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Article

Unusual Reactivity of Methylene Group Adjacent to Pyridine-2-Carboxamido Moiety in Iron(III) and Cobalt(III) Complexes

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The Fe(III) and Co(III) complexes of the ligand *N*-(2-picolyl)picolinamide (pmpH; H represents the dissociable amide hydrogen), namely, [Fe(pmp)$_2$]BF$_4$ (**1**) and [Co(pmp)$_2$]ClO$_4$ (**2**), have been synthesized and structurally characterized. The –CH$_2$– moiety of pmp$^-$ in [M(pmp)$_2$]$^+$ (M = Fe, Co) is very reactive and is readily converted to carbonyl (C=O) group upon exposure to dioxygen. Such conversion results in [M(bpca)$_2$]ClO$_4$ complexes (M = Fe (**3**), Co (**5**); bpcaH = bis(2-pyridylcarbonyl)amine) which have been characterized by spectroscopy and X-ray diffraction. The structure of **5** is reported here for the first time. The reactivity of the –CH$_2$– moiety of pmp$^-$ has so far precluded the isolation of **1** although other metal complexes of pmp$^-$ have been reported years ago. The CH$_2$ → C=O transformation arises from the tendency of the coordinated pmp$^-$ ligand to achieve further conjugation in the ligand framework and provides a better way to synthesize the metal complexes of bpcaH ligand. Reaction of **3** with NaH affords Fe(II) complex [Fe(bpca)$_2$] (**4**) without any reduction of the ligand frame.

Introduction

In our attempts to develop the chemistry of iron(III),[1−5] cobalt(III),[6−10] and copper(II)[11−14] complexes with ligands containing pyridine-2-carboxamide groups, we have noticed an unusual reactivity of −CH$_2$− groups attached to such a moiety. The results included here involve the ligand *N*-(2-picolyl)picolinamide (pmpH; H represents the dissociable amide hydrogen) first reported by Nonoyama and co-workers.[15] A close scrutiny of the literature revealed that although metal complexes of the ligand pmpH have been synthesized,[15,16] the iron(III) (or iron(II)) complex of this ligand is conspicuously absent. During the past 10 years, several synthetic protocols to isolate discrete metal complexes of ligands with pyridine-2-carboxamide group(s) have been developed in this laboratory.[1−14,17−26] Initially, all such methods used to isolate [Fe(pmp)$_2$]$^+$, the iron(III) complex

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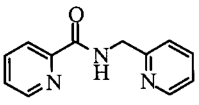
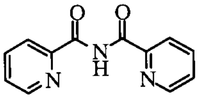
of pmp$^-$ (pmp$^-$ is the deprotonated form of pmpH), failed in our hands. Instead, [Fe(bpca)$_2$]$^+$, the iron(III) complex of ligand bpcaH (bpcaH = bis(2-pyridylcarbonyl)amine), was obtained in high yield.[27]



pmpH



bpcaH

The ligand bpca$^-$ (bpca$^-$ is the deprotonated form of bpcaH) is a tridentate ligand that coordinates a variety of metal ions through the three nitrogen atoms and readily forms ML$_2$ type complexes. A variety of [M(bpca)$_2$]$^{n+}$ complexes have been reported in the literature, and the list includes the complexes of iron(II),[27] iron(III),[27] manganese(II),[28] nickel(II),[29] copper(II),[30] zinc(II),[27] rhodium(II),[31,32] and rhodium(III).[32] Interest in the use of such [M(bpca)$_2$] units as components for larger supermolecular arrays has been on the rise, and recently, [M(bpca)$_2$], where M = nickel(II)[29] and manganese(II),[33,34] has afforded interesting extended structures with iron(II) centers. It is important to note here that the initial report for the synthesis of the tridentate ligand bpcaH involved the hydrolysis of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine in the presence of copper(II) ions.[35,36] This is the first report of the synthesis of complexes of bpca$^-$ directly from preformed [M(pmp)$_2$]$^{n+}$species.

In this account, we report the synthesis and structure of the iron(III) and cobalt(III) complexes of pmp$^-$, [Fe(pmp)$_2$]BF$_4$ (**1**) and [Co(pmp)$_2$]ClO$_4$ (**2**), respectively.[37] These complexes are the only metal complexes of pmp$^-$ other than copper(II)[16] that have been characterized by X-ray diffraction. In addition, we report the conversion of complexes **1** and **2** to [Fe(bpca)$_2$]ClO$_4$ (**3**) and [Co(bpca)$_2$]ClO$_4$ (**5**), respectively, upon exposure to O$_2$. While the structure of **3** has been reported in a earlier account,[27] the structure of **5** is reported here for the first time, and this complex adds to the list of hitherto known [M(bpca)$_2$]$^+$ compounds. Once formed, the iron(III) center in complex **3** can be reduced to iron(II) to afford neutral complex [Fe(bpca)$_2$] (**4**). The conversion of the ligand frame of pmp$^-$ to bpca$^-$ (in air at room temperature) proceeds only when they are ligated to iron(III) or cobalt(III) centers. Otherwise, pmpH is stable in air and does not convert into bpcaH in neutral or basic solutions.

