueous solution was adjusted to 5 with dilute HNO₃, and 2.45 g (28.8 mmol) of NaNO₃ was added with stirring. The volume of this mixture was reduced to 35 mL. It was then filtered, and the filtrate was allowed to evaporate at room temperature. After 2 days, the crystals were collected and washed with cold water. Yield: 1.125 g (81%). ¹H NMR (D₂O, 500 MHz; δ from TSP): 3.74 (2H, q), 3.88 (1H, m), 4.42 (1H, m), 4.54 (2H, m), 4.65 (1H, m), 4.74 (1H, m), 6.16 (1H, t), 6.89 (1H, t), 7.19 (1H, d), 7.69 (1H, d), 8.04 (1H, d), 8.19 (1H, d), 8.28 (1H, d), 8.49 (1H, t), 8.76 (1H, t). Electronic absorption spectrum (λ_{max}, nm (ε, M⁻¹ cm⁻¹): in water, 562 (sh, 102), 452 (sh, 262), 315 (sh, 5200); in methanol, 562 (103), 412 (sh, 659), 330 (sh, 3600), 280 (sh, 8900).

[Co(PyPz₂P)(H₂O)](H₃O)(PF₆)₂·2CH₃OH (**2b**). This complex was synthesized by the procedure described above except for the use of NH₄PF₆ in place of NaNO₃. The complex was crystallized from methanol. Yield: 160 mg (14%).

[Co(PyPz₂P)(OH)] (**3**). A batch of 350 mg (0.714 mmol) of complex **2a** was dissolved in 5 mL of methanol, and to this green solution was added a solution of 130 mg (0.714 mmol, 1 equiv) of tetramethylammonium hydroxide pentahydrate in 5 mL of methanol. The color rapidly changed to deep red. After this solution was stirred for 1 h, the methanol was removed and the red solid was dissolved in 10 mL of CH₂Cl₂ and filtered. Slow evaporation of the filtrate under vacuum afforded complex **3** as a microcrystalline solid. Yield: 290 mg (95%). ¹H NMR (D₂O, 500 MHz; δ from TSP): 3.55 (1H, m), 3.85 (1H, t), 3.91 (1H, m), 4.20 (1H, m), 4.36 (1H, d), 4.44 (2H, m), 4.65 (1H, d), 6.15 (1H, t), 6.81 (1H, t), 7.20 (1H, d), 7.64 (1H, d), 7.94 (1H, d), 8.08 (1H, d), 8.16 (1H, d), 8.38 (1H, t), 8.60 (1H, d). Electronic absorption spectrum (λ_{max}, nm (ε, M⁻¹ cm⁻¹): in water, 554 (sh, 75), 452 (236), 310 (4 400), 230 (sh, 18 000).

Na[Co(PyPz₂P)₂] (**4a**). To a solution of 500 mg (1.41 mmol) of **1** in 15 mL of methanol was added dropwise a solution of 275 mg (0.95 mmol) cobalt nitrate hexahydrate dissolved in 10 mL of water. After 5 min of stirring, 113 mg (2.82 mmol) of NaOH in 5 mL was added followed by 3.0 mL of 30% H₂O₂. The solution was then stirred for 14 h. Next, the methanol was removed from the reaction mixture, and

the pH of the mostly aqueous solution was adjusted to 7 with dilute HNO₃. A solution of 722 mg (8.5 mmol) of NaNO₃ in 2 mL of water was added to it, and the volume of the mixture was reduced to 10 mL. It was then filtered, and the filtrate was allowed to evaporate at room temperature. After 48 h, the brownish green crystals (hexagonal plates) were collected and washed with cold water and air-dried. Yield: 300 mg (54%). ¹H NMR (D₂O, 500 MHz; δ from TSP): 2.46 (8H, t), 3.72 (8H, t), 6.22 (4H, t), 7.18 (4H, d), 7.42 (4H, d), 8.24 (4H, d), 8.63 (2H, t). Electronic absorption spectrum (λ_{max}, nm (ε, M⁻¹ cm⁻¹): in water, 580 (74), 450 (sh, 530), 314 (11 400), 280 (sh, 13 000), 243 (sh, 25 000).

