

intercept Cr(IV) have been partially successful. Manganese(II), a known Cr(IV) scavenger,¹⁷ was found to increase the rate of the Cr(VI)-L-cysteine reaction.¹⁸ The increase in rate due to Mn(II) can be rationalized if, as seems likely, the Mn species produced were to react with Cr(VI). Thus, the above experiments point toward a two-electron process, a result that is at least consistent with the earlier inference from the stoichiometric results; however, they do not unequivocally preclude the participation of Cr(V) even though no direct or indirect evidence supports its involvement.

- (16) The authors wish to thank Drs. William B. Smith and Christopher Saint of Texas Christian University for assistance with the EPR measurements.
 (17) See, e.g.: Watanabe, W.; Westheimer, F. H. *J. Chem. Phys.* **1949**, *17*, 61.
 (18) A detailed account of these experiments is to be submitted for publication.

Concluding Remarks

The rate law for the Cr(VI)-L-cysteine reaction at neutral pH has been established as a special case of the more general rate law for the reaction in acidic media, and the redox stoichiometry was found to be 3:1 L-Cys:Cr(VI). By contrast, however, the Cr(III) product observed in neutral solution is radically different from that in acidic solution. These results have been interpreted in terms of several mechanisms featuring two-electron-transfer steps in the rate-determining processes.

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Reexamination of a Cytochrome Oxidase Model. A Noncoupled Iron-Copper Binuclear Complex

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A heterobinuclear complex $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$ (I) (mac = the macrocyclic adduct of 2,6-diacetylpyridine and hydrazine; Bpm = bipyrimidine), previously postulated to contain a Fe(Bpm)Cu bridge, had been studied as a possible model for cytochrome oxidase. Four important questions arise with this complex. (1) The high-spin state of the Fe(II) conflicts with reports of low-spin Fe(II) in closely analogous environments. Our study removes the discrepancy: the complexes are all low spin except in adducts with $\text{M}(\text{acac})_2$. (2) Can mac bend enough to permit coordination of the cis Bpm nitrogens, given that the only reported structural evidence is for planar mac? Our structure of $[\text{Fe}(\text{mac})\text{bpy}](\text{ClO}_4)_2$ demonstrates appropriate mac bending, though not quite in the way that had been proposed. (3) $\text{Cu}(\text{acac})_2$ is fairly resistant to the addition of an extra donor atom, and even more resistant to two donors as required for Bpm, and the observed magnetic properties can be explained by ligand-exchange reactions. We have eliminated this possibility with FAB mass spectral data. (4) The unpaired electrons of Cu and Fe appear to be coupled in I. To check whether a peculiarity of Bpm sometimes prevents electron coupling, we demonstrate the generality of coupling through $\text{M}(\text{Bpm})\text{M}$ bridges with $\text{M} = \text{Ni}, \text{Co}, \text{and Mn}$. Thus, binuclear complexes of Cu, Ni, Co, and Mn are now known to be antiferromagnetic, the first finding that fails to support a CuBpmFe bridge. A further experiment virtually eliminates the possibility of a Bpm bridge. Electronic spectra indicate the formation, from $[\text{Fe}(\text{mac})\text{bpy}]^{2+}$, that Bpm is not necessary to form the binuclear complex. Possible mechanisms for the binucleation involve hydrogen bonding or, more likely, one of the uncoordinated mac N atoms, in which light the electrochemistry of the complex can now be reexamined. Crystal data for $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2](\text{ClO}_4)_2 \cdot \text{FeCl}_2 \cdot \text{O}_8\text{N}_8\text{C}_{28}\text{H}_{28}$, $P2_1/n$, $Z = 4$, $a = 8.943$ (3) Å, $b = 24.332$ (8) Å, $c = 15.954$ (5) Å, $\beta = 100.77$ (4)°.