Experimental Section

Materials. 2-Picolinic acid, 2-(2-aminomethyl)pyridine, ferrocenium tetrafluoroborate ([Fe(Cp)$_2$]BF$_4$), and iron(II) tetrafluoroborate hexahydrate (Fe(BF$_4$)$_2$·6H$_2$O) were purchased from Aldrich Chemical Co. and used without further purification. *N,N′*-Dimethylformamide (DMF), acetonitrile (CH$_3$CN), tetrahydrofuran (THF), methanol (CH$_3$OH), and diethyl ether (Et$_2$O) were distilled from BaO, CaH$_2$, Na/benzophenone, Mg, and Na, respectively. All other solvents were used without further purification. [Fe(DMF)$_6$](ClO$_4$)$_3$ was synthesized by following a published procedure.[38] The acid chloride of 2-picolinic acid was synthesized by heating 2-picolinic acid in excess thionyl chloride followed by removal of unreacted thionyl chloride under vacuum. Air-sensitive compounds (compounds **1** and **2**) were handled on Schlenk lines or under dinitrogen in a glovebox.

Caution!!! Although no explosions were encountered in this work, perchlorate salts could detonate upon heating. These complexes should be handled with care and only in small amounts.

Synthesis of Compounds. *N*-(2-Picolyl)picolinamide (pmpH). A batch of 1.36 g (11.0 mmol) of 2-picolinic acid chloride was placed in 40 mL of THF, and a solution of 1.19 g (11.0 mmol) of 2-(aminomethyl)pyridine dissolved in 40 mL of THF was added to it dropwise at 0 °C. Next, 4.45 g (44.0 mmol) of triethylamine was added, and the resulting solution was allowed to stir overnight at room temperature. The Et$_3$N·HCl(s) was then filtered from the reaction mixture, and the solvent was removed to yield crude pmpH as a light yellow oil. This oil was dissolved in methylene chloride (CH$_2$Cl$_2$), and the solution was washed with aqueous 0.1 M NaOH (3×10 mL). The CH$_2$Cl$_2$ portion was collected and dried over MgSO$_4$. It was then filtered, and the solvent was removed in vacuo to yield a light yellow oil that crystallized upon standing. The solid was collected and washed several times with Et$_2$O to afford pure pmpH in the crystalline form.[39] Yield: 80%. ^{1}H NMR (303 K, CDCl$_3$, 250 MHz): δ (ppm from TMS), 4.80 (d 2H), 7.19 (t 1H), 7.33 (d 1H), 7.42 (t 1H), 7.65 (t 1H), 7.84 (t 1H), 8.22 (d 1H), 8.59 (m 2H), 8.93 (s 1H). Selected IR frequency (KBr disk): ν_{CO} 1670 cm^{-1}.

[Fe(pmp)$_2$]BF$_4$ (1). A batch of 0.035 g of NaOCH$_3$ (0.52 mmol) was dissolved in 3 mL of CH$_3$OH and added to 0.10 g (0.47 mmol) of pmpH dissolved in 15 mL of CH$_3$OH. To this solution of the deprotonated ligand was added dropwise a solution of 0.08 g (0.23 mmol) of Fe(BF$_4$)$_2$·6H$_2$O dissolved in 10 mL of CH$_3$OH, and the resulting red mixture was stirred for 1 h. Next, a solution of 0.10 g (0.38 mmol) of [Fe(Cp)$_2$]BF$_4$ in 10 mL of CH$_3$OH was added slowly to the reaction mixture. Red crystals of [Fe(pmp)$_2$]BF$_4$ were deposited in good yield from this solution within 1 h. Yield: 60%. Anal. Calcd for C$_{24}$H$_{20}$N$_6$O$_2$FeBF$_4$: C, 50.83; H, 3.55; N, 14.82. Found: C, 50.39; H, 3.41; N, 14.91. Selected IR stretching

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(39) This synthetic procedure affords pmpH as a white crystalline solid. In previous works, pmpH was isolated as a light yellow oil.[15,16]

frequencies (KBr disk, cm^{-1}): 1654 (s, ν_{CO}), 1604 (m), 1377 (m), 1057 (vs, ν_{BF4}), 767 (m).

$[Co(pmp)_2]ClO_4$ (2). A batch of 0.02 g (0.31 mmol) of $NaOCH_3$ was added to 0.066 g (0.31 mmol) of pmpH dissolved in 5 mL of CH_3OH. Next, a solution of 0.057 g (0.15 mmol) of $Co(ClO_4)_2\cdot 6H_2O$ in 5 mL of CH_3OH was added to the reaction mixture to afford a light brown solution. Addition of 0.04 g (0.16 mmol) of $[Fe(Cp)_2]BF_4$ dissolved in 2 mL of CH_3OH caused the solution to change color from light brown to red. $[Co(pmp)_2]ClO_4$ was deposited as a red microcrystalline precipitate within 20 min. The crystals were collected and washed several times with dry CH_3OH. Yield: 65%. Anal. Calcd for $C_{24}H_{20}N_6O_6CoCl$: C, 49.45; H, 3.46; N, 14.42. Found: C, 49.81; H, 3.41; N, 14.81. Selected IR stretching frequencies (KBr disk, cm^{-1}): 1648 (s, ν_{CO}), 1604 (m), 1397 (m), 1087 (vs, ν_{ClO4}), 765 (m), 622 (m). Absorption spectrum in CH_3CN, λ_{max} nm (ϵ, M^{-1} cm^{-1}): 515 (460), sh 410 (230).