0.5[Co(H₂O)₆][Co(PyPz₂P)₂]·5.4H₂O (**4b**). To 200 mg (0.26 mmol) of complex **4a** in 5 mL of water was added dropwise 75 mg of (0.26 mmol) cobalt nitrate hexahydrate dissolved in 2 mL of water. A greenish brown precipitate was formed instantly. It was filtered, and the precipitate was washed with 5 mL of cold water. The solid was then redissolved in 8 mL of water by heating (70 °C), and the mixture was filtered. The filtrate was then stored at room temperature. Dark brown parallelepipeds were deposited within 14 h. They were collected by filtration and dried in air. Yield: 120 mg (50%).

Other Physical Measurements. Infrared spectra were obtained with a Perkin-Elmer 1600 FTIR spectrophotometer. Absorption spectra were monitored on a Perkin-Elmer Lambda 9 spectrophotometer. A Bruker ESP-300 spectrometer was used to record the EPR spectra at X-band frequencies. NMR spectra were recorded on a Varian 500 MHz Unity Plus instrument interfaced with a Sun OS 4.1.3 computer.

X-ray Data Collection and Structure Solution and Refinement. Orange plates of complex **2b**, suitable for X-ray analysis, were obtained by slow evaporation of a methanolic solution of the complex. X-ray data were collected at 140(2) K on a Siemens P3 diffractometer equipped with an Enraf Nonius low-temperature apparatus. The structure was solved in *P* $\bar{1}$ using direct methods, and an absorption correction was applied.⁶ Brown parallelepipeds of complex **4b**, suitable for X-ray analysis, were obtained during slow evaporation of the reaction mixture at room temperature. The X-ray data were collected at 123(2) K with a Siemens R3m/V diffractometer equipped with an Enraf Nonius low-temperature apparatus. The structure was solved in *P* $\bar{1}$ using direct methods. The data were corrected for Lorentz and polarization effects. An absorption correction was also applied.⁶ [Co(H₂O)₆]²⁺ lies on an inversion center. There are also 5.4 water molecules in the lattice. Four are nicely ordered, while there are three sites for O12 and O13 is only 40% occupied. All calculations were carried out on a 486/DX50 computer using the SHELXTL Version 5.03 program.⁷

Machine parameters, crystal data, and data collection parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 2. The two sets of crystallographic data (including positional coordinates) have been submitted as Supporting Information.

Results and Discussion

In the present study, [Co(PyPz₂P)(H₂O)]X, (X = NO₃⁻ (**2a**), [(H₃O)(PF₆)₂]⁻ (**2b**)) has been synthesized via chemical (H₂O₂) oxidation⁸ of a mixture of Co(II) acetate and PyPz₂PH₂ in aqueous methanol. Ligation of the deprotonated amido nitrogens of **1** to Co(III) is ensured by the addition of 2 equiv of a strong base. Following removal of methanol, the reaction mixture must be adjusted to pH 5 for the formation of [Co(PyPz₂P)(H₂O)]⁺. Addition of excess NaNO₃ to this solution and subsequent slow evaporation affords crystalline complex **2a**. Complex **2b** is obtained when NH₄PF₆ is added to the aqueous solution instead of NaNO₃. The yield of complex

(6) Parkins, S.; Moezzi, B.; Hope, H. XABS2: An empirical absorption corrections program. *J. Appl. Crystallogr.* **1995**, 53–56.

(7) Sheldrick, G. *SHELXTL*, Version 5.03; Siemens Industrial Automation, Inc.: Madison, WI, 1994. Tables of neutral atom scattering factors, *f'* and *f''*, and absorption coefficients were taken from: *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.

(8) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 458, 735–738.

Table 1. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for [Co(PyPz₂P)(H₂O)](H₃O)(PF₆)₂·2CH₃OH (**2b**) and 0.5[Co(H₂O)₆][Co(PyPz₂P)₂]₂·5.4H₂O (**4b**)

	complex 2b	complex 4b
formula	C ₁₉ H ₃₀ N ₇ O ₆ F ₁₂ P ₂ Co	C ₃₄ H _{50.8} N ₁₄ O _{12.4} Co _{1.5}
mol wt	801.37	942.48
cryst color, habit	orange plate	brown parallelepiped
<i>T</i> , K	140(2)	123(2)
cryst syst	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	11.842(2)	12.471(3)
<i>b</i> , Å	11.920(3)	14.070(3)
<i>c</i> , Å	12.755(2)	14.171(5)
α , deg	111.21(2)	71.58(2)
β , deg	103.866(13)	68.08(2)
γ , deg	106.992(13)	71.74(2)
<i>V</i> , Å ³	1479.9(5)	2134.0(10)
<i>Z</i>	2	2
<i>d</i> _{calcd} , g cm ⁻³	1.798	1.467
abs coeff, μ , mm ⁻¹	0.813	0.667
GO F^a on F^2	1.031	1.013
<i>R</i> ₁ , ^b %	6.06	5.86
<i>R</i> _{w2} , ^c %	14.38	12.23

