3258 *Inorg. Chem.* **1999,** *38,* 3258−3260

Carboxamido Nitrogens Are Good Donors for Fe(III): Syntheses, Structures, and Properties of Two Low-Spin Nonmacrocyclic Iron(III) Complexes with Tetracarboxamido-N Coordination

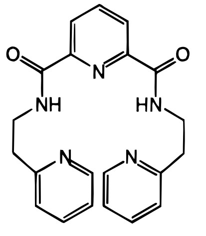
Dana S. Marlin,[†] Marilyn M. Olmstead,[‡] and Pradip K. Mascharak*,[†]

Department of Chemistry and Biochemistry, University of California, Santa Cruz, California 95064, and Department of Chemistry, University of California, Davis, California 95616

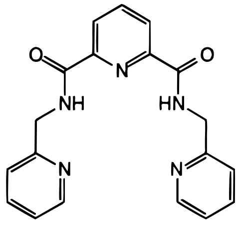
Received December 22, 1998

Introduction

The recent discovery of ligation of deprotonated carboxamido nitrogens from the peptide backbone to iron centers in nitrogenase[1] and nitrile hydratase[2,3] has raised interest in the coordination chemistry of peptide complexes of tervalent iron. For a long time, such coordination was assumed to be improbable since Fe(III) precipitates out at pH values which are much lower than that required for the formation of the deprotonated carboxamido donor center.[4] However, in the past few years, we[5−7] and others[8−10] have structurally characterized stable Fe(III) complexes with coordinated carboxamido nitrogens. It now appears that anionic carboxamido nitrogens are good donors for iron in a +3 or higher oxidation state[11−13] and Fe(III) complexes with even four such nitrogen donors can be synthesized quite readily.[10,14] As part of our continuing research in the area of designed ligands with built-in peptide groups, we have recently reported the copper[15] and cobalt[16] complexes of the pentadentate dipeptide ligand, *N*,*N*-bis[2-(pyridyl)ethyl]pyridine-2,6-dicarboxamide (Py_3PH_2, H atoms are the dissociable carboxamido H atoms). The deprotonated dianionic ligand



Py_3PH_2



$MePy_3PH_2$

Py_3P^{2-} binds Cu(II), Co(II), and Co(III) centers in a pentadentate fashion with five nitrogens situated in two deprotonated carboxamido groups and three pyridine rings. Quite in contrast, our attempts to synthsize the Fe(III) complex of this ligand inevitably afforded the bis complex $[Fe^{III}(Py_3P)_2]^-$ in which two Py_3P^{2-} ligands are coordinated to Fe(III) via the $N_{amide}-N_{pyridine}-N_{amide}$ portion of each ligand. In no case were we able to isolate a complex in which the nitrogens of the pendant pyridine rings are coordinated to the metal. An analogous ligand *N*,*N*-bis[2-(2-pyridyl)methyl]pyridine-2,6-dicarboxamide ($MePy_3PH_2$) also showed similar behavior. In this paper, we report the syntheses, structures, and properties of the two bis complexes. The chemistry of these two ligands clearly indicates that the exceptional stability provided by four carboxamido nitrogens to the Fe(III) center outweighs the chelate effect of the pentadentate ligands. The two complexes $Na[Fe(Py_3P)_2]$ (**1**) and $Na[Fe(MePy_3P)_2]$ (**2**) are the second and third examples of tetracarboxamido Fe(III) complexes derived from nonmacrocyclic ligands. The first example of such a complex has recently been reported by Mukherjee and co-workers.[14]

Experimental Section

Preparation of Compounds. 2,6-Pyridinedicarbonyl dichloride, 2(2-aminoethyl)pyridine, 2(2-aminomethyl)pyridine, and $Fe(ClO_4)_3{\cdot}xH_2O$ were obtained from Aldrich Chemical Co. and used without further purification. $[Fe(DMF)_6](ClO_4)_3$ was prepared by a published procedure.[17] *N*,*N*′-dimethylformamide (DMF) was distilled under vacuum from BaO, and CH_3CN was distilled from CaH_2 prior to use.