$[Fe(bpca)_2]ClO_4$ (3). Method A: A batch of 0.015 g (0.62 mmol) of NaH was added to 0.12 g (0.56 mmol) of pmpH dissolved in 10 mL of DMF. To this solution of the deprotonated ligand was added slowly a solution of 0.22 g (0.28 mmol) of $[Fe(DMF)_6](ClO_4)_3$ in 10 mL DMF with stirring when a red color developed. The reaction mixture turned deeper red after 10 h. Next, the DMF was removed in vacuo to afford a brown-red residue. It was then dissolved in 5 mL of CH_3CN, and the solution was exposed to air. The color changed from red to brown within 2 min. Finally, the solution was filtered, and THF was added to afford brown crystals of $[Fe(bpca)_2]ClO_4$. Yield: 45%. Method B: **3** was obtained directly by the aerial oxidation of **1** in DMF. A 0.1 g portion of **1** was dissolved in 5 mL of DMF, and the solution was exposed to air and stirred for 1 h. The reddish brown solution was then evaporated to dryness, and the residue was recrystallized from CH_3CN/THF. Anal. Calcd for $C_{24}H_{16}N_6O_8FeCl$: C, 47.43; H, 2.65; N, 13.83. Found: C, 47.39; H, 2.51; N, 13.91. Selected IR stretching frequencies (KBr disk, cm^{-1}): 1724 (vs, ν_{CO}), 1654 (s), 1604 (m), 1328 (s), 1292 (m), 1085 (vs, ν_{ClO4}), 760 (m), 701 (m), 662 (m).

$[Fe(bpca)_2]$ (4). Method A: A slurry of 0.042 g (1.70 mmol) of NaH in 2 mL of DMF was added to 0.17 g (0.80 mmol) of pmpH dissolved in 10 mL of DMF. Next, a solution of 0.31 g (0.39 mmol) of $[Fe(DMF)_6](ClO_4)_3$ in 5 mL of DMF was slowly added to it with stirring. The resulting red mixture was stirred overnight at room temperature. It was then filtered, and 2 mL of Et_2O was added to the filtrate. The compound $[Fe(bpca)_2]$ was isolated as dark crystals with green sheen.[40] Method B: **4** was synthesized directly by reducing **3** with NaH in DMF. Addition of THF to the dark DMF solution afforded black crystals of **4** upon standing at room temp for 10 h. Yield: 45%. Anal. Calcd for $C_{24}H_{16}N_6O_4Fe$: C, 56.70; H, 3.17; N, 16.54. Found: C, 56.49; H, 3.21; N, 16.39. Selected IR stretching frequencies (KBr disk, cm^{-1}): 1686 (s, ν_{CO}), 1578 (m), 1350 (s), 766 (m), 712 (m), 627 (m).

$[Co(bpca)_2]ClO_4\cdot CH_3OH$ (5·CH_3OH). Method A: A solution of 0.04 g (0.56 mmol) of $NaOCH_3$ in 3 mL of CH_3OH was added to 0.11 g (0.52 mmol) of pmpH dissolved in 10 mL of CH_3OH. To this solution of the deprotonated ligand was added 0.095 g (0.26 mmol) of $Co(ClO_4)_2\cdot 6H_2O$ in 5 mL of CH_3OH, and the light brown mixture was stirred for 1 h. It was then placed in a stoppered flask, and dioxygen was allowed to slowly diffuse into the reaction mixture. Orange-red crystals of **5** were obtained in 70% yield within 12 h. Method B: The procedure outlined in method A was followed with the exception that the oxidation step was performed by the addition of 3 equiv of 30% H_2O_2. In this reaction, the mixture deposits **5** as an orange colored precipitate. Method C: In this method, solutions of **2** in DMF or CH_3CN were exposed to dioxygen. Addition of THF or CH_3OH to this solution afforded crystalline **5**·CH_3OH after 12 h. The yields of **5** in methods B and C were 75% and 50%, respectively. Anal. Calcd for $C_{25}H_{20}N_6O_9CoCl$: C, 46.71; H, 3.14; N, 13.08. Found: C, 46.35; H, 3.21; N, 13.11. Selected IR stretching frequencies (KBr disk, cm^{-1}): 1723 (s, ν_{CO}), 1655 (m), 1605 (m), 1340 (s), 1090 (vs, ν_{ClO4}), 763 (m), 700 (m), 624 (m). Absorption spectrum in CH_3CN, λ_{max} nm (ϵ, M^{-1} cm^{-1}): 480 (370), sh 360 (550).