^a GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(M - N)]^{1/2}$ (*M* = number of reflections, *N* = number of parameters refined). ^b *R*₁ = $\sum||F_o| - |F_c||/\sum|F_o|$. ^c *R*_{w2} = $[\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

2a (81%) is clearly superior to that of complex **2b** (14%), although crystals of the latter were suitable for crystallographic studies.

The bis complex [Co(PyPz₂P)₂]⁻ (anion of complexes **4a,b**) is best synthesized when one starts with cobalt(II) sources with noncoordinating anions (NO₃⁻, ClO₄⁻, BF₄⁻) and a cobalt:ligand ratio of 1:1.5, adds the base first, and follows it by the addition of H₂O₂ (see Experimental Section). This procedure results in precipitation of the small amount of Co(OH)₂ at the initial stage and raises the cobalt:ligand ratio and allows one to collect complex **4a** in high yield and in pure form. A higher ratio of ligand (> 1.5) invariably leads to contamination of the product (**4a**) by unreacted ligand which could be removed by repeated washing of the product with chloroform. Interestingly, complex **4a** is not formed to a significant amount when Co(II) acetate tetrahydrate is used as the starting material. Complex **4a** forms thin plates which are not suitable for X-ray work. Hence, in the present study, the [Co(H₂O)₆]²⁺ salt of [Co(PyPz₂P)₂]⁻ (**4b**) has been isolated by mixing the anionic complex [Co(PyPz₂P)₂]⁻ with Co(NO₃)₂ in water. Complex **4b** is highly crystalline and readily forms brown parallelepipeds which are suitable for X-ray crystallography. In a few preparations of complex **4a**, small amounts (a few crystals) of complex **4b** have also been noticed during the course of the present work.

Addition of 1 equiv of (CH₃)₄NOH·5H₂O to a solution of complex **2a** (or complex **2b**) in methanol affords [Co(PyPz₂P)(OH)] (**3**) in nearly quantitative yield. Deprotonation of the ligated water molecule in [Co(PyPz₂P)(H₂O)]⁺ can be easily followed by the color of the solution (vide infra). Removal of methanol and redissolution in CH₂Cl₂ allows separation of complex **3** from [(CH₃)₄N]NO₃ which is insoluble in CH₂Cl₂. The two complexes **2** and **3** can be readily separated from each other on a cation exchanger.

Conversion of [Co(PyPz₂P)(H₂O)]NO₃ (2a**) to Na[Co(PyPz₂P)₂] (**4a**).** Addition of Na₂PyPz₂P, the disodium salt of PyPz₂PH₂, to a methanolic solution of complex **2a** followed by heating results in quantitative formation of complex **4a** (eq 1), a process that can be monitored by ¹H NMR spectroscopy. The

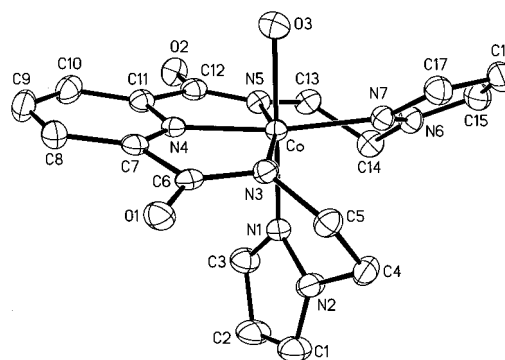
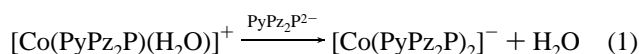
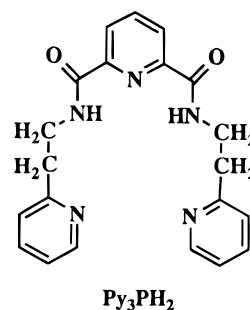


