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A Novel Diiron Complex: a Bimetallic System with Both High- and Low-spin Fe(II) Centers

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Abstract

The bimetallic complexes $[(H_2O)_4Fe(bpm)Fe(CN)_4]$ and $[(H_2O)_4Co(bpm)Fe(CN)_4]$, where bpm = 2,2′-bipyrimidine have been prepared and characterized by UV–Vis, IR, and Mössbauer spectroscopies. The Mössbauer spectrum of the diiron system is similar to the sum of the spectra of d^6 low-spin $Fe(CN)_4bpm^{2-}$ and d^6 high-spin $Fe(H_2O)_4bpm^{2+}$. The Co/Fe mixed-metal bimetallic system shows only a single d^6 low-spin Fe(II) center in the ^{59}Fe Mössbauer spectrum. The diiron system is the first small molecular unit reported where low-spin and high-spin Fe(II) centers exist in close proximity.

Introduction

There have been several articles concerning the preparation of transition metal complexes of the form $M(bpm)_{3-n}L_{2n}$ (where bpm = 2,2′-bipyrimidine and M = Cr [1], Co [2], Mo [3], W [1], Ru [4–8], Fe [9–12] or Ni [13]). The interest in bpm as a ligand derives from its ability to chelate simultaneously two metal centers. This results in the formation of a metal–ligand–metal framework that has a characteristically short metal–metal distance and a bridging ligand π-system that allows good electronic communication between the metal centers [14]. In fact, there is better communication in these systems than in many of the monodentate bridges that have been previously used [15–18]. When we initiated this study, there were no literature reports of the bpm ligand bridging first-row metal centers. In an effort to prepare an unsymmetrical, spin-paired diiron system, we took an aqueous solution of $Fe(CN)_4bpm^{2-}$ and added one equivalent of Fe^{2+}. Before we had the opportunity to add four coordination site equivalents of a strong-field ligand for the second iron center, the precipitate that is described in this work had formed rendering the supernatant solution colorless.

Experimental

Materials

Analytical reagent grade chemicals and solvents were used for all preparations described in this work. Water, which was used for all syntheses, was redistilled from alkaline permanganate in an all-glass apparatus. The bpm (Alfa, Inorganics) had a proton-decoupled ^{13}C NMR spectrum in D_2O corresponding to $C_\alpha = 159.0$ ppm and $C_\beta = 123.4$ ppm *versus* TMS (dioxane at 69.4 ppm *versus* TMS used as an internal reference). Potassium bromide for infrared spectra were spectroquality and dried in a vacuum oven before use.

Syntheses

The monometallic complex, $K_2[Fe(CN)_4bpm]$ was prepared by a procedure reported previously [9].

$[Fe(H_2O)_4bpm]Cl_2$

The tetraaquo-2,2′-bipyrimidineiron(II) dichloride was prepared by dissolving 0.311 g (1.56 mmol) of $FeCl_2 \cdot 4H_2O$ in 20 ml of H_2O. To this solution, 0.418 g (2.64 mmol) of solid bpm was added followed by the addition of 200 ml of acetone to produce a gray precipitate. The precipitate was collected, washed with ether, and dried under vacuum. A typical reaction gave 90% yield.

$[(H_2O)_4Fe(bpm)Fe(CN)_4]$

This electrically neutral diiron complex was prepared by the direct combination of $Fe(aq)^{2+}$ and $Fe(CN)_4bpm^{2-}$ in aqueous solution. A sample of 0.50 g (1.3 mmol) of $K_2[Fe(CN)_4bpm]$ was dissolved

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in 40 ml of argon-deoxygenated water. A solution of 0.25 g (1.4 mmol) of $FeCl_2 \cdot 4H_2O$ in 10 ml of water was added to the above solution in a dropwise fashion. In approximately two minutes, a black–green precipitate formed which gave a 95% yield of the product after washing with ethanol then ether and drying under vacuum.