Ligands. Py_3PH_2 was synthesized by following a published procedure.[15] $MePy_3PH_2$ was prepared as follows. A solution of 5 g (24.5 mmol) of 2,6-pyridinedicarbonyl dichloride in 100 mL of $CHCl_3$ was added dropwise to a solution of 7.95 g (73.5 mmol) of 2(2-aminomethyl)pyridine in 200 mL of $CHCl_3$ at 0 °C. The mixture was then heated to reflux for 2 h and filtered, and the solvent was removed by rotary evaporation. The solid thus obtained was recrystallized from acetone and dried under vacuum (~70% yield). ^1H NMR (303 K, $CDCl_3$, 250 MHz): δ (ppm from TMS) 4.61 (d, 4H), 7.05 (t, 2H), 7.22 (d, 2H), 7.54 (t, 2H), 7.91 (t, 1H), 8.23 (d, 2H), 8.36 (d, 2H), 9.21 (t, 2H). ^{13}C NMR (298 K, $CDCl_3$): δ (ppm from TMS) 44.35, 122.48, 124.70, 137.08, 138.73, 148.52, 148.93, 157.15, 163.64.

$Na[Fe(Py_3P)_2]{\cdot}DMF$ (1·DMF). A solution of 0.24 g (0.64 mmol) of Py_3PH_2 and 0.03 g (1.27 mmol) of NaH in 5 mL of DMF was slowly added to a solution of 0.25 g (0.32 mmol) of $[Fe(DMF)_6](ClO_4)_3$ in 5 mL of DMF. The resultant orange red solution was stirred for 1 h, and then the solvent was removed under vacuum. The red solid was washed with 5 mL of acetonitrile and redissolved in 3 mL of DMF. Slow diffusion of diethyl ether into this solution afforded large red blocks

---

[†] University of California, Santa Cruz, CA.

[‡] University of California, Davis, CA.

(1) Peters, J. W.; Stowell, M. H.; Soltis, M.; Finnegan, M. G.; Johnson, M. K.; Rees, D. C. *Biochemistry* **1997**, *36*, 1181.

(2) Nagashima, S.; Nakasako, M.; Dohmae, N.; Tsujimura, M.; Takio, K.; Odaka, M.; Yohda, M.; Kamiya, N.; Endo, I. *Nature Struct. Biol.* **1998**, *5*, 347.

(3) Huang, W.; Jia, J.; Cummings, J.; Nelson, M.; Schneider, G.; Lindqvist, Y. *Structure* **1997**, *5*, 691.

(4) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385.

(5) Tao, X.; Stephan, D. W.; Mascharak, P. K. *Inorg. Chem.* **1987**, *26*, 754.

(6) Brown, S. J.; Olmstead, M. M.; Mascharak, P. K. *Inorg Chem.* **1990**, *29*, 3229.

(7) Noveron, J. C.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1998**, *37*, 1138.

(8) Che, C.-M.; Leung, W.-H.; Li, C.-K.; Cheng, H.-Y.; Peng, S.-M. *Inorg. Chim. Acta* **1992**, *196*, 43.

(9) Ray, M.; Mukherjee, R. N.; Richardson, J. F.; Buchannan, R. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2451.

(10) Bartos, M. J.; Kidwell, C.; Kauffmann, K. E.; Gordon-Wylie, S. W.; Collins, T. J.; Clark, G. C.; Münck, E.; Weintraub, S. T. *Angew. Chem., Intl. Ed. Engl.* **1995**, *34*, 1216.

(11) Kostka, K. L.; Fox, B. G.; Hendrich, M. P.; Collins, T. J.; Rickard, C. E. F.; Wright, L. J.; Münck, E. *J. Am. Chem. Soc.* **1993**, *115*, 6746.

(12) Collins, T. J.; Fox, B. G.; Hu, Z. G.; Kostka, K. L.; Münck, E.; Rickard, C. E. F.; Wright, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 8724.

(13) Collins, T. J.; Kostka, K. L.; Münck, E.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 5637.

(14) Ray, M.; Ghosh, D.; Shirin, Z.; Mukherjee, R. *Inorg. Chem.* **1997**, *36*, 3568.

(15) Chavez, F. A.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1996**, *35*, 1410.

(16) Chavez, F. A.; Nguyen, C. V.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1996**, *35*, 6282.

(17) Hodgkinson, J.; Jordan, R. B. *J. Am. Chem. Soc.* **1973**, *95*, 763.