Table 1. Summary of Crystal Data and Intensity and Structure Refinement Parameters for $[Fe(pmp)_2]BF_4$ (**1**), $[Co(pmp)_2]ClO_4$ (**2**), and $[Co(bpca)_2]ClO_4\cdot CH_3OH$ (**5**·CH_3OH)

	complex **1**	complex **2**	complex **5**
formula	$C_{24}H_{20}BF_4FeN_6O_2$	$C_{24}H_{20}ClCoN_6O_6$	$C_{25}H_{20}ClCoN_6O_9$
mol wt	567.12	582.84	642.85
cryst color, habit	red plate	red plate	orange plate
T, K	91(2)	91(2)	91(2)
cryst syst	monclinic	monclinic	triclinic
space group	Pn	Pn	$P1$
a, Å	8.6168(16)	8.5758(11)	8.8361(9)
b, Å	8.8823(16)	8.9060(12)	11.4944(12)
c, Å	15.505(3)	15.490(3)	14.4695(14)
α, deg	90	90	110.182(4)
β, deg	99.972(7)	99.770(5)	102.203(7)
γ, deg	90	90	101.096(3)
V, Å^3	1168.8(4)	1165.9(3)	1290.6(2)
Z	2	2	2
d_{calcd}, g cm^{-3}	1.611	1.660	1.654
abs coef, μ, mm^{-1}	0.714	0.907	0.837
GOF^a on F^2	1.017	1.036	1.050
R_1,^{b}%	5.67	4.62	3.77
R_{w2},^{c}%	11.91	10.92	9.49

^{a} GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). ^{b} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $R_{w2} = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

X-ray Data Collection and Structure Solution and Refinement. Red crystals of **1** suitable for X-ray analysis were obtained upon slow addition of $[Fe(Cp)_2]BF_4$ to a solution of $[Fe(pmp)_2]$ in CH_3OH. Single crystals of **2** were obtained from diffusion of Et_2O into a solution of the complex dissolved in CH_3CN. Orange crystals of **5**·CH_3OH were grown by carefully placing a layer of CH_3OH on the top of a solution of the complex in CH_3CN.

Diffraction experiments were performed on a Bruker SMART 1000 diffractometer, and data were collected at 91 K. The structures were solved by using the SHELXS-97 package, and the data were corrected for absorption effects. In the case of **2** and **5**, the structures were refined using SHELXTL 6.10 program while SHELXL-97 was used for the refinement of the structure of **1**. Machine parameters, crystal data, and data collection parameters are summarized in Table 1 while selected bond distances and angles are listed in Table 2. Complete crystallographic data for complexes **1**, **2**, and **5**·CH_3OH have been submitted as Supporting Information.

Other Physical Measurements. Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. A Perkin-Elmer 1600 FTIR spectrophotometer was used to monitor the infrared spectra.

Results and Discussion

Our interest in the chemistry of Fe(II) and Fe(III) complexes with carboxamido nitrogens as donors prompted

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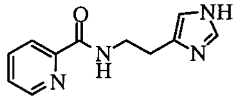
[40] Structural analysis revealed that the complex was $[Fe(bpca)_2]\cdot NaClO_4$. The presence of ClO_4^- was also confirmed by IR spectroscopy (ν_{ClO4} at 1089 cm^{-1}). Crystallization of this complex from DMF/THF solutions eventually afforded pure $[Fe(bpca)_2]$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**, **2**, and **5**$\cdot$$CH_3OH$