Introduction

Since the first report of magnetic coupling in heterobinuclear and heterotrinnuclear complexes,¹ there has been steadily increasing interest in such compounds.²⁻¹⁰ One kind of bridge

between dissimilar metal atoms, imidazolate (Im^-), is of interest because of the existence of such a bridge in bovine superoxide dismutase¹¹ and the postulate of a Cu- Im -Fe bridge in cytochrome *c* oxidase.¹²⁻¹⁴ In the latter case, the iron is in a heme environment. To simulate this, a model compound was devised¹⁴ with iron(II) bonded to the conjugated N_4 tetradentate mac¹⁵ (Figure 1), which, from the perspective

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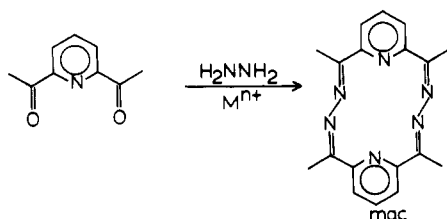


Figure 1. Synthesis and structure of mac.

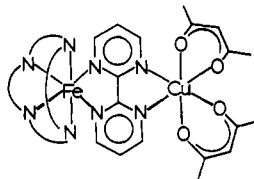


Figure 2. Previously proposed structure of $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$ (I).

of the iron, is heme-like. $\text{Fe}(\text{mac})^{2+}$ forms adducts with bpy and phen.¹⁵ Therefore, the closely related ligand bipyrimidine, Bpm, was used as the bridge between the two metal atoms to simulate imidazole bridging. Like imidazole, Bpm can act as an electron-transfer bridge, and it has the additional advantage of a chelating ability on two sides of the pyrimidine rings. When bis(pentane-2,4-dionato)copper(II), $\text{Cu}(\text{acac})_2$, was reacted with $[\text{Fe}(\text{mac})(\text{Bpm})]^{2+}$, a color and spectral change indicated the formation of a new product that analyzed as $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$ (I) for which the structure in Figure 2 was proposed. The electrochemistry of the compound was interpreted on the basis of this structure.

It has not been possible to establish the structure directly by X-ray crystallography as suitable single crystals could not be obtained. The indirect study of the structure can be divided into a consideration of four main questions.

(1) Goedken et al.¹⁵ reported low-spin iron in $[\text{Fe}(\text{mac})(\text{CH}_3\text{CN})_2]^{2+}$ and $[\text{Fe}(\text{mac})\text{bpy}]^{2+}$. This implies a low-spin configuration for $[\text{Fe}(\text{mac})(\text{Bpm})]^{2+}$ because of the similarity of bpy and Bpm in their geometry, donor properties, and crystal field strengths, yet Wilson et al.¹⁴ reported a high-spin state for the iron in $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$. If the structure is as proposed (Figure 2), the addition of Cu to the Bpm could indeed slightly weaken the Fe–Bpm bonds to slightly (and fortuitously) favor a high-spin state in a previously low-spin complex. We have examined the magnetism of these complexes to clarify these points.

(2) The conjugated macrocyclic ligand, mac (Figure 1), is planar in the only complex, $[\text{Fe}(\text{mac})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$, for which the structure has been determined.¹⁵ The proposed adduction of $[\text{Fe}(\text{mac})]^{2+}$ with the bidentate bpy would require bending of the macrocycle. For steric reasons, any bending that does occur would not involve the linking of trans coordination sites by adjacent donor N atoms as shown in Figure 2. Bending of mac should be resisted by somewhat reduced stability due to the loss of delocalization energy of the planar $14-\pi$ aromatic system.¹⁶ We have therefore determined the crystal structure of a model for these $[\text{Fe}(\text{mac})]^{2+}$ adducts, $[\text{Fe}(\text{mac})\text{bpy}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.