10.1021/ic981461c CCC: $18.00

Table 1. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for Na[Fe(Py$_3$P)$_2$]·DMF (**1**·DMF) and Na[Fe(MePy$_3$P)$_2$]·1.5CH$_3$CN·0.5DMF (**2**·1.5CH$_3$CN·0.5DMF)

	1	**2**
empirical formula	$C_{45}H_{45}N_{11}NaO_5Fe$	$C_{42.5}H_{38}N_{12}NaO_{4.5}Fe$
fw	898.76	867.69
cryst size, mm	0.50 × 0.40 × 0.30	0.30 × 0.30 × 0.10
cryst habit	block	plate
cryst color	red	orange
cryst system	monoclinic	triclinic
space group	$P2_1$	$P\bar{1}$
a, Å	10.723(2) ($\alpha = 90°$)	10.694(3) ($\alpha = 97.26(2)°$)
b, Å	14.018(3) ($\beta = 99.67(2)°$)	10.955(3) ($\beta = 94.30(2)°$)
c, Å	14.268(3) ($\gamma = 90°$)	18.573(5) ($\gamma = 107.79(2)°$)
vol, Å^3	2114.2(7)	2040.3(10)
Z	2	2
density (calcd), g cm^{-3}	1.412	1.412
abs coeff, mm^{-1}	0.428	0.441
max and min transm	0.935 and 0.884	0.9572 and 0.8790
R1[a]	0.0326	0.0562
wR2[b]	0.0766	0.1244

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

of **1**·DMF in 20% yield. Anal. Calcd for $C_{45}H_{45}N_{11}NaO_5Fe$: C, 60.11; H, 5.05; N, 17.15. Found: C, 59.98; H, 5.17; N, 17.32.

Na[Fe(MePy$_3$P)$_2$]·1.5CH$_3$CN·0.5DMF (2·1.5CH$_3$CN·0.5DMF). To a stirring solution of 0.92 g (2.6 mmol) of MePy$_3$PH$_2$ and 0.13 g (5.3 mmol) of NaH in 5 mL of DMF was added a solution of 1.03 g (1.32 mmol) of [Fe^{III}(DMF)$_6$](ClO4)$_3$ in 5 mL of DMF, and a deep red solution resulted. After 1 h, a batch of 20 mL of acetonitrile was added to it and the mixture was stored at room temperature. A microcrystalline red solid was isolated in 70% yield after 12 h. Anal. Calcd for $C_{42.5}H_{38}N_{12}NaO_{4.5}Fe$: C, 58.81; H, 4.42; N, 19.38. Found: C, 58.48; H, 4.27; N, 19.78.

X-ray Data Collection and Structure Solution and Refinement. Red blocks of **1**·DMF were grown by slow diffusion of diethyl ether into a DMF solution of the complex while orange plates of **2**·1.5CH$_3$CN·0.5DMF were obtained by diffusion of diethyl ether into DMF/CH$_3$CN solution. The structure of **1** consists of discrete [Fe(Py$_3$P)$_2$]$^-$ anions, and the Na$^+$ ions are coordinated to oxygens of the ligated carboxamido groups, oxygen from the lattice DMF molecule, and one or two nitrogens of the pendant pyridine rings. The structure of **2** is very similar except for disorder around the Na$^+$ ions. The disorder has been modeled with two different arrangements (each 50% occupancy) of solvent molecules around the Na$^+$ ions (see Supporting Information). Diffraction experiments were performed on a Siemens R3m/V machine equipped with a low-temperature apparatus. Data were collected at 130 K, and the structures were solved by direct methods (SHELXL-97, Sheldrick, 1997). The crystal data for the two complexes are included in Table 1 while selected bond distances and angles are listed in Table 2.

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. EPR spectra at X-band frequencies were obtained with a Bruker ESP-300 spectrometer. Electrochemical measurements were performed with standard Princeton Applied Research instrumentation using a Pt electrode and an aqueous saturated calomel electrode (SCE).

Results and Discussion

Syntheses of Na[Fe(Py$_3$P)$_2$] (**1**) and Na[Fe(MePy$_3$P)$_2$] (**2**) are noteworthy for several reasons. First, the bis complexes are formed regardless of the ligand to metal stoichiometry. When the Fe:ligand ratio is 1:1, the bis complexes are formed despite the presence of the remaining 0.5 equiv of Fe(III) in the reaction mixture. This indicates that the anionic carboxamido nitrogens provide exceptional stability to Fe(III) centers. Further support to this conclusion comes from the fact that addition of strong ligands such as CN$^-$, N$_3^-$, and DMAP (DMAP = (dimethylamino)pyridine) to solutions of **1** or **2** does not promote any further reaction. Second, unlike the previous syntheses of Fe(III) carboxamido complexes, which generally involve formation of the Fe(II) complexes followed by oxidation,[9,11−14] the present syntheses begin with Fe(III) sources. Third, both complexes are very stable in a variety of solvents including water. Although they are conveniently synthesized in DMF, these complexes show no reactivity when dissolved in water. Other Fe(III) and Fe(IV) complexes with coordinated carboxamido nitrogens also show stability in aqueous medium.[11−14] Thus, the common notion that the strongly basic carboxamido nitrogens are readily attacked by water appears unlikely in this chemistry. Also, aqueous solutions of **1** and **2** do not afford any oxo- or hydroxo-bridged dimeric (or polymeric) Fe(III) complexes which are often recognized as thermodynamically very stable entities in the hydrolytic coordination chemistry of iron.[18,19]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Na[Fe(Py$_3$P)$_2$]·DMF (**1**·DMF) and Na[Fe(MePy$_3$P)$_2$]·1.5CH$_3$CN·0.5DMF (**2**·1.5CH$_3$CN·0.5DMF)