[$H_2O_4Co(bpm)Fe(CN)_4$]

The Fe(II)/Co(II) heterobimetallic complex was prepared in a procedure analogous to that used for the diiron complex substituting 1.00 g (4.20 mmol) of $CoCl_2 \cdot 6H_2O$ for the ferrous chloride. The typical yield for this reaction is 96% based on the initial amount of $K_2[Fe(CN)_4bpm]$ dissolved in solution.

Instrumentation

Electronic absorption spectra of solutions were recorded on a Bausch-Lomb Spectronic 2000 UV–Vis spectrophotometer using matched quartz cells. Electronic spectra of insoluble bimetallic complexes were recorded as dilute solutions in DMSO. Owing to the very limited solubility of the diiron and iron/cobalt complexes even in DMSO, molar extinction coefficients could not be determined with any accuracy.

All infrared spectra were recorded using a Nicolet 5 DX FT IR Spectrometer system. Typically fifty scans were used for both the background and sample spectra. The sample compartment was purged with dried nitrogen to remove moisture and carbon dioxide. The samples were prepared as KBr pellets (1 mg sample per 100 mg KBr) using a Wig-L-Bug amalgamator and a Wilks mini-press.

All Mössbauer spectra were recorded at 77 K. The instrumentation included and Austin Science Associates constant acceleration spectrometer in conjunction with a Canberra Series 30 multichannel analyzer. The source was manufactured by New England Nuclear and consisted of 50–45 mCi of ^{57}Co in a rhodium matrix. Doppler velocity calibration was achieved by a non-linear, least-squares routine fitted to the line positions of the National Bureau of Standards Iron Foil Mössbauer Standard 1541. All of the center shifts are referenced to the α-Fe foil. The spectra obtained were fitted using a modified version of the NBS program MONBS4 which fits Lorentzian curve shapes on a parabolic baseline. In the case of $[(H_2O)_4Fe(bpm)Fe(CN)_4]$, one of the peak positions for the high-spin iron center could not be fitted. The method for approximating the center shift and quadrupolar splitting of this complex will be discussed in a later section.

Results and Discussion

The reaction of equimolar amounts of $K_2[Fe(CN)_4bpm]$ and $FeCl_2 \cdot 4H_2O$ in aqueous solution immediately results in a clear solution with the formation of an insoluble, greenish-black precipitate. The mass of the precipitate and the fact that it is insoluble in water, limits the number of possibilities for the molecular formula. The possibility of a simple (yet insoluble) salt of the form $Fe[Fe(CN)_4bpm]$ is ruled out since it would require greater than 100% of the theoretical yield and it is not consistent with the infrared and visible spectral data. A comparison of the CN^- stretching frequencies (Table 1) and the C–C and C–N skeletal vibrations in bpm show substantial shifts in frequencies between the $Fe(CN)_4bpm^{2-}$ and the Fe/Fe bimetallic complex. In addition, both the Fe/Fe and Fe/Co bimetallic complexes display additional peaks in the 3400–3500 cm^{-1} region which could be assigned to the coordinated H_2O ligand. (Exact position is difficult to determine due to small amounts of residual water in the dried KBr.) The formulation which is consistent with the solubility properties, as well as all spectroscopic data is the electrically-neutral, bimetallic complex, $[(H_2O)_4Fe(bpm)Fe(CN)_4]$. This proposed complex corresponds to a theoretical reaction yield of 95% for the synthetic reaction. The analogous reaction using $CoCl_2 \cdot 6H_2O$ in place of $FeCl_2 \cdot 4H_2O$ generates a species with different spectroscopic properties than the $Fe(CN)_4bpm^{2-}$ iron and we assign the Fe/Co species as the neutral complex, $[(H_2O)_4Co(bpm)Fe(CN)_4]$, formed in 96% yield. The structure of these compounds appears in Fig. 1.

