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Synthesis of a Clathrochelate Complex with an Appended Pyridine and Its Coordination to a Cobaloxime Complex

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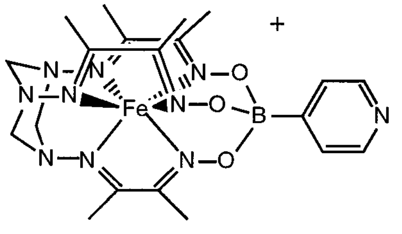
Introduction

Numerous approaches have been taken to incorporate multiple metal sites into a clathrochelate-based molecule. Hendrickson, Gagne, Sinn, and co-workers[1] have developed a clathrochelate system in which two metal ions are encapsulated within a single ligand cage derived from the condensation of 2 mol of 2,2′,2″-triaminotriethylamine and 3 mol of 2-hydroxy-5-methylisophthalaldehyde. A similar approach has been utilized by Voloshin and co-workers[2] and Sahoo and co-workers[3] to encapsulate two metal ions using a diacetylazine oxime ligand system which is closed off by either tin- or boron-containing capping groups. Drago and Elias[4] and Chaudhuri and co-workers[5−7] have utilized tris(dioximato) complexes as bridging ligands which are "capped" by metal complexes to produce trinuclear species in which the central metal ion is encapsulated. Wherland and co-workers[8] have synthesized a tris(dioximato)cobalt clathrochelate which is capped by ferrocenylboronate groups, thereby producing a trimetallic complex. The iron analogue of this trinuclear complex has been synthesized and studied by Voloshin and his group.[9]

We have been exploring methods of linking clathrochelate complexes to other metal complexes for the purpose of electron-transfer studies. Studies of clathrochelate systems based on bifunctional oxime−hydrazone chelating ligands have resulted in the successful synthesis of binuclear clathrochelate species[10,11] and clathrochelates appended to and bridged by ferrocenyl species.[12] In this paper, this series of complexes is extended by the synthesis of a clathrochelate complex with an appended pyridyl group. The ability of this pyridyl group to link the clathrochelate to another metal complex is demonstrated by coordination of the clathrochelate to a cobaloxime complex.



$[Fe(BMXY)_3(CH_2)_3(BC_5H_4N)]^+$

Experimental Section

Materials. 2,3-Butanedione oxime hydrazone (BMXY) was prepared by the reaction of 2,3-butanedione monooxime (Aldrich) with an excess of hydrazine monohydrate in ethanol as described previously.[13] 4-Pyridineboronic acid was prepared by the method of Fischer and Havinga.[14] Dibromo(1,2-cyclohexanedione dioxime)(1,2-cyclohexanedione dioximato)cobalt(III) was prepared by a variation[15] of the procedure used by Marzilli and co-workers.[16] All other reagents were obtained commercially ($FeBr_2$, Strem; all others, Aldrich) and used as received.

[4-Pyridyl[[3,3′,3″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(2-butanone) trioximato](3−)-O^2,$O^{2'}$,$O^{2''}$]borato(1−)]iron(1+) Hexafluorophosphate(1−), $[Fe(BMXY)_3(CH_2)_3(BC_5H_4N)]PF_6\cdot C_2H_5OH$. A 0.90 g (7.8 mmol) sample of BMXY was dissolved in 15 mL of absolute ethanol, and the solution was outgassed with N_2. Solid ferrous bromide (0.56 g; 2.6 mmol) was added, and the mixture was stirred until a dark red solution was produced. A 0.31 g (2.6 mmol) sample of 4-pyridineboronic acid was added, and the mixture was stirred for 1 h. The solution was cooled, and the red product, $[Fe(BMXY)_3(BC_5H_4N)]$-Br, was collected via suction filtration and washed with ethanol followed by ethyl ether. Yield: 0.54 g (0.95 mmol). A second crop of the complex was isolated as the hexafluorophosphate salt by treating the filtrate with a solution of 0.5 g (3.1 mmol) of NH_4PF_6 dissolved in a minimum of absolute ethanol and concentrating the resultant mixture. This second crop (0.53 g; 0.85 mmol) produced a combined yield of 70% for the intermediate.