Figure 1. Computer-generated thermal ellipsoid (probability level 50%) plot of [Co(PyPz₂P)(H₂O)]⁺ (cation of complex **2b**) with the atom labeling scheme. Hydrogen atoms are omitted for clarity.

transformation complex **2a** → complex **4a** is irreversible; heating of a mixture of complex **4a** and cobalt(II) nitrate in water with H₂O₂ does not result in formation of complex **2a**. The superior thermodynamic stability of [Co(PyPz₂P)₂]⁻ relative to [Co(PyPz₂P)(H₂O)]⁺ presumably arises from the high crystal field stabilization due to coordination of four deprotonated amido nitrogens to the Co(III) center.

Structure of [Co(PyPz₂P)(H₂O)](H₃O)(PF₆)₂·2CH₃OH (2b**).** The structure of [Co(PyPz₂P)(H₂O)]⁺, the cation of complex **2b**, is shown in Figure 1, while selected bond distances and bond angles are listed in Table 2. The coordination geometry around cobalt is octahedral. The equatorial positions are occupied by two deprotonated amido nitrogens, one pyridine nitrogen, and one 2-pyrazole nitrogen, while the axial positions are occupied by the second 2-pyrazole nitrogen and one H₂O molecule. There are two disordered PF₆⁻ ions, one hydronium ion, and two methanol molecules for each [Co(PyPz₂P)(H₂O)]⁺ in the unit cell. The hydronium ion is sufficiently far as to not interact with [Co(PyPz₂P)(H₂O)]⁺. The overall structure of [Co(PyPz₂P)(H₂O)]⁺ is very similar to that of [Co(Py₃P)(H₂O)]⁺ (**5**), the Co(III) complex of an analogous ligand Py₃PH₂.⁹ In



complex **2b**, the Co–N_{py} (py = pyridine) distance (1.849(3) Å) is shorter than other Co^{III}–N_{py} bond distances (1.950–2.00 Å)¹⁰ as a result of the pyridine N being a member of two five-membered chelate rings.⁹ Since no cobalt(III)–pyrazole complex has been structurally characterized, comparison of the Co^{III}–N_{pz} bond distance in complex **2b** with the Co^{III}–N_{pz} bond distance in any other complex is not possible. There are two

- (9) Chavez, F. A.; Nguyen, C. V.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1996**, *35*, 6282.
 (10) (a) Zhu, D.-R.; You, X.-Z.; Shi, X.-H.; Fun, H.-K.; Sivakumar, K. *Acta Crystallogr.* **1996**, *C52*, 1146. (b) Beattie, J. K.; Hambley, T. W.; Klepetko, J. A.; Masters, A. F.; Turner, P. *Polyhedron* **1996**, *15*, 2141. (c) Xu, D.; Lei, L.; Xu, Y.; Cheng, C. *Acta Crystallogr.* **1992**, *C48*, 1399. (d) Goher, M. A. S.; Wang, R.-J.; Mak, T. C. W. *Polyhedron* **1992**, *11*, 829. (e) Billing, D. G.; Dobson, S. M.; Patrick, G.; Carlton, L. *Acta Crystallogr.* **1991**, *C47*, 1964. (f) Ondracek, J.; Jursik, F.; Maixner, J.; Kratochvil, B. *Acta Crystallogr.* **1990**, *C46*, 1821.

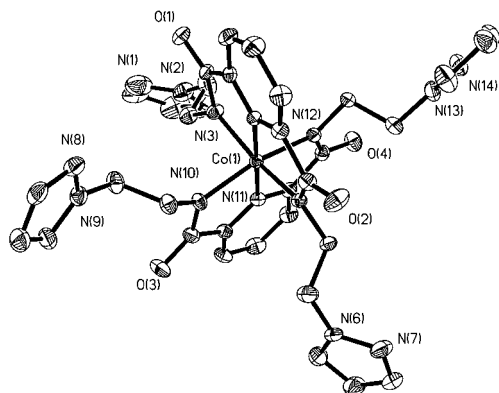


Figure 2. Computer-generated thermal ellipsoid (probability level 50%) plot of $[\text{Co}(\text{PyPz}_2\text{P})_2]^-$ (**4b**) with the atom labeling scheme. Hydrogen atoms are omitted for clarity.