TABLE 1. Electronic and Infrared Data for Mono- and Bimetallic Complexes

Complex	Electronic[a] ν_{max} (μm^{-1})	Vibrational[b] ν_{CN} (cm^{-1})
$K_2[Fe(CN)_4bpm]$ [c]	1.86 2.48 4.03	2057
$[Fe(H_2O)_4bpm]Cl_2$	3.3	
$[(H_2O)_4Fe(bpm)Fe(CN)_4]$ [d]	1.45	2100
$[(H_2O)_4Co(bpm)Fe(CN)_4]$ [d]	1.54	2106

[a]Obtained in aqueous solution at room temperature, unless noted otherwise. [b]Obtained as KBr pellets, values correspond only to cyanide stretch region. [c]Ref. 10. [d]Solvent is DMSO.

The qualitative electronic spectra of the complexes are listed in Table 1. The spectra of $Fe(CN)_4bpm^{2-}$, $[(H_2O)_4Fe(bpm)Fe(CN)_4]$ and $[(H_2O)_4Co(bpm)Fe(CN)_4]$ are all dominated by a low-energy, high-intensity, metal-to-ligand charge-transfer (MLCT) transition from a d_π orbital on the low-spin Fe(II) to a π^* orbital on bpm. These transitions occur at 1.86, 1.45 and 1.54 μm^{-1}, respectively. The shift to lower frequency is typical of a bimetallic Fe(II) complex

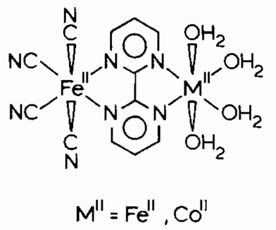

Fig. 1. Structure of the Bimetallic Complexes $[(H_2O)_4Fe(bpm)Fe(CN)_4]$ and $[(H_2O)_4Co(bpm)Fe(CN)_4]$.

bridged by a chelating aromatic, nitrogen heterocycle [19] and is due to the stabilization of the π^* orbitals in bpm by the remote binding of the Lewis acid $Fe^{II}(H_2O)_4$ or $Co^{II}(H_2O)_4$ moiety. The fact that the shift to lower energy is larger for the less electronegative Fe(II) high-spin center as compared to the Co(II) high-spin center agrees with this interpretation.

The varying positions of the MLCT bands discussed above in addition to the variation in ν_{CN} in the infrared spectrum mentioned previously (Table 1) are further indications that the Fe/Fe and Co/Fe systems are molecular units and not mixed salts. (Elemental analyses were inconsistent for the cyanoferrate complexes, probably due to incomplete combustion of cyanoferrate complexes as previously observed*.

The positions of the major CN^- stretch in the infrared spectra are listed in Table 1. Increases in π-backbonding, which delocalize electron density back into π-antibonding orbitals on the CN^- ligand, should lower ν_{CN}. The hexacyanoferrate complex, $K_4[Fe(CN)_6]$, displays its most intense CN^- band at 2043 cm^{-1} under the conditions used in this study. Substitution of bpm ligands for two CN^- ligands raises ν_{CN} (2057 cm^{-1}) because of the greater π-backbonding ability of bpm *versus* CN^-. Further increases in ν_{CN} are observed when $Fe(H_2O)_4^{2+}$ or $Co(H_2O)_4^{2+}$ (2100 and 2106 cm^{-1}, respectively) are coordinated to remote sites on bpm. The combina-

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*Many Fe(II) cyano complexes have presented difficulties in the past for commercial elemental analysis [20].