	1	**2**
Fe−N(2)	1.946(2)	1.958(3)
Fe−N(3)	1.876(2)	1.881(3)
Fe−N(4)	1.968(2)	1.943(3)
Fe−N(7)	1.964(2)	1.950(3)
Fe−N(8)	1.875(2)	1.881(3)
Fe−N(9)	1.971(2)	1.971(3)
N(2)−Fe−N(3)	81.24(10)	81.02(12)
N(2)−Fe−N(4)	161.80(9)	162.04(12)
N(2)−Fe−N(7)	94.67(10)	91.04(12)
N(2)−Fe−N(8)	99.91(10)	99.15(12)
N(2)−Fe−N(9)	90.18(9)	90.55(12)
N(3)−Fe−N(7)	97.65(10)	96.33(12)
N(3)−Fe−N(8)	178.32(10)	177.61(13)
N(3)−Fe−N(9)	100.09(10)	101.78(12)
N(4)−Fe−N(7)	91.57(9)	92.61(12)
N(4)−Fe−N(8)	97.93(9)	98.79(12)
N(4)−Fe−N(9)	89.06(9)	91.42(12)
N(7)−Fe−N(8)	81.06(10)	81.28(12)
N(7)−Fe−N(9)	162.12(9)	161.84(12)
N(8)−Fe−N(9)	81.15(10)	80.61(12)

Structures. The structures of the anions of **1** and **2** are shown in Figure 1. In both complexes, the iron atom is coordinated by two ligands in a *mer* geometry and the four deprotonated carboxamido nitrogens reside in the equatorial plane. The pendant pyridine arms are oriented in space in a propellerlike fashion (Figure 1). The overall structure is more compact in the case of **2** (Table 2). The average Fe(III)−N$_{amido}$ distances in **1** and **2** are 1.962(3) and 1.955(3) Å, respectively. These values are greater than the average Fe(III)−N$_{amido}$ distances observed in Fe(III) complexes of macrocyclic anionic ligands with four carboxamido nitrogens (1.927(16), 1.877(8) Å).[10−13] In the case of the nonmacrocyclic Fe(III) complex with four carboxamido nitrogens,[14] the average Fe(III)−N$_{amido}$ distance is somewhat longer (1.971(3) Å). The average Fe(III)−N$_{py}$ (py = pyridine) distances in **1** and **2** are noticeably shorter (1.875(2) and 1.881(3) Å, respectively) than typical Fe(III)−N$_{py}$ distances in complexes with pyridine donor groups.[20,21] We believe that formation of two adjacent five-membered chelate rings in the Fe(III)/N$_{amide}$−N$_{pyridine}$−N$_{amide}$ portion of the

---

(18) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344.
(19) Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1.
(20) Arulsamy, N.; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 4531.
(21) Bernhardt, P. V.; Comba, P.; Mahu-Rickenbach, A.; Steblere, S.; Steiner, S.; Varnagy, K.; Zehnder, M. *Inorg. Chem.* **1992**, *31*, 4194.