$\text{Co}^{\text{III}}-\text{N}_{\text{pz}}$ distances in complex **2b**. We believe that the $\text{Co}-\text{N1}$ distance of 1.929(3) Å is a reasonable value for the $\text{Co}^{\text{III}}-\text{N}_{\text{pz}}$ distance. The other $\text{Co}^{\text{III}}-\text{N}_{\text{pz}}$ distance, namely, $\text{Co}-\text{N7}$ (1.946(3) Å), is longer presumably due to the *trans*-influence of the pyridine nitrogen. The $\text{Co}-\text{N}_{\text{amido}}$ bond lengths in complex **2b** ($\text{Co}-\text{N3}$ (1.942(3) Å) and $\text{Co}-\text{N5}$ (1.934(3) Å) are somewhat longer than the corresponding bond lengths in complex **5** (1.929(6) and 1.930(6) Å, respectively) but compare well with the $\text{Co}-\text{N}_{\text{amido}}$ bond lengths observed in other cobalt(III)-peptido complexes.^{11,12} Finally, the $\text{Co}-\text{OH}_2$ bond in complex **2b** is noticeably longer (1.963(3) Å) than the same bond in complex **5** (1.945(4) Å). Stronger σ donation of the 2-pyrazole nitrogen compared to the pyridine nitrogen¹³ could be responsible for this lengthening.

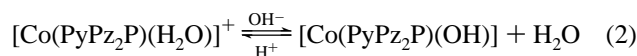
Structure of $0.5[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{PyPz}_2\text{P})_2] \cdot 5.4\text{H}_2\text{O}$ (4b**).** The structure of the anion of complex **4b** is illustrated in Figure 2, and selected bond distances and bond angles are included in Table 2. In this complex, two $\text{PyPz}_2\text{P}^{2-}$ ligands are coordinated to one cobalt(III) center (Figure 2). Each $\text{PyPz}_2\text{P}^{2-}$ ligand employs one pyridine nitrogen and two deprotonated amido nitrogens to bind cobalt in this pseudooctahedral complex. In both ligands, the pyridine, keto groups, and amido nitrogens are nearly planar (0.0222 and 0.0333 Å) with a 87.3° angle between the two planes. The average of the four $\text{Co}-\text{N}_{\text{amido}}$ bond lengths of complex **4b** is 1.957 Å. Although this value is somewhat longer than the $\text{C}-\text{N}_{\text{amido}}$ bond lengths seen in complex **2b** and other cobalt(III)-peptido complexes,^{11,12} it is very close to the average $\text{Co}-\text{N}_{\text{amido}}$ bond length (1.966(4) Å) in the $[\text{Et}_4\text{N}][\text{CoL}_2]$ complex where $\text{H}_2\text{L} = 2,6\text{-bis}(N\text{-phenylcarbamoyl})\text{pyridine}$.¹⁴ The four pendant pyrazole rings of complex **4b** are oriented in space in a propellerlike fashion (Figure 2). In the unit cell, two anions are symmetrically distributed about one $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. One 2-pyrazole nitrogen from each $[\text{Co}(\text{PyPz}_2\text{P})_2]^-$ unit is within hydrogen bonding distance to water molecules of the hexaaquacobalt(II) cation.

Table 2. Selected Bond Distances (Å) and Angles (deg)