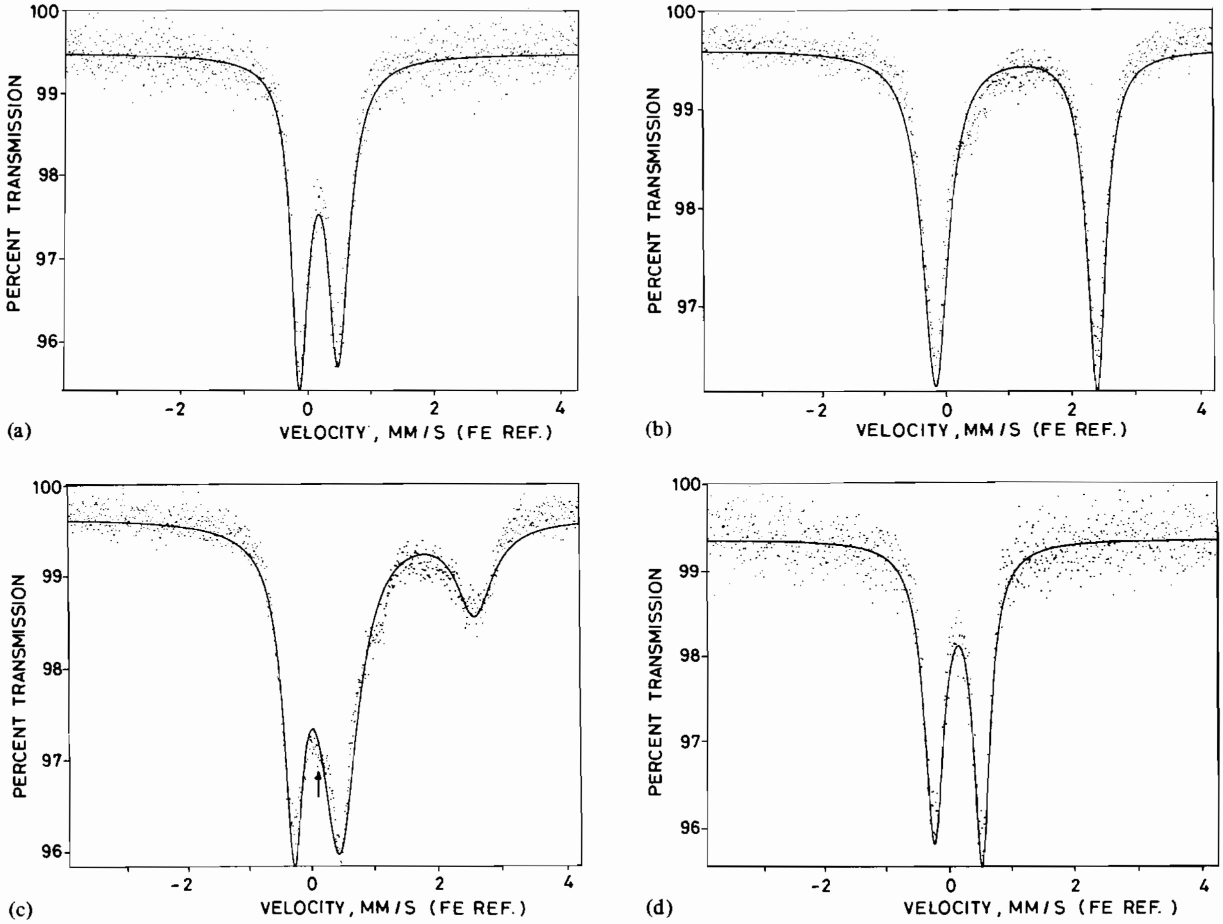

Fig. 2. Mössbauer spectra of (a) $K_2[Fe(CN)_4bpm]$, (b) $[Fe(H_2O)_4bpm]Cl_2$, (c) $[(H_2O)_4Fe(bpm)Fe(CN)_4]$ and (d) $[(H_2O)_4Co(bpm)Fe(CN)_4]$ at 77 K in the solid state. MONBS4 fits are shown for (a), (b) and (d) as discussed in the text.

TABLE 2. ^{57}Fe Mössbauer Spectra of Monometallic Fe(II) and Bimetallic Fe(II)–M(II) (M(II) = Fe(II) or Co(II)) Complexes Bridged by 2,2'-Bipyrimidine[a]

Complex	δ (mm/s)[b]	ΔEq (mm/s)[c]
$K_2[Fe(CN)_4bpm]$	0.12	0.59
$[Fe(H_2O)_4bpm]Cl_2$	1.12	2.57
$[(H_2O)_4Fe(bpm)Fe(CN)_4]$	0.06	0.72
	1.28[d]	2.42
$[(H_2O)_4Co(bpm)Fe(CN)_4]$	0.12	0.62