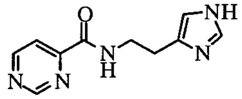
Complex **1**			
Fe−N1	1.986(3)	N2−C6	1.371(6)
Fe−N2	1.887(4)	N2−C7	1.396(6)
Fe−N3	1.978(3)	N5−C18	1.329(6)
Fe−N4	1.978(3)	N5−C19	1.452(6)
Fe−N5	1.890(4)	C6−O1	1.175(6)
Fe−N6	1.970(3)	C18−O2	1.229(5)
N1−Fe−N2	82.41(16)	N3−Fe−N5	98.60(15)
N1−Fe−N3	164.08(14)	N3−Fe−N6	91.21(14)
N1−Fe−N4	91.94(14)	N4−Fe−N5	81.65(16)
N1−Fe−N5	97.19(15)	N4−Fe−N6	163.70(13)
N1−Fe−N6	88.95(14)	N5−Fe−N6	82.10(16)
N2−Fe−N3	81.86(15)	N2−C6−C5	109.7(4)
N2−Fe−N4	96.70(15)	N2−C7−C8	108.4(4)
N2−Fe−N5	178.3(2)	N5−C18−C17	109.4(4)
N2−Fe−N6	99.54(15)	N5−C19−C20	107.6(3)
N3−Fe−N4	92.35(14)	N2−C6−O1	129.0(5)
Complex **2**			
Co−N1	1.947(2)	N2−C6	1.367(4)
Co−N2	1.881(3)	N2−C7	1.397(4)
Co−N3	1.941(2)	N5−C18	1.335(4)
Co−N4	1.945(3)	N5−C19	1.445(4)
Co−N5	1.882(3)	C6−O1	1.195(5)
Co−N6	1.940(2)	C18−O2	1.230(4)
N1−Co−N2	83.24(11)	N3−Co−N5	97.71(11)
N1−Co−N3	165.63(10)	N3−Co−N6	91.18(10)
N1−Co−N4	91.77(10)	N4−Co−N5	82.77(12)
N1−Co−N5	96.52(11)	N4−Co−N6	166.03(11)
N1−Co−N6	88.54(10)	N5−Co−N6	83.32(12)
N2−Co−N3	82.58(11)	N2−C6−C5	108.9(3)
N2−Co−N4	95.93(11)	N2−C7−C8	107.8(3)
N2−Co−N5	178.67(15)	N5−C18−C17	109.0(3)
N2−Co−N6	97.98(11)	N5−C19−C20	106.9(3)
N3−Co−N4	91.95(10)	N2−C6−O1	128.4(4)
Complex **5**$\cdot$$CH_3OH$			
Co−N1	1.9434(14)	N2−C7	1.375(2)
Co−N2	1.8944(14)	N5−C18	1.372(2)
Co−N3	1.9382(14)	N5−C19	1.380(2)
Co−N4	1.9413(15)	O1−C6	1.213(2)
Co−N5	1.8944(13)	O2−C7	1.217(2)
Co−N6	1.9455(14)	O3−C18	1.2183(19)
N2−C6	1.377(2)	O4−C19	1.2159(19)
N1−Co−N2	83.49(6)	N3−Co−N5	97.82(6)
N1−Co−N3	166.50(6)	N3−Co−N6	90.27(6)
N1−Co−N4	91.25(6)	N4−Co−N5	83.26(6)
N1−Co−N5	95.68(6)	N4−Co−N6	166.20(6)
N1−Co−N6	91.55(6)	N5−Co−N6	83.01(6)
N2−Co−N3	83.01(6)	N2−C6−C5	109.67(14)
N2−Co−N4	96.88(6)	N2−C7−C8	109.61(14)
N2−Co−N5	179.16(6)	N5−C18−C17	109.56(13)
N2−Co−N6	96.86(6)	N5−C19−C20	109.33(13)
N3−Co−N4	90.15(6)	O3−C18−N5	128.44(15)

us to isolate Fe(III) complex(es) of the ligand pmpH which, as mentioned earlier, has been unknown until this work. The present synthesis of pmpH involves coupling of picolinic acid chloride with 2-amino(methyl)pyridine in THF, a reaction that affords the ligand in the crystalline form. The Fe(III) complexes of the type $[FeL_2]^{n+}$, where L = ligands with carboxamide donor group, are usually synthesized by reacting Fe(III) salts with deprotonated ligands in DMF solutions.[1] This synthetic procedure, however, failed in our hands initially when we performed similar reactions with pmpH in air. Soon, we discovered that the presence of dioxygen in the reaction mixture caused oxidation of the $-CH_2-$ unit of the ligated pmp^- ligand to C=O group. As a consequence, we isolated $[Fe(bpca)_2]^+$, the Fe(III) complex of bpcaH reported previously by Folgado and co-workers.[27] Once the role of dioxygen and the unexpected reactivity of the methylene moiety of pmpH were eminent, we took a different approach to synthesize $[Fe(pmp)_2]^+$. This new method involves oxidation of $[Fe(pmp)_2]$ (prepared in situ by mixing an Fe(II) salt with pmp^- under dinitrogen) with $[Fe(Cp)_2]BF_4$ in methanol. The reaction is clean, and $[Fe(pmp)_2]BF_4$ crystallizes out of methanol in high yield. The absence of dioxygen in this method allows isolation of the desired Fe(III) complex. It is now evident that the unusual reactivity of the methylene moiety of pmpH is the reason for the conspicuous absence of the iron complex(es) of this ligand in the literature.

The reactivity of the $-CH_2-$ unit in pmpH is novel and deserves further comments. We have previously reported $[FeL_2]^+$ complexes with two very similar tridentate ligands, namely PypepH and PrpepH.[4,5] Both $[Fe(Pypep)_2]^+$ and $[Fe(Prpep)_2]^+$ are structurally very similar to $[Fe(pmp)_2]^+$ and contain FeN_6 chromophores that include carboxamido nitrogens. The ligand PypepH is particularly notable because it differs from pmpH by just one methylene spacer between the pyridine-2-carboxamide moiety and the N-containing ring. Despite all the similarities, $[Fe(Pypep)_2]^+$ and $[Fe(Prpep)_2]^+$ are stable in air and exhibit no reactivity in the $-CH_2-$ links.