$[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})](\text{H}_3\text{O})(\text{PF}_6)_2 \cdot 2\text{CH}_3\text{OH}$ (2b)			
Bond Distances			
$\text{Co}-\text{N1}$	1.929(3)	$\text{N1}-\text{N2}$	1.366(4)
$\text{Co}-\text{N3}$	1.942(3)	$\text{O1}-\text{C6}$	1.257(4)
$\text{Co}-\text{N4}$	1.849(3)	$\text{O2}-\text{C12}$	1.250(5)
$\text{Co}-\text{N5}$	1.934(3)	$\text{O5}-\text{C18}$	1.437(7)
$\text{Co}-\text{N7}$	1.946(3)	$\text{N4}-\text{C11}$	1.342(5)
$\text{Co}-\text{O3}$	1.963(3)	$\text{C7}-\text{C8}$	1.383(5)
Bond Angles			
$\text{N1}-\text{Co}-\text{N3}$	84.54(13)	$\text{N5}-\text{Co}-\text{N7}$	93.73(13)
$\text{N1}-\text{Co}-\text{N4}$	93.27(13)	$\text{N1}-\text{Co}-\text{O3}$	175.82(13)
$\text{N1}-\text{Co}-\text{N5}$	91.38(13)	$\text{N3}-\text{Co}-\text{O3}$	91.31(12)
$\text{N1}-\text{Co}-\text{N7}$	94.26(13)	$\text{N4}-\text{Co}-\text{O3}$	86.70(13)
$\text{N3}-\text{Co}-\text{N4}$	82.40(13)	$\text{N5}-\text{Co}-\text{O3}$	92.76(13)
$\text{N3}-\text{Co}-\text{N5}$	163.69(13)	$\text{N7}-\text{Co}-\text{O3}$	86.09(13)
$\text{N3}-\text{Co}-\text{N7}$	102.30(13)	$\text{C7}-\text{N4}-\text{Co}$	118.2(3)
$\text{N4}-\text{Co}-\text{N5}$	82.07(13)	$\text{N3}-\text{C6}-\text{O1}$	128.1(3)
$0.5[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{PyPz}_2\text{P})_2] \cdot 5.4\text{H}_2\text{O}$ (4b)			
Bond Distances			
$\text{Co1}-\text{N3}$	1.955(3)	$\text{N1}-\text{N2}$	1.391(6)
$\text{Co1}-\text{N4}$	1.850(3)	$\text{O1}-\text{C6}$	1.260(4)
$\text{Co1}-\text{N5}$	1.957(3)	$\text{N1}-\text{C1}$	1.384(6)
$\text{Co1}-\text{N10}$	1.959(3)	$\text{N6}-\text{N7}$	1.361(4)
$\text{Co1}-\text{N11}$	1.860(3)	$\text{Co2}-\text{O5}$	2.079(3)
$\text{Co1}-\text{N12}$	1.957(3)	$\text{O2}-\text{C12}$	1.249(4)
Bond Angles			
$\text{N3}-\text{Co1}-\text{N4}$	81.59(13)	$\text{N5}-\text{Co1}-\text{N10}$	90.56(12)
$\text{N3}-\text{Co1}-\text{N5}$	163.51(12)	$\text{N5}-\text{Co1}-\text{N12}$	90.42(12)
$\text{N3}-\text{Co1}-\text{N10}$	91.69(13)	$\text{N10}-\text{Co1}-\text{N11}$	82.02(13)
$\text{N3}-\text{Co1}-\text{N11}$	96.50(13)	$\text{N10}-\text{Co1}-\text{N12}$	163.60(12)
$\text{N3}-\text{Co1}-\text{N12}$	92.00(13)	$\text{N11}-\text{Co1}-\text{N12}$	81.68(13)
$\text{N4}-\text{Co1}-\text{N5}$	81.92(12)	$\text{N3}-\text{C6}-\text{O1}$	126.9(3)
$\text{N4}-\text{Co1}-\text{N10}$	98.71(13)	$\text{O5}-\text{Co2}-\text{O6}$	91.00(11)
$\text{N4}-\text{Co1}-\text{N11}$	177.96(13)	$\text{O1}-\text{C6}-\text{C7}$	121.3(3)
$\text{N4}-\text{Co1}-\text{N12}$	97.64(13)	$\text{N2}-\text{N1}-\text{C1}$	104.2(5)

The metric features of the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion are quite regular (Table 2).

Reversible Conversion of $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]^+$ (2a** or **2b**) to $[\text{Co}(\text{PyPz}_2\text{P})(\text{OH})]$ (**3**).** In aqueous solution, the absorption spectrum of $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]^+$ changes with pH. The greenish brown color changes to brownish orange as the pH is increased. In Figure 3, the changes in the electronic absorption spectrum of complex **2a** with pH in aqueous solution at 25 °C are shown. As the pH is increased from 3 to 11, absorptions at 564 and 300 nm diminish with concomitant formation of new bands at 554 and 311 nm. These spectral changes arise from the removal of a proton from the ligated water in $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]^+$ (eq 2). At pH = 9, the absorption spectrum of complex



2a is identical to that of complex **3**. The conversion of complex **2a** to complex **3** is reversible. As the pH is lowered to 4, the spectrum of complex **3** reverts back to the spectrum of complex **2a**. The results of the pH titration (inset, Figure 3) afford a pK_a value of 7 for the coordinated water in complex **2a** (and complex **2b**). Similar weak acid behavior of coordinated water has also been observed with $[\text{Co}(\text{Py}_3\text{P})(\text{H}_2\text{O})]^+$ (**5**), which also yields a pK_a value of 7.⁹