The combined yields of both salts were dissolved in 90 mL of acetonitrile, and the mixture was treated with 6 mL (15-fold molar excess) of formaldehyde solution (37% in H_2O). One drop of hexafluorophosphoric acid (60% in H_2O) was added as a catalyst. After the solution was stirred for 15 h, an excess of NH_4PF_6 (2.5 g; 15 mmol) in a minimum of ethanol was added and the mixture was rotary-evaporated until solid formed. The crude product was collected via suction filtration and washed with ethanol followed by ethyl ether. The product was purified by redissolving it in a minimum of acetonitrile and passing the solution down a neutral alumina column (Brockmann Activity III) using acetonitrile as the eluant. The first band to elute was collected and rotary-evaporated to half of its original volume. The concentrate was treated with approximately 100 mL of absolute ethanol, and the resulting solution was rotary-evaporated to produce a dark red crystalline product, which was isolated via suction filtration, washed successively

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[1] Timken, M. D.; Marritt, W. A.; Hendrickson, D. N.; Gagne, R. A.; Sinn, E. *Inorg. Chem.* **1985**, *24*, 4202.

[2] Voloshin, Y. Z.; Varzatskii, O. A.; Tkachenko, E. Y.; Maletin, Y. A.; Degtyarov, S. P.; Kochubey, D. I. *Inorg. Chim. Acta* **1997**, *255*, 255.

[3] Bhattacharya, U.; Pujapanda, P. K.; Rout, A. K.; Sahoo, B. *Indian J. Chem.* **1993**, *32A*, 91.

[4] Drago, R. S.; Elias, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 6570.

[5] Chaudhuri, P.; Winter, M.; Della Vedova, B. P. C.; Fleischhauer, P.; Haase, W.; Florke, U.; Haupt, H.-J. *Inorg. Chem.* **1991**, *30*, 4777.

[6] Birkelbach, F.; Weyhermuller, T.; Lengen, M.; Gerdan, M.; Trautwein, A. X.; Wieghardt, K.; Chaudhuri, P. *J. Chem. Soc., Dalton Trans.* **1997**, 4529.

[7] Burdinski, D.; Birkelbach, F.; Weyhermuller, T.; Florke, U.; Haupt, H.-J.; Lengen, M.; Trautwein, A. X.; Eckhard, B.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **1998**, *37*, 1009.

[8] Murgia, M. A.; Borchardt, D.; Wherland, S. *Inorg. Chem.* **1990**, *29*, 1982.

[9] Voloshin, Y. Z.; Kron, T. E.; Belsky, V. K.; Zavodnik, V. E.; Maletin, Y. A.; Kozachkov, S. G. *J. Organomet. Chem.* **1997**, *536−537*, 207.

[10] Belinski, J. A.; Squires, M. E.; Kuchna, J. M.; Bennett, B. A.; Grzybowski, J. J. *J. Coord. Chem.* **1988**, *19*, 159.

[11] Grzybowski, J. J.; Allen, R. D.; Belinski, J. A.; Bieda, K. L.; Bish, T. A.; Finnegan, P. A.; Hartenstein, M. L.; Regitz, C. S.; Ryalls, D. M.; Squires, M. E.; Thomas, H. J. *Inorg. Chem.* **1993**, *32*, 5266.

[12] Bieda, K. L.; Kranitz, A. L.; Grzybowski, J. J. *Inorg. Chem.* **1993**, *32*, 4209.

[13] Forster, M. O.; Dey, B. B. *J. Chem. Soc.* **1912**, *101*, 2234.

[14] Fischer, F. C.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 439.