PypepH



PrpepH

In an earlier work, Nonoyama and co-workers synthesized $[Co(pmp)_2]ClO_4$ (**2**) via reaction of $Co(ClO_4)_2\cdot 6H_2O$ with pmpH in aqueous ethanol. NaOH was used as the base in this reaction, and aerial oxidation of Co(II) afforded Co(III) complex **2** in reasonable yield. We have repeated this synthesis in methanol using $NaOCH_3$ as the base. However, we have noted that storage of $[Co(pmp)_2]ClO_4$ in CH_3OH in the presence of air results in formation of $[Co(bpca)_2]ClO_4$. Successful isolation of **2** in crystalline form (suitable for X-ray diffraction) has only been achieved by avoiding exposure of the reaction mixture to air. Conversion of **2** into $[Co(bpca)_2]ClO_4$ is fairly rapid when **2** is allowed to react with H_2O_2. In quite a contrast to this behavior, no oxidation of $-CH_2-$ unit is observed with $[Co(Pypep)_2]^+$ and $[Co(Prpep)_2]^+$.[9,10]

Structure of 1. The structure of the cation of **1** is presented in Figure 1. The iron(III) center resides in an octahedral geometry that is defined by the six nitrogen atoms from two pmp^- ligands. The complex is isolated as the *mer* isomer, and the two carboxamido nitrogen atoms occupy positions trans to each other.

In **1**, the $Fe-N_{amido}$ bond lengths (1.887(4) and 1.890(4) Å) are shorter than the $Fe-N_{amido}$ bond lengths found in the similar complex $[Fe(Pypep)_2]ClO_4$ (1.957(2) and 1.958(2) Å).[5] The average $Fe-N_{py}$ distance (1.978 Å) in **1** lies within the expected range observed for $Fe(III)-N_{py}$ bonds.[1,5]

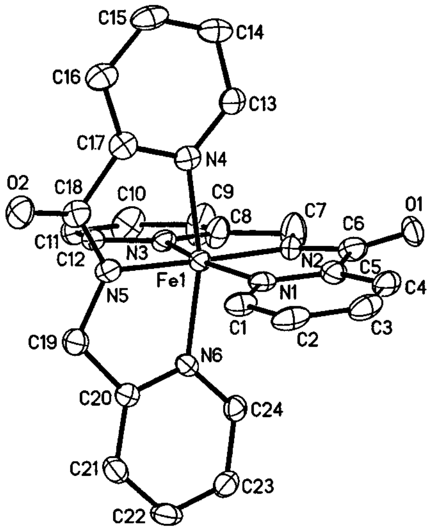


Figure 1. Thermal ellipsoid (probability level 50%) plot of $[Fe(pmp)_2]^+$ (cation of **1**) with the atom-labeling scheme. H atoms are omitted for the sake of clarity.

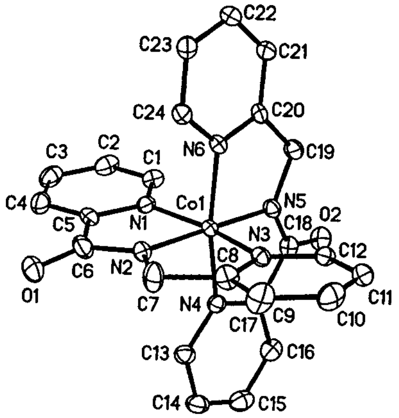


Figure 2. Thermal ellipsoid (probability level 50%) plot of $[Co(pmp)_2]^+$ (cation of **2**) with the atom-labeling scheme. H atoms are omitted for the sake of clarity.

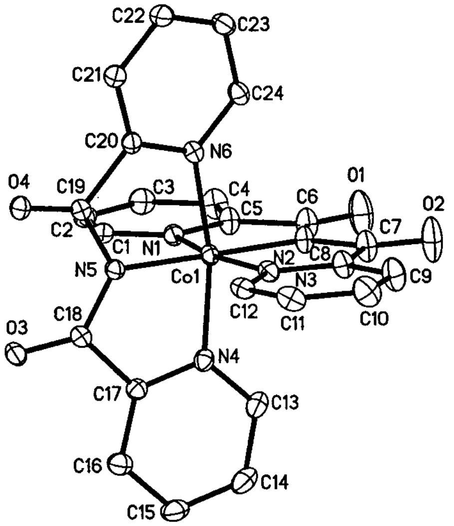
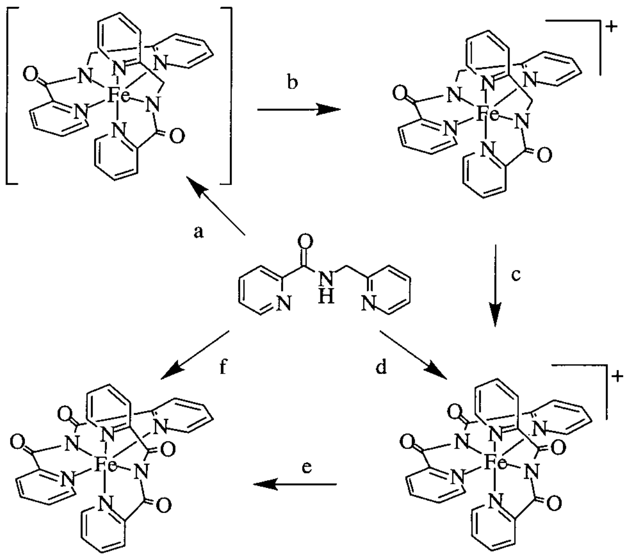


Figure 3. Thermal ellipsoid (probability level 50%) plot of $[Co(bpca)_2]^+$ (cation of **5**) with the atom-labeling scheme. H atoms are omitted for the sake of clarity.