NMR Spectra. The ^1H and ^{13}C NMR spectra of complexes **2a, b, 3**, and **4a** have been recorded in various solvents at 25 °C. Results of these measurements indicate that the methylene protons (associated with C4, C5, C13, and C14; see Figure 1) of complexes **2a, b** and **3** are nonequivalent. For example, the methylene protons of complex **2a** resonate between 3.7 and 4.9 ppm in the ^1H NMR spectrum of complex **2a** in D_2O . The

- (11) (a) Farinas, E. F.; Tan, J. D.; Baidya, N.; Mascharak, P. K. *J. Am. Chem. Soc.* **1993**, *115*, 2996. (b) Tan, J. D.; Hudson, S. E.; Brown, S. J.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 3841. (c) Muettterties, M.; Cox, M. B.; Arora, S. K.; Mascharak, P. K. *Inorg. Chim. Acta* **1989**, *160*, 123. (d) Brown, S. J.; Hudson, S. E.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1989**, *111*, 6446. (e) Delany, K.; Arora, S. K.; Mascharak, P. K. *Inorg. Chem.* **1988**, *27*, 705, and references cited therein.
- (12) (a) Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1991**, *113*, 8419. (b) Mak, S.-T.; Wong, W.-T.; Yam, V. W.-W.; Lai, T.-F.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1991**, 1915.
- (13) Fantucci, P.; Valenti, V. *J. Chem. Soc., Dalton Trans.* **1992**, 1981.
- (14) Ray, M.; Ghosh, D.; Shirin, Z.; Mukherjee, R. *Inorg. Chem.* **1997**, *36*, 3568.