[15] Jameson, D. L.; Grzybowski, J. J.; Hammels, D. E.; Castellano, R. K.; Hoke, M. E.; Freed, K.; Basquill, S.; Mendel, A.; Shoemaker, W. J. *J. Chem. Educ.* **1998**, *75*, 447.

[16] Trogler, W. C.; Stewart, R. C.; Epps, L. A.; Marzilli, L. G. *Inorg. Chem.* **1974**, *13*, 1564.

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Table 1. Crystallographic Data for $[Fe(BMXY)_3(CH_2)_3\{(BC_5H_4N)Co(NOXH)_2Br\}]PF_6\cdot0.5\ MeOH$ (**1**)

formula	$C_{32.50}H_{48}BBrCoF_6FeN_{14}O_{7.5}P$	Z	2
fw	1105.32	cryst color, habit	red thin plate
space group	$P\bar{1}$	D(calc), g cm^{-3}	1.597
a, Å	9.1044(2)	μ(Mo Kα), cm^{-1}	16.66
b, Å	14.7918(2)	temp, K	213(2)
c, Å	17.7688(2)	diffractometer	Siemens P4/CCD
α, deg	84.5085(2)	radiation (λ, Å)	Mo Kα (0.710 73)
β, deg	76.4880(2)	$R(F)$,^{a} %	7.19
γ, deg	81.7951(2)	$R(wF^2)$,^{a} %	17.82
V, Å^3	2298.04(4)		

[a] Quantity minimized: $R(wF^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. $R = \sum\Delta/\sum|F_o|$; $\Delta = |F_o - F_c|$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [2F_c^2 + \mathrm{Max}(F_o^2, 0)]/3$.

with ethanol and ethyl ether, and dried in vacuo at 78 °C. Yield: 0.86 g (50% overall). UV−vis (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 494 (1.4×10^4). NMR (CD_3CN): ^{1}H δ 2.47 (s, 9H), 2.53 (s, 9H), 3.50 (d, J = 13 Hz, 3H), 5.24 (d, J = 13 Hz, 3H), 7.70 (d, J = 6 Hz, 2H), 8.57 (d, J = 6 Hz, 2H); ^{13}C{^{1}H} δ 13.2, 16.9, 73.9, 126.4, 148.3, 153.5, 167.7. Anal. Calcd for $C_{22}H_{34}N_{10}O_4BFePF_6$: C, 37.00; H, 4.80; N, 19.61. Found: C, 36.65; H, 5.17; N, 19.87.

Coordination to a Cobaloxime Complex. $[Fe(BMXY)_3(CH_2)_3\{(BC_5H_4N)Co(NOXH)_2Br\}]PF_6$ (1). A 0.078 g (0.11 mmol) sample of dibromo(1,2-cyclohexanedione dioxime)(1,2-cyclohexanedione dioximato)cobalt(III) suspended in 20 mL of methanol was treated with 0.076 g (0.11 mmol) of $[Fe(BMXY)_3(CH_2)_3(BC_5H_4N)]PF_6\cdot C_2H_5OH$. A 0.015 mL (0.11 mmol) portion of triethylamine was added, and the reaction mixture was stirred until the green solid that had appeared completely dissolved and was replaced by a red crystalline solid. The product was isolated via suction filtration, washed with a small amount of methanol, and dried in vacuo at 78 °C. Yield: 0.11 g (91%). UV−vis (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 489 (1.2×10^4). NMR (DMSO-d_6): ^{1}H δ 1.65 (br, 8H), 2.41 (s, 9H), 2.51 (s, 9H), 2.86 (br, 8H), 3.60 (d, J = 13 Hz, 3H), 5.40 (d, J = 13 Hz, 3H), 7.78 (br, 2H), 8.00 (br, 2H), 10.5 (br, 2H); ^{13}C{^{1}H} δ 13.3, 17.0, 20.6, 25.5, 73.9, 128.8, 148.4, 153.2, 154.0, 167.9. Anal. Calcd for $C_{28}H_{42}N_{14}O_7BFeCoBrPF_6$: C, 35.25; H, 4.22; N, 17.99. Found: C, 35.38; H, 4.44; N, 17.36.