(3) The structure in Figure 2 requires $\text{Cu}(\text{acac})_2$ to add two extra ligand donor atoms, which does not occur readily even in solution. Mono adducts with such bases as pyridine are well-known, but when compounds containing two such bases per copper are isolated, only one of these is actually coordinated to the metal.¹⁷ Thus, adduction of $\text{Cu}(\text{acac})_2$ to Bpm seems unlikely, especially as no analogous adduct with bpy

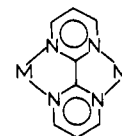


Figure 3. Bpm bridging in homonuclear complexes.

has been reported. Moreover, no magnetic coupling was observed between the metal atoms;¹⁴ this is unexpected for Bpm (vide infra). These magnetic properties could be explained by a metal-exchange reaction that would place the copper into a very stable planar environment within the mac ring, the iron being associated with the other ligands. The FAB mass spectrum was examined to determine this.

(4) The ability of Bpm to binucleate is well established,^{18,19} but it should provide a superexchange pathway^{20–23} that can transmit electron spin information from the iron and copper if these are linked to it. This expectation was checked experimentally with a series of Bpm-bridged homobinuclear complexes (Figure 3) in which magnetic coupling was invariably observed for a series of first-row transition metals.²³

Experiments to test the first three of these questions appeared to lend support to the proposed structure in Figure 2. We have therefore carried out reactions to form analogues of $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$ in which Bpm is absent.

Experimental Section

Syntheses. 2,2'-Bipyrimidine. The preparation given differs slightly from that previously described.²⁴ DMF was distilled prior to use from calcium hydride. The copper bronze reagent was activated by Vogel's method and stored in a vacuum desiccator prior to use.²⁵ Copper bronze (12 g), 2-bromopyrimidine (10 g), and DMF (50 mL) were placed in a 250-mL 2-neck round-bottom flask equipped with a reflux condenser and drying column. Workup of the reaction mixture in the reported manner²⁴ yielded 2.82 g (56%) of brown crude bipyrimidine. This was recrystallized from ethyl acetate and petroleum ether to yield 2.05 g (41%) or light tan material (mp 110–112 °C; lit. mp 113–115 °C). The product was further purified prior to reactions by sublimation at 90 °C. This yielded a pure white solid. The mass spectrum of this material showed the parent peak at 158 and the pyrimidine unit at 79.

$[\text{Fe}(\text{mac})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ was prepared as previously described.¹⁵ $[\text{Fe}(\text{mac})\text{bpy}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. Equimolar solutions of $[\text{Fe}(\text{mac})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ and bpy in acetonitrile were mixed. On mixing, the color changed from green to red. The acetonitrile was recovered by rotary evaporation, and the resulting red residue was recrystallized from CH_2Cl_2 ; yield 90%. Small well-shaped crystals developed in 2–3 days. Other solvent systems resulted in the destruction of the complex.

$[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2](\text{ClO}_4)_2$. The literature sample, kindly provided by Dr. L. Wilson, was used.¹⁴

Magnetic Measurements. The magnetic susceptibilities were measured on polycrystalline samples at fields of about 100 G and at temperatures ranging from 4 to 100 K with use of a superconducting susceptometer. Calibration and measuring techniques are described elsewhere.^{26,27}

FAB Mass Spectra. Conventional mass spectroscopy is not appropriate for $\text{I}(\text{ClO}_4)_2$ since it is a perchlorate salt. A recently developed technique, fast atom bombardment (FAB), which is particularly suited for nonvolatile salts,²⁸ was used.

Crystal data for $[\text{Fe}(\text{mac})\text{bpy}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$: $\text{FeCl}_2\text{O}_{10}\text{N}_8\text{C}_{28}\text{H}_{28}$;