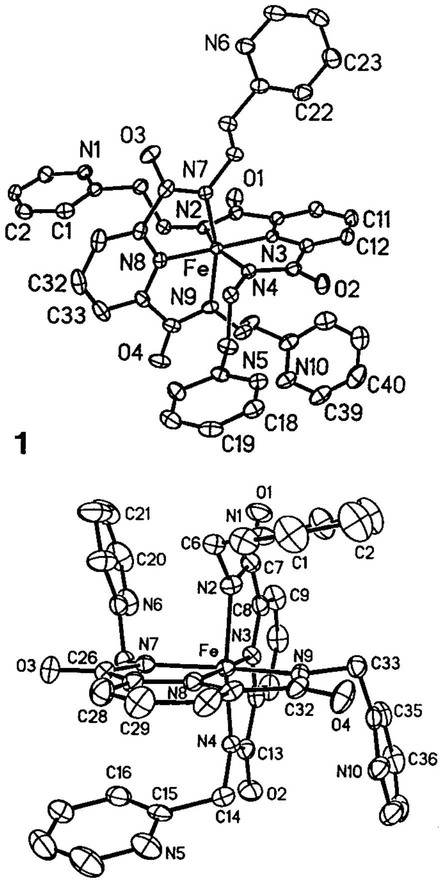


Figure 1. Thermal ellipsoid plot of the anions of **1** and **2** (50% probability level) showing the numbering scheme. H atoms are omitted for the sake of clarity.

complexes as well as strong donor capacity of the carboxamido nitrogens gives rise to the short Fe(III)$-$N$_{py}$ distances in **1** and **2**.

Properties. Coordination of carboxamido nitrogens to Fe(III) in **1** and **2** is readily indicated by the red shift of the ν_{C-O} to 1593 cm^{-1} from 1654 cm^{-1} for Py$_3$PH$_2$ and 1665 cm^{-1} for MePy$_3$PH$_2$. Also, the N$-$H stretching frequencies of the free ligands (Py$_3$PH$_2$, 3318 cm^{-1}; MePy$_3$PH$_2$, 3307 cm^{-1}) are absent in the IR spectra of the iron complexes. Complexes **1** and **2** dissolve in solvents such as DMF, H$_2$O, and MeOH to give orange-red solutions. The color arises from strong ligand-to-metal charge-transfer (LMCT) absorption around 450 nm.[14] For example in DMF, **1** and **2** exhibit complex absorption with λ_{max} at 455 nm (ϵ = 9000 M^{-1} cm^{-1}) and 445 nm (ϵ = 8400 M^{-1} cm^{-1}), respectively. In water, both complexes exhibit absorption at 430 nm.

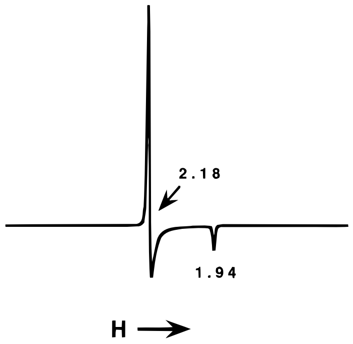


Figure 2. X-band EPR spectrum (100 K) of **2** in DMF glass. Selected *g* values are indicated. Spectrometer settings: microwave frequency, 9.43 GHz; microwave power, 10 mW; modulation frequency, 100 kHz; modulation amplitude, 2 G.

The Fe(III) centers in **1** and **2** are low-spin due to the strong donor capacity of carboxamido nitrogens. In DMF glass (100 K), both complexes exhibit axial EPR signals with $g_{\perp}$=2.18 and $g_{\|}$ = 1.94 (Figure 2). Since the half-wave potential ($E_{1/2}$) values for **1** and **2** in DMF are $-$0.95 and $-$1.05 V vs SCE, it appears that MePy$_3$P^{2-} provides more stability to Fe(III) center compared to Py$_3$P^{2-}.

In conclusion, the syntheses of the two stable low-spin Fe(III) complexes with four carboxamido nitrogens in the first coordination sphere demonstrate that coordination of such donors to the Fe(III) center is quite feasible. Also, the resulting complexes are very stable in water, a fact that indicates that coordination to Fe(III) centers lowers the inherent basicity of the carboxamido nitrogens and prevents hydrolytic decomposition. Finally, the propensity for formation of bis complexes with Py$_3$PH$_2$ and MePy$_3$PH$_2$ demonstrates that the high affinity of Fe(III) centers toward carboxamido nitrogens could compete with the chelate effect of multidentate ligands.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-9818492).

Supporting Information Available: Figure depicting the coordination of Na$^+$ in the crystal lattice of **2**$\cdot$1.5CH$_3$CN$\cdot$0.5DMF (Figure S1) and tables listing crystal structure data for Na[Fe(Py$_3$P)$_2$]$\cdot$DMF (**1**$\cdot$DMF) and Na[Fe(MePy$_3$P)$_2$]$\cdot$1.5CH$_3$CN$\cdot$0.5DMF (**2**$\cdot$1.5CH$_3$CN$\cdot$0.5DMF) including atomic coordinates and isotropic thermal parameters, bond distances and angles, anisotropic thermal parameters, and H-atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

IC981461C