Scheme 1



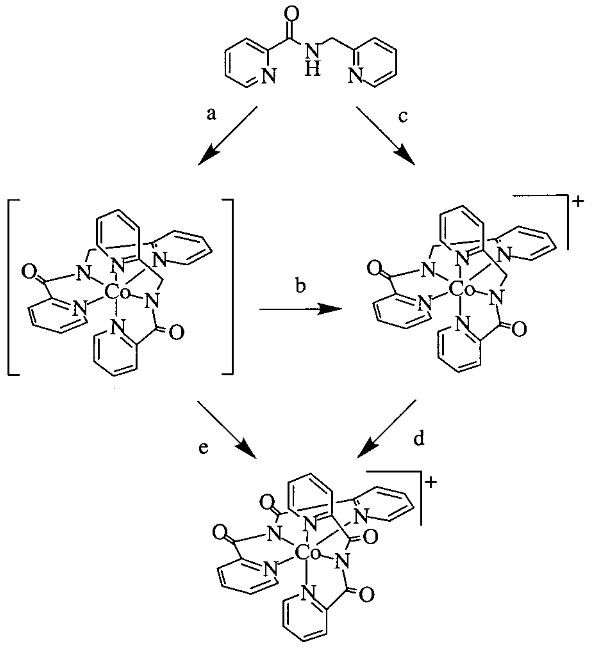
Structure of 2. The structure of $[Co(pmp)_2]^+$, shown in Figure 2, reveals that the complex is isostructural with **1**. However, the Co$-N_{amido}$ bond lengths (1.881(3) and 1.882(3) Å) are slightly shorter than the Fe$-N_{amido}$ bond lengths observed in **1**. Also, the average length of the four Co$-N_{py}$ bonds (1.943 Å) is shorter than that of the four Fe$-N_{py}$ bonds observed in **1** (1.978 Å). As a result, the overall structure of **2** is more compact than that of **1**. Much like the iron case, the Co$-N_{amido}$ bonds in **2** are shorter than the corresponding bonds in $[Co(Pypep)_2]^+$ (av: 1.933(3) Å).[10]

Structure of 5·CH_3OH. The structure of the cation of **5** is shown in Figure 3. In this structure, the cobalt(III) center resides in an octahedral geometry that is defined by the six nitrogen donor atoms of two bpca$^-$ ligands. Because of the short bite of the rigid pyridine-2-carboxamido moieties, all four $N_{py}-Co-N_{amido}$ angles are approximately 83°, a value observed in other $[M(bpca)_2]^+$ complexes. [27,32]

Comparison of the Structures of $[M(pmp)_2]^+$ and $[M(bpca)_2]^+$. Upon close inspection of the crystal structures of **1**−**3** and **5**, it becomes evident that the angles generated by pmp$^-$ and bpca$^-$ are very similar in the Fe(III) and Co(III) complexes. For example, the $N_{amido}-CH_2-C_{py}$ and the $N_{amido}-CO-C_{py}$ angles in **1** and **2** are very similar to each other (average value ~108° and 109°, respectively). In addition, the four $N_{amido}-CO-C_{py}$ angles in **3** and **5** (average = 109.7°) are all very close to 109°. It is thus clear that conversion of the $-CH_2-$ units to $-CO-$ groups (a change in hybridization from sp^3 to sp^2) hardly changes the angles at this carbon center in these complexes. Indeed, only small changes in the metric parameters are observed during the $[M(pmp)_2]^+ \rightarrow [M(bpca)_2]^+$ transformations (Table 2).

Reactivity of 1 and 2. Scheme 1 represents the various reactions of the iron complexes of pmpH. Formation of Fe(II) complex $[Fe(pmp)_2]$ from pmp$^-$ and $Fe(BF_4)_2·6H_2O$ in methanol (reaction a) has been confirmed by UV−vis spectroscopy. This Fe(II) complex (formed in situ) is converted into $[Fe(pmp)_2]BF_4$ (**1**) by the addition of 1 equiv of $[Fe(Cp)_2]BF_4$ in CH_3OH under anaerobic conditions (step