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Table I. Positional Parameters for $[\text{Fe}(\text{N}_6\text{C}_{18}\text{H}_{18})\text{bpy}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$

atom	x	y	z
Fe	0.1416 (6)	0.0976 (2)	0.1729 (3)
Cl(1)	0.411 (1)	0.0748 (4)	0.6993 (5)
Cl(2)	0.457 (2)	0.2354 (4)	0.3299 (7)
O(11)	0.394 (3)	0.1263 (11)	0.740 (2)
O(12)	0.443 (3)	0.0367 (10)	0.764 (1)
O(13)	0.272 (4)	0.0503 (12)	0.650 (2)
O(14)	0.528 (4)	0.0763 (13)	0.651 (2)
O(22)	0.577 (4)	0.2072 (13)	0.380 (2)
O(23)	0.470 (5)	0.2811 (18)	0.340 (3)
O(24)	0.343 (4)	0.2096 (12)	0.356 (2)
O(W1)	0.009 (2)	0.1564 (8)	0.550 (1)
O(W2)	0.184 (3)	0.2549 (10)	0.572 (1)
N(3)	0.017 (3)	0.1325 (10)	0.246 (1)
N(4)	-0.040 (3)	0.1020 (11)	0.307 (1)
N(12)	0.338 (3)	0.0934 (10)	0.137 (1)
N(13)	0.347 (3)	0.1070 (10)	0.046 (1)
N(19)	0.168 (3)	0.1732 (9)	0.143 (1)
N(20)	0.274 (3)	0.0914 (11)	0.282 (1)
N(1A)	-0.014 (3)	0.0874 (10)	0.070 (1)
N(1B)	0.083 (3)	0.0182 (9)	0.182 (1)
O(21)	0.455 (5)	0.216 (1)	0.247 (2)
C(1)	0.092 (3)	0.210 (1)	0.186 (2)
C(2)	0.002 (4)	0.185 (1)	0.242 (2)
C(5)	0.058 (4)	0.073 (1)	0.355 (2)
C(6)	0.233 (4)	0.082 (1)	0.359 (2)
C(7)	0.342 (4)	0.074 (1)	0.432 (2)
C(8)	0.482 (5)	0.074 (2)	0.425 (2)
C(9)	0.543 (4)	0.077 (1)	0.347 (2)
C(10)	0.432 (4)	0.085 (1)	0.279 (2)
C(11)	0.462 (4)	0.091 (1)	0.189 (2)
C(14)	0.302 (4)	0.153 (1)	0.028 (2)
C(15)	0.232 (4)	0.190 (1)	0.080 (2)
C(16)	0.223 (4)	0.248 (1)	0.057 (2)
C(17)	0.148 (4)	0.285 (1)	0.103 (2)
C(18)	0.091 (4)	0.265 (1)	0.172 (2)
C(2A)	-0.104 (3)	0.043 (1)	0.066 (2)
C(3A)	-0.223 (4)	0.035 (1)	0.003 (2)
C(4A)	-0.285 (4)	0.068 (1)	-0.059 (2)
C(5A)	-0.209 (4)	0.118 (1)	-0.055 (2)
C(6A)	-0.078 (4)	0.129 (1)	0.012 (2)
C(2B)	-0.041 (4)	0.003 (1)	0.131 (2)
C(3B)	-0.111 (4)	-0.044 (1)	0.140 (2)
C(4B)	-0.036 (5)	-0.081 (2)	0.196 (2)
C(5B)	0.108 (4)	-0.061 (1)	0.252 (2)
C(6B)	0.153 (4)	-0.018 (1)	0.236 (2)
C(2M)	-0.079 (4)	0.216 (1)	0.307 (2)
C(5M)	0.009 (4)	0.034 (1)	0.421 (2)
C(11M)	0.621 (4)	0.102 (1)	0.172 (2)
C(14M)	0.340 (4)	0.165 (1)	-0.057 (2)
H(3A)	-0.27 (3)	-0.003 (10)	-0.00 (1)
H(4A)	-0.38 (3)	0.059 (10)	-0.10 (2)
H(5A)	-0.24 (3)	0.147 (10)	-0.10 (2)
H(6A)	-0.03 (3)	0.166 (10)	0.02 (2)
H(3B)	-0.20 (3)	-0.049 (10)	0.11 (2)
H(4B)	-0.08 (3)	-0.119 (9)	0.20 (2)
H(5B)	0.16 (3)	-0.086 (11)	0.29 (2)
H(6B)	0.25 (3)	-0.009 (11)	0.27 (2)
H(7)	0.30 (3)	0.069 (10)	0.48 (1)
H(8)	0.56 (3)	0.068 (11)	0.48 (2)
H(9)	0.65 (3)	0.072 (10)	0.34 (2)
H(16)	0.26 (3)	0.260 (10)	0.01 (2)
H(17)	0.14 (3)	0.325 (10)	0.09 (2)
H(18)	0.05 (3)	0.290 (10)	0.21 (2)
H(W1)	0.06 (3)	0.169 (8)	0.52 (1)
H(W2)	-0.06 (2)	0.137 (8)	0.55 (1)
H(W3)	0.17 (3)	0.214 (10)	0.54 (1)
H(W4)	0.17 (3)	0.235 (9)	0.56 (1)
H(51)	0.08 (3)	0.036 (9)	0.47 (1)
H(52)	-0.09 (3)	0.045 (9)	0.43 (1)
H(53)	0.00 (3)	-0.001 (10)	0.41 (1)