Crystallographic Structure Determination. Crystals of **1** suitable for an X-ray diffraction study were isolated from mixtures that contained 1:1 molar ratios of $[Fe(BMXY)_3(CH_2)_3(BC_5H_4N)]PF_6\cdot C_2H_5OH$ to $[Co^{III}\{(NOXH_2)NOXH\}Br_2]$ in minimum amounts of methanol which were allowed to sit undisturbed for 2 weeks.

The single-crystal X-ray diffraction experiment was performed on a Siemans P4/CCD diffractometer. Crystal, data collection, and refinement parameters are given in Table 1. No symmetry higher than triclinic was observed for the data of **1**. The E statistics suggested the centrosymmetric option, $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix, least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and all hydrogen atoms were treated as idealized contributions. Compound **1** is a hemimethanolate; the protons of the disordered solvent molecule were not located but were included in the global refinement parameters. A thermal ellipsoid plot of the complex cation of **1** is shown in Figure 1. All software and sources of the scattering factors are contained in the SHELXTL (5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Physical Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker NR/80 FT spectrometer (AF series). Acetonitrile-d_3 and dimethyl-d_6 sulfoxide were used as solvents, and tetramethylsilane was used as the internal reference. Visible and UV spectra were obtained using a Milton-Roy Spectronic 3000 diode array spectrometer with acetonitrile as the solvent. Elemental analyses were performed by Galbraith Labs, Inc., Knoxville, TN.

For all electrochemical measurements, acetonitrile (Aldrich, anhydrous, 99+%) that had been outgassed with purified nitrogen was used as the solvent and tetra-n-butylammonium tetrafluoroborate (TBAB) was used as the electrolyte. Cyclic voltammetry was performed using a Bioanalytical Systems CV-50W voltammetric analyzer coupled to a Gateway 2000 computer. A 20 mL cylindrical cell was used in conjunction with a platinum disk working electrode, a platinum wire counter electrode, and a 3.0 M NaCl/silver/silver chloride reference electrode.[17]

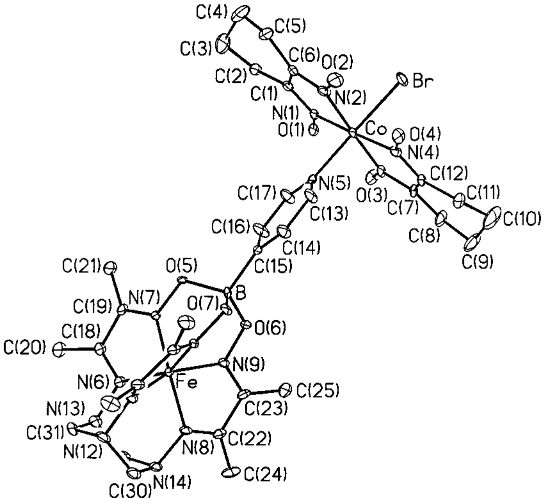

Figure 1. Thermal ellipsoid plot of $[Fe(BMXY)_3(CH_2)_3\{(BC_5H_4N)Co(NOXH)_2Br\}]PF_6\cdot0.5CH_3OH$ drawn at 30% probability. Hydrogen atoms, counterions, and the disordered solvent molecule have been omitted for clarity.