Scheme 2

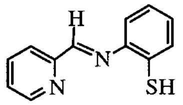


b). Further oxidation of $[Fe(pmp)_2]^+$ to $[Fe(bpca)_2]^+$ (**3**) occurs readily upon exposure of the solution of **1** in DMF to air (step c). The synthesis of complex **3** can also be accomplished by the direct addition of $[Fe(DMF)_6](ClO_4)_3$ to pmp^- (deprotonated by the addition of 1 equiv of NaH) in DMF in the presence of air (step d). We have also found that **3** can be converted to **4** by reacting **3** with 1 equiv of NaH in DMF solutions (step e). The Fe(II) center in **4** is stable in air and does not convert back to **3**. Finally, the conversion of the pmp^- ligand to $bpca^-$ *and* the reduction of the Fe(III) center of **3** can be achieved in a single step (step f). Step f in Scheme 1 is similar to step d except for the fact that 2 equiv of NaH are used to deprotonate pmpH and the reaction is performed in air. Because **3** can be converted to **4** in DMF by the addition of NaH, it is most likely that the excess NaH in the reaction mixture reduces the Fe(III) center of **3** to the Fe(II) center found in **4** in the reaction mixture. In this case, NaH acts as both the base and the reductant.

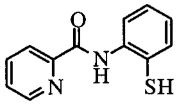
The formations of Co(III) complexes **2** and **5** are included in Scheme 2. Complex **2** can be obtained in crystalline form by oxidizing $[Co(pmp)_2]$ (formed in situ) with $[Fe(Cp)_2]BF_4$ in methanol under anaerobic conditions (steps a, b). If the methanolic solution of $[Co(pmp)_2]$ is exposed to air for a brief period (~1 min), red microcrystalline precipitate of **2** is also obtained in good yield (step c). However, when the reaction mixture is stirred over a period of 10 h, one collects **5** as orange crystals in high yield (step d). The rate of the conversion of $[Co(pmp)_2]$ to **5** is greatly increased when the oxidation of the cobalt(II) species is performed in CH_3OH following the addition 1.5 equiv of 30% H_2O_2 (step e). In this reaction, the oxidation of the cobalt(II) center and the $-CH_2-$ group occurs almost immediately. Finally, it appears that the methylinic carbon centers of pmpH are much less reactive toward oxidation in the case of **2** when compared to **1**. The time necessary for the conversion of **2** to **5** in DMF is longer compared to that for the conversion of **1** to **3**.

The formation of **1** as well as the conversion of **1** to **3** (and **3** to **4**) can be followed by monitoring the changes in the IR spectrum. For example, the carbonyl stretching frequency (ν_{CO}) shifts from 1670 cm^{-1} in free pmpH to 1654 cm^{-1} upon formation of **1**. When the $-CH_2-$ unit of coordinated pmp^- ligand in **1** is converted to the C=O group to afford **3**, a new ν_{CO} is observed at 1724 cm^{-1}. This ν_{CO} is shifted to red in the case of **4** and gives rise to a band at 1701 cm^{-1}. A similar series of changes can be observed in the IR spectrum of the cobalt(III) complexes **2** and **5**. Complex **2** exhibits ν_{CO} at 1650 cm^{-1} (much like **1**) which shifts to 1720 cm^{-1} in **5**.

We believe that the reactivity of the $-CH_2-$ group in both Fe(III) and Co(III) complexes of pmp^- arises from the tendency to achieve conjugation throughout the entire ligand frame upon conversion to $bpca^-$. Formation of a carbonyl (C=O) group is energetically favorable and could also be a driving force. The latter suggestion gets support from a similar reactivity noted by us recently in the case of cobalt(III) complex $[Co(PyAS)_2]^+$.[41] The ligand PyASH is a tridentate Schiff base ligand that we designed and isolated to model the coordination sphere of the active site of the cobalt-containing nitrile hydratase.[42-44] The imine (−C=N−) linkage in the complex $[Co(PyAS)_2]^+$ changes to a carboxamido (−C(O)−N−) group (the product being $[Co(PyPepS)_2]^-$)[7] when the parent complex is stored in air. This conversion of the imine group to a carboxamido moiety in the $PyAS^-$ → $PyPepS^{2-}$ transformation also adds a carbonyl group in the system.



PyASH



$PyPepSH_2$

Conclusion

In summary, an improved synthesis of ligand pmpH is reported. We have synthesized and structurally characterized the Fe(III) complex $[Fe(pmp)_2]^+$ and the homologous Co(III) complex $[Co(pmp)_2]^+$. These two species are the only known $[ML_2]^+$ type complexes of pmp^-. $[Fe(pmp)_2]^+$ and $[Co(pmp)_2]^+$ readily afford $[Fe(bpca)_2]^+$ and $[Co(bpca)_2]^+$, respectively, upon exposure to air. The crystal structure of $[Co(bpca)_2]ClO_4$ is reported here for the first time. The unusual reactivity of the $-CH_2-$ group of pmpH explains the absence of $[Fe(pmp)_2]^+$ in previous accounts and provides

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a better way to synthesize the metal complexes of bpcaH ligand.

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Supporting Information Available: X-ray crystallographic files (in CIF format) and tables for the structure determination of $[Fe(pmp)_2]BF_4$, $[Co(pmp)_2]ClO_4$, and $[Co(bpca)_2]ClO_4 \cdot CH_3OH$. This material is available free of charge via the Internet at http://pubs.acs.org.

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