mol wt 765; space group $P2_1/n$; $Z = 4$; $a = 8.943$ (3), $b = 24.332$ (8), $c = 15.954$ (5) Å; $\beta = 100.77$ (4)°; $V = 3410$ Å³; $\rho = 1.49$ g cm⁻³; $\mu(\text{Mo K}\alpha) = 6.7$ cm⁻¹; crystal dimensions (distances in mm of faces from centroid) (100) 0.09, (100) 0.09, (110) 0.01, (110) 0.10, (110) 0.11, (110) 0.11, (001) 0.26, (001) 0.26; maximum/minimum

Table II

Bond Lengths and Selected Interatomic Distances (Å)			
Fe-N(3)	1.96 (1)	N(19)-C(1)	1.38 (1)
Fe-N(12)	1.95 (1)	N(19)-C(15)	1.33 (1)
Fe-N(19)	1.92 (1)	N(20)-C(6)	1.38 (2)
Fe-N(20)	1.92 (1)	N(20)-C(10)	1.42 (2)
Fe-N(1A)	1.96 (1)	<Cl-O>	1.37 (3)
Fe-N(1B)	2.01 (1)	<N-C>	1.34 ^a
N(3)-N(4)	1.39 (1)	<C-CM>	1.54 (2) ^b
N(3)-C(2)	1.29 (1)	<C-H>	0.97
N(4)-C(5)	1.26 (2)	<O-H>	0.80
N(12)-N(13)	1.50 (1)		
Bond Angles (deg)			
N(3)-Fe-N(12)	147.8 (5)	N(1A)-Fe-N(1B)	77.4 (5)
N(3)-Fe-N(19)	81.0 (4)	Fe-N(3)-N(4)	120.7 (8)
N(3)-Fe-N(20)	79.5 (5)	Fe-N(3)-C(2)	117.2 (9)
N(3)-Fe-N(1A)	99.2 (5)	N(4)-N(3)-C(2)	121.8 (11)
N(3)-Fe-N(1B)	100.8 (4)	N(3)-N(4)-C(5)	114.8 (13)
N(12)-Fe-N(19)	79.5 (4)	Fe-N(12)-N(13)	118.9 (9)
N(12)-Fe-N(20)	79.9 (5)	Fe-N(12)-C(11)	122.5 (10)
N(12)-Fe-N(1A)	106.6 (5)	N(13)-N(12)-C(11)	116.9 (11)
N(12)-Fe-N(1B)	103.4 (4)	N(12)-N(13)-C(14)	111.4 (10)
N(19)-Fe-N(20)	102.3 (5)	Fe-N(19)-C(1)	113.9 (7)
N(19)-Fe-N(1A)	91.1 (5)	Fe-N(19)-C(15)	125.5 (8)
N(19)-Fe-N(1B)	168.4 (5)	Fe-N(20)-C(6)	127.2 (11)
N(20)-Fe-N(1A)	166.1 (5)	Fe-N(20)-C(10)	115.7 (8)
N(20)-Fe-N(1B)	89.3 (5)		

^a Bipyridyl distances. ^b Methyl C distances.

transmission coefficients 0.94/0.90.

Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ - 2θ scan technique was used, as previously described,²⁹ with scan widths (0.5 + 0.35 tan θ) to record the intensities for all nonequivalent reflections for which $1.4^\circ < 2\theta < 48^\circ$.

The intensities of four standard reflections showed no greater fluctuations during data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and absorption. Of the 3918 independent intensities, there were 1512 with $F_o^2 < 2\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.³⁰ Only these data were used in the final refinement of the structural parameters.

Structure Determination. The position of the iron atom was determined from a three-dimensional Patterson function, and the other non-hydrogen atoms were determined from Fourier difference functions. Due to the small crystal size, a small data set was obtained, and anisotropic thermal parameters were not introduced for O, N, or C atoms. Further Fourier syntheses permitted location of the hydrogen atoms, which were included in the final refinement for three cycles of least squares and then held fixed. The model converged with $R = 8.0\%$ and $R_w = 8.4\%$. A final Fourier difference function was featureless. Tables of the observed and calculated structure factors are available.³¹ The principal programs used are as described previously.²⁹

Results and Discussion

$[\text{Fe}(\text{mac})\text{bpy}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ was found to have a constant corrected magnetic susceptibility of 1.3×10^{-3} cgs over the range of 4–300 K,³¹ which clearly corresponds to low-spin iron(II),³² in agreement with the report that $[\text{Fe}(\text{mac})\text{-(Bpm)}]^{2+}$ is low spin.¹³ The high-spin states of iron(II) in $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$ now needs to be explained as does the absence of magnetic coupling in the proposed FeBpmCu bridge.

Structure of $[\text{Fe}(\text{mac})\text{bpy}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. Figure 4 shows the $[\text{Fe}(\text{mac})\text{bpy}]^{2+}$ ion, which clearly has a bent mac ring to accommodate the cis bidentate coordination of bpy. As is

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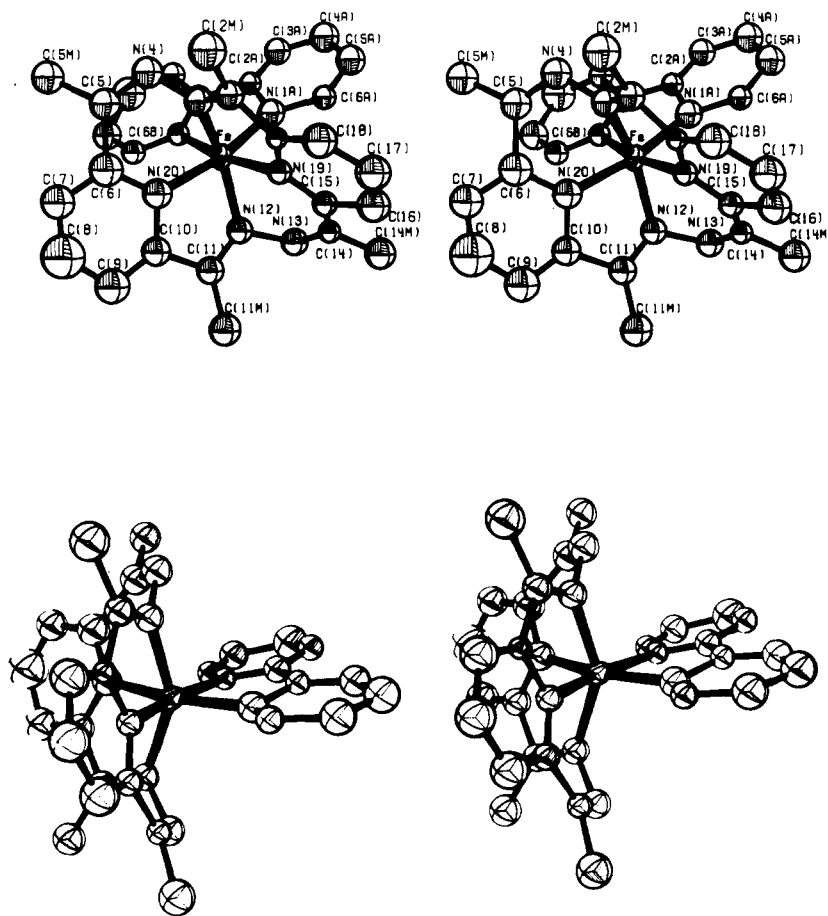