Results and Discussion

Synthesis. The synthesis of the "clathropyridine" complex, $[Fe(BMXY)_3(CH_2)_3(BC_5H_4N)]PF_6$, closely follows the established protocol for synthesizing clathrochelate complexes based on oxime−hydrazone ligands.[10−12] The one difference encountered is the occurrence of protonation on the pyridine ring. The protonated product, $[Fe(BMXY)_3(CH_2)_3(BC_5H_4NH)](PF_6)_2$, is isolated from the acid-catalyzed capping reaction with formaldehyde, and the complex remains protonated on recrystallization from acetonitrile/ethanol. Passage of an acetonitrile solution of the protonated complex down a neutral alumina column (Brockmann Activity III) produces a red crystalline sample of the deprotonated complex on evaporation and treatment with ethanol. NMR and elemental analysis data show that the compound contains an ethanol of crystallization which resists removal in vacuo at 78 °C. It is likely that this ethanol of solvation is hydrogen-bonded to the deprotonated pyridine nitrogen.

Nuclear Magnetic Resonance Spectra. Complete formation of the clathrochelate ligand is indicated by the appearance of the pair of doublets (5.0−5.4 and 3.3−3.8 ppm; J = 13 Hz) in the ^{1}H NMR spectrum which arise because of geminal coupling between the axial and equatorial methylene protons in the 1,3,5-triazacyclohexane capping group. Proton NMR spectroscopy is also very useful in determining whether the pyridine group is protonated or deprotonated. A broad resonance centered at 4.1 ppm is observable for the protonated species; however, this broad resonance can be difficult to observe. A more easily observed indicator of protonation is the distance between the signals in the AA′BB′ splitting pattern of the pyridine protons. In the protonated species, these signals are separated by 0.2 ppm; on deprotonation, the separation of these signals increases to 0.8 ppm. ^{1}H NMR spectroscopy of the "clathropyridine−

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(17) The ferrocene/ferrocenium couple occurs at a potential of +0.45 V under the described experimental conditions.

cobaloxime" complex shows that this separation of the resonances due to the pyridine protons can also be utilized to determine whether the pyridine is coordinated or not to the "cobaloxime." Coordination produces a 0.2 ppm signal separation very similar to that observed on protonation.

The ^{13}C spectra of the complexes illustrate the high degree of symmetry in these molecules. The spectrum of the clathropyridine complex exhibits only seven signals: two for the methyl carbons (13.2 and 16.9 ppm), two for the azomethine carbons (153.5 and 167.7 ppm), one for the capping methylene (73.9 ppm), and two for the pyridine ring carbons (148.3 and 126.4 ppm). It should be noted that the third pyridine carbon is not observed due to the fact that the boron nuclear spins are not decoupled from the carbon nuclear spin, which results in a highly split and broadened signal that is further reduced in intensity because it experiences no nuclear Overhauser enhancement. On coordination of the clathropyridine complex to the cobaloxime, the number of signals in the ^{13}C spectrum increases accordingly, with the observation of a third azomethine signal (153.2 ppm) and two more methylene signals (20.6 and 25.48 ppm).

Electrochemical Studies. Cyclic voltammetric studies of iron clathrochelate complexes of this family usually reveal a quasireversible oxidation to Fe^{3+} and a quasireversible reduction nominally to Fe^{+}. For example, the complex capped with phenylboronic acid, $[Fe(BMXY)_3(CH_2)_3(BC_6H_5)]PF_6$,[10] undergoes oxidation at +1.19 V ($\Delta = 66$ mV) and reduction at −1.00 V ($\Delta = 70$ mV). The clathropyridine complexes behave differently depending on whether they are protonated or not. Cyclic voltammetry of the protonated species, $[Fe(BMXY)_3(CH_2)_3(BC_5H_4NH)](PF_6)_2$, exhibits an oxidative couple at +1.23 V ($\Delta = 66$ mV) and a reductive couple at −0.96 V ($\Delta = 66$ mV). In addition to these redox couples, a second reduction which is completely irreversible appears at a cathodic peak potential of −0.58 V and is assigned to the reduction of the H^+ that is protonating the pyridine nitrogen. The deprotonated species, $[Fe(BMXY)_3(CH_2)_3(BC_5H_4N)]PF_6$, reveals a comparable quasireversible reduction at −0.96 V ($\Delta = 65$ mV), no reduction at −0.58 V, and an irreversible oxidation with an anodic peak potential of +1.34 V which has an "*n*" value greater than 1 and is likely due to an ECE mechanism involving the deprotonated pyridine. The cyclic voltammogram of the clathropyridine−cobaloxime species (Figure 2) is quite complex owing to the numerous irreversible and quasireversible processes associated with the cobaloxime species; however, superimposed on this complex background, the typical quasireversible couples of the oxidative and reductive processes of the clathrochelate complex can be observed at approximately +1.2 and −0.95 V.