[a]Solid samples, run at 77 K, spectral fit using modified version of National Bureau of Standards program called MONBS4. [b]Isomer shift referenced to α-iron, fitted to line positions of National Bureau of Standards, Iron Foil Mössbauer Standard 1541, unless noted otherwise. [c]Quadruple splitting. [d]MONBS4 fitted only a three-line spectrum. One peak of the doublet of high-spin Fe(II) appears between the two peaks for the low-spin Fe(II). See text for method of approximating δ and ΔEq.

tion of the inductive effect of the remote metal center and the stabilization of the π-system on the bridging ligand (bpm), enable more π-electron density to be localized on bpm and still less in the π* system of CN^-. The Mössbauer spectra of $K_2[Fe(CN)_4bpm]$, $[Fe(H_2O)_4bpm]Cl_2$, $[(H_2O)_4Fe(bpm)Fe(CN)_4]$ and $[(H_2O)_4Co(bpm)Fe(CN)_4]$ are illustrated in Fig. 2. and summarized in Table 2. The determination of the center shifts and quadrupolar splitting for all complexes except $[(H_2O)_4Fe(bpm)Fe(CN)_4]$ used the MONBS4 program. The spectrum of $K_2[Fe(CN)_4$-bpm] is typical [21] of a low-spin Fe(II) complex in an asymmetric ligand field, a center shift of 0.12 mm/s (*versus* α-Fe) and the relatively small quadrupolar splitting value of 0.59 mm/s. The $[Fe(H_2O)_4$-bpm]Cl_2 complex has a center shift of 1.12 mm/s, the large positive value indicative of less s-electron density felt by the nucleus due to greater screening by the d-electrons not involved in π-backbonding in the tetraaquo *versus* the tetracyano complexes. The larger quadrupolar splitting (2.57 mm/s) in the tetraaquo complex is characteristic of the $(\pi^*)^4(\sigma^*)^2$ unsymmetrical d-electron configuration of a high-spin Fe(II) species.

The Fe(II)–Co(II) bimetallic complex shows a Mössbauer spectrum similar to that of the low-spin Fe(II) in $Fe(CN)_4bpm^{2-}$. This is not surprising given the rather weak Co(II)–bpm bonds consistent with the $(\pi^*)^5(\sigma^*)^2$ d-electron configuration for high-spin Co(II). The fact that the Fe(II)–Fe(II) bimetallic complex shows small changes in the center shifts of both the high-spin and low-spin centers *versus* the monometallic fragments is indicative of the electronic interaction of the two Fe(II) centers through the electronically communicative bpm bridging ligand [1–6, 14]. For the Fe(II)–Fe(II) bimetallic system only the two low-spin lines and the high-velocity component of the high-spin Fe(II) center are fit by the MONBS4 line-fit program. This three-line fit is illustrated in Fig. 2c by the solid line. The arrow on Fig. 2c represents the fourth peak which lies between the two low-spin components and which could not be fitted with MONBS4. A visual examination of the Fe(II)–Fe(II) spectrum (Fig. 2c) and comparison with the high- and low-spin sites in the other complexes in Fig. 2, shows the presence of the low-velocity component of the high-spin Fe(II) site between the low-spin peaks at ~0.1 mm/s. In order to find the isomer shift and quadrupolar coupling for the two Fe centers in Fig. 2c, the following procedure was used. Since the low-velocity peak in the low-spin doublet has minimal overlap with the unfitted high-spin peak, it was assumed that this peak was purely due to low-spin Fe(II). Subtraction of this peak and a peak of identical magnitude and half-width from the high-velocity, low-spin Fe(II) peak, resulted in the isomer shift and quadrupolar splitting values of the high-spin center in the Fe(II)–Fe(II) complex reported in Table 2.

To our knowledge this is the first literature report of a high-spin Fe(II)/low-spin Fe(II) complex in a single, small molecular weight unit. Given the apparent interaction of the metal centers in the Fe(II)–Fe(II) system with respect to the lack of interaction in the Co(II)–Fe(II) system, this new class of polymetallic complexes has the potential to show interesting temperature dependent magnetic properties.

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