Figure 4. Two views of $[\text{Fe}(\text{mac})\text{bpy}]^{2+}$.

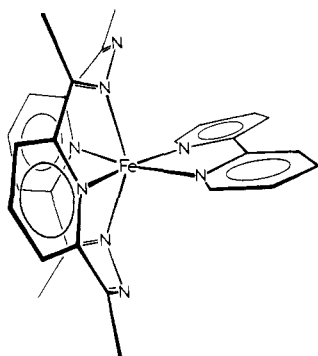


Figure 5. Structure of $[\text{Fe}(\text{mac})\text{bpy}]^{2+}$.

evident from Figures 4 and 5, the bending of the ring involves bridging of four adjacent donor sites on the metal such that a very distorted octahedron is preserved.

The macrocycle coordinates via four of the six nitrogen atoms such that there are two five-membered Fe-N-C-C-N coordination rings, each of which is adjacent to a six-membered Fe-N-N-C-C-N ring. Each of the two five-membered rings is essentially planar, unlike the six-membered rings that are involved in the bending of mac. The FeN₂ fragments of the five-membered rings, Fe-N(3)-N(19) and Fe-N(12)-N(20), are inclined at 77° of one another, instead of the 90° required of a regular octahedron. These fragments make angles of 9.2 and 4.6° with their associated pyridine rings, indicating that the bending is not uniform. The bpy ligand is also distorted with a twist of 6.9° between the two rings.

The distortion of the coordinated octahedron is also indicated by the deviation of the cis and trans bond angles from 90 and 180°, respectively. The diacetylpyridine nitrogens N(19) and N(20) are cis to one another with a N(19)-Fe-

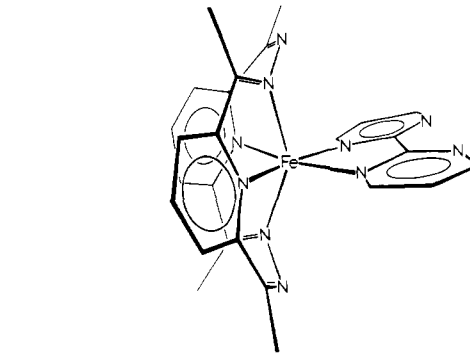


Figure 6. Proposed structure of $[\text{Fe}(\text{mac})(\text{Bpm})]^{2+}$.

N(20) bond angle of 102.3°. These nitrogens are trans to the two bipyridyl nitrogens, forming bond angles of 168.4 and 166.1°. The hydrazine nitrogens are trans to each other, forming a bond angle of 147.8°. The iron to nitrogen bond lengths in the present complex are similar to those reported in the parent complex $[\text{Fe}(\text{mac})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$. The greatest change is in the iron hydrazine to nitrogen bond lengths that increase by 0.04–0.07 Å in the present complex. The difference between N(3)-N(4) and the chemically equivalent N(12)-N(13) bond is presumably due to the uneven folding of the macrocycle.