X-ray Crystallographic Studies. The X-ray crystal structure of $[Fe(BMXY)_3(CH_2)_3\{(BC_5H_4N)Co(NOXH)_2Br\}]PF_6{\cdot}0.5\,MeOH$ indicates that the environment around cobalt(III) is essentially octahedral with Co−N(macrocycle) bond lengths ranging from 1.883 to 1.892 Å. The Co−N(pyridine) bond length is 1.968 Å, and the Co−Br bond length is 2.389 Å. Iron(II) is in a distorted trigonal prismatic environment with Fe−N bond lengths ranging from 1.907 to 1.930 Å. The twist angle between the two N_3 faces, which measures the distortion from trigonal prismatic geometry, is found to be 21.3°. The crystal structure of a similar iron clathrochelate complex, $[Fe(BMXY)_3(HCOC_2H_5)_3(BC_6H_5)]BF_4$, has been examined by Voloshin[18] and found to have a distorted trigonal prismatic environment around iron (twist angle 18.3°), with Fe−N bonds averaging approximately 1.91 Å. The dioxime-based clathrochelate complex $[Fe(NOX)_3(BC_4H_9)_2]$ is also quite similar in geometry with a twist angle of 20.3° and Fe−N bond lengths averaging 1.92 Å.[19]

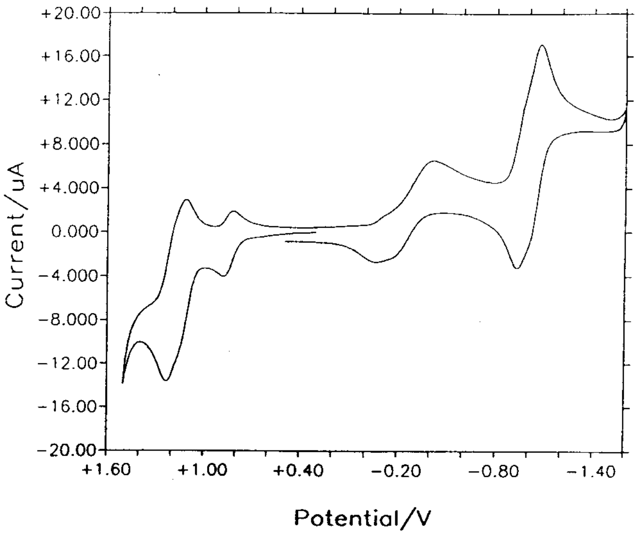

Figure 2. Cyclic voltammogram of $[Fe(BMXY)_3(CH_2)_3\{(BC_5H_4N)Co(NOXH)_2Br\}]PF_6$ (1.0 mM) in CH_3CN (0.1 M in TBAB). The initial potential is +0.30 V versus the saturated silver chloride electrode, and scanning is begun anodically at 100 mV/s.

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Supporting Information Available: Tables of detailed crystallographic data, atomic positional parameters, thermal parameters, and bond lengths and angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Voloshin, Y. Z.; Stash, A. I.; Varzatshii, O. A.; Belsky, V. K.; Maletin, Y. A.; Strizhakova, N. G. *Inorg. Chim. Acta* **1999**, *284*, 180.

(19) Kubow, S. A.; Takeuchi, K. J.; Grzybowski, J. J.; Jircitano, A. J.; Goedken, V. L. *Inorg. Chim. Acta* **1996**, *241*, 21.