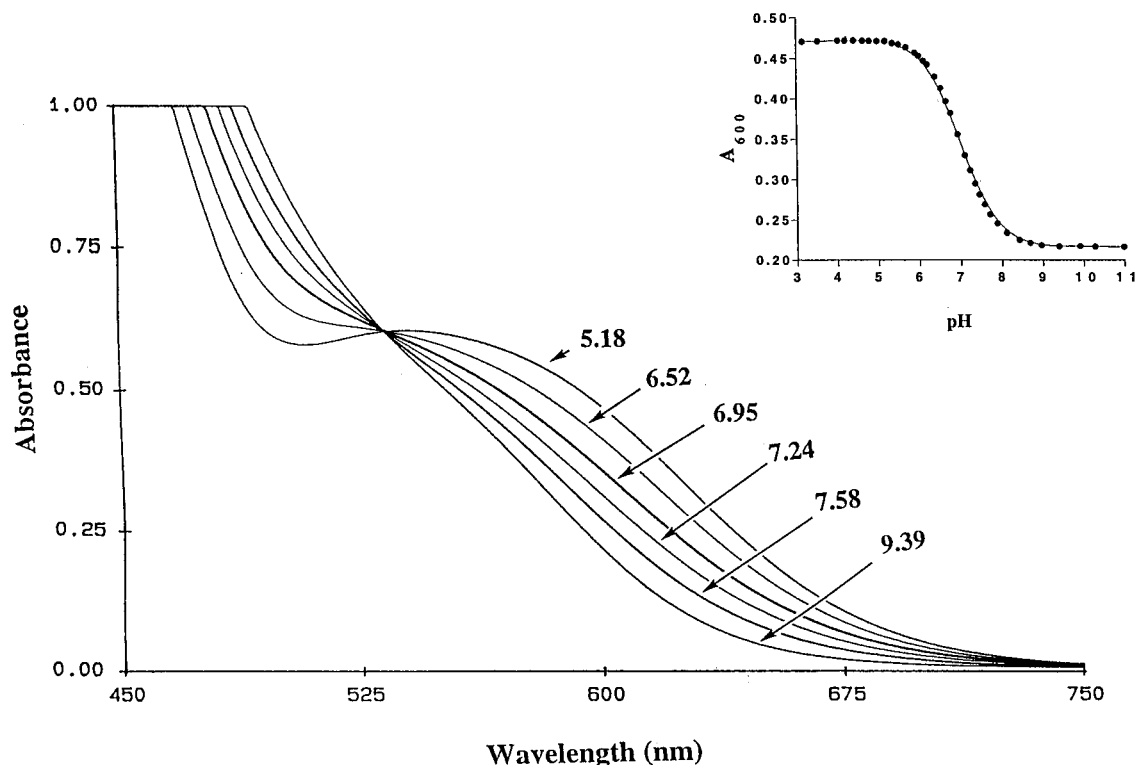


Figure 3. Changes in the electronic absorption spectrum of $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]\text{NO}_3$ (**2a**) with pH monitored in aqueous solution. Only the changes in the visible band are shown. Inset: Plot of pH vs absorbance at 600 nm.

pyrazole protons (associated with C1–C3 and C15–C17; see Figure 1) are also nonequivalent. Thus, there are two sets of three resonances for the pyrazole protons at 6.2, 6.9, 7.2, 7.7, 8.2, and 8.8 ppm. These nonequivalent resonances indicate that the ligand framework is quite rigid and held in specific orientation in the $\{\text{Co}(\text{PyPz}_2\text{P})\}$ moiety. Conversion of $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]^+$ (**2a** or **2b**) to $[\text{Co}(\text{PyPz}_2\text{P})(\text{OH})]$ (**3**) results in noticeable spreading out of the methylene resonances as well as minor shifts in the positions of the pyrazole peaks (see Experimental Section).

When the ^1H NMR spectrum of complex **2a** is monitored in $(\text{CD}_3)_2\text{SO}$ at 25 °C, several resonances shift relative to their positions in the D_2O spectrum. These changes are associated with the replacement of the ligated D_2O molecule (the complex is brownish green) by a $(\text{CD}_3)_2\text{SO}$ molecule (the complex is green). Water binds to the $\text{Co}(\text{III})$ center in complex **2a** more strongly than DMSO. This is apparent from the fact that when D_2O is added to the $(\text{CD}_3)_2\text{SO}$ solution of complex **2a**, the color immediately changes from green to brownish green while the reverse addition does not bring about any change in the NMR spectrum.

The ^1H NMR spectrum of complex **4a** is noticeably simple compared to the spectrum of complex **2a**, **2b**, or **3**. This simplification is indicative of free rotation of the ligand arms and high symmetry of the metal complex. The methylene resonances are shifted upfield relative to their positions in $\text{Na}_2\text{-PyPz}_2\text{P}$ (3.84 and 4.43 ppm in D_2O) and, unlike the other complexes, are not spread out in the region 3–5 ppm. The

latter fact indicates that in complex **4a**, the CH_2 groups are not held in any specific orientation(s) in space. The three pyrazole protons also give rise to only one set of resonances at 6.2, 7.2, and 7.4 ppm. Taken together, the NMR patterns confirm that the pendant $\text{CH}_2\text{-CH}_2\text{-Pz}$ arms are quite free to move in solution.

In summary, three cobalt complexes, namely, $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})]^+$, $[\text{Co}(\text{PyPz}_2\text{P})(\text{OH})]$, and $[\text{Co}(\text{PyPz}_2\text{P})_2]^-$, of the ligand PyPz_2PH_2 have been synthesized and the structures of $[\text{Co}(\text{PyPz}_2\text{P})(\text{H}_2\text{O})(\text{H}_3\text{O})(\text{PF}_6)_2 \cdot 2\text{CH}_3\text{OH}]$ (**2b**) and $0.5[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{PyPz}_2\text{P})_2] \cdot 5.4\text{H}_2\text{O}$ (**4b**) have been determined by X-ray crystallography. Complex **2b** is the first example of a structurally characterized complex in which 2-pyrazole nitrogens are coordinated to a $\text{Co}(\text{III})$ center.

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Supporting Information Available: Atom labeling schemes for the ligand frames and the cation of **4b** (Figures S1 and S2), ^1H NMR spectra of **2a** and **4a** in D_2O and in $(\text{CD}_3)_2\text{SO}$ (Figures S3 and S4), and tables containing spectral properties of **2a**, **b**, **3**, and **4a**, **b** and crystal data and intensity collection and refinement parameters, positional coordinates, bond distances and angles, H atom coordinates, and anisotropic and isotropic thermal parameters for **2b** and **4b** (28 pages). Ordering information is given on any current masthead page.

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