If the adducted ligand had been Bpm instead of bpy, the two other donor sites of the Bpm would now indeed be available for coordination to a second metal atom (Figure 6). This fact certainly does not take away from the postulate of structures of the type proposed in Figure 2.

Fast-Atom-Bombardment Mass Spectrum. The FAB mass spectrum of $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2](\text{ClO}_4)_2$ shows that the iron is in the macrocycle environment (m/e 374) and that the

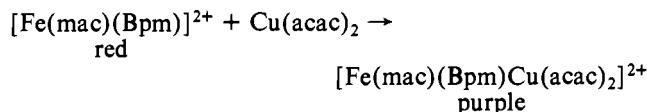
Table III. Values of $-JS^2$ (cm^{-1}) for $(\text{hfa})_2\text{M}(\text{Bpm})\text{M}(\text{hfa})_2$ Complexes

$(\text{hfa})_2\text{Ni}(\text{Bpm})\text{Ni}(\text{hfa})_2$	6.46
$(\text{hfa})_2\text{Co}(\text{Bpm})\text{Co}(\text{hfa})_2$	7.94
$(\text{hfa})_2\text{Mn}(\text{Bpm})\text{Mn}(\text{hfa})_2$	2.88

copper is bound to the acetylacetonate ligand (m/e 266). A separate peak (m/e 158) is observed for the Bpm, but no peak is found for its adduct with either copper or iron. The mass spectral results show that all components of the compound are present and that no metal exchange occurs. No molecular ion is observed, as expected, given the ionic nature of the compound.

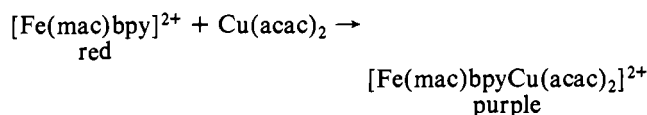
Magnetic Interaction in $\text{L}_2\text{M}(\text{Bpm})\text{ML}_2$ Complexes ($\text{M} = \text{Cu, Ni, Co, Mn}$). A series of compounds was formed by using β -diketonate ligands (L) with bivalent transition metals (M) and using Bpm to form a binucleating bridge between pairs of identical metal atoms. The complex $\text{Cu}_2(\text{Bpm})(\text{hfa})_4$ has been examined previously and shown to exhibit antiferromagnetic interactions,¹⁴ although no crystal structure determination directly verified Bpm bridging. The crystal structure of $(\text{hfa})_2\text{Co}(\text{Bpm})\text{Co}(\text{hfa})_2$ has recently been determined,²³ and it clearly shows a Co(Bpm)Co-bridged species. The analogous complexes with Ni(II) and Mn(II) are very similar and formed by the same reaction. All exhibit magnetic coupling between the metal atoms (Table III). Thus, in all cases where a Bpm is known to bridge paramagnetic metal atoms, coupling is observed. The coupling is substantial even when metals with several unpaired electrons are involved. The reported absence of coupling in $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$ therefore argues against the existence of a Bpm bridge.

$[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$ and $[\text{Fe}(\text{mac})\text{bpyCu}(\text{acac})_2]^{2+}$. The structure of $[\text{Fe}(\text{mac})\text{bpy}]^{2+}$ (Figures 4 and 5) removes any doubt that the macrocycle can bend. This, coupled with the FAB data on I, seemed to support the structure proposed for I. The formation of heterobinuclear I from $[\text{Fe}(\text{mac})(\text{Bpm})]^{2+}$ is associated with a color change from red to purple, which is not merely the sum of the two reacting species:



An equally spectacular change is observed in the spectrum (Figure 7), indicating the formation of a new product.

The postulate of a Bpm bridge is the simplest explanation. To test the possibility of Bpm bridging, the same experiment was carried out on $[\text{Fe}(\text{mac})\text{bpy}]^{2+}$, which cannot form a type 1 adduct since it has no backside nitrogens:



The color again changes from red to purple, and the spectral change (Figure 7) is strikingly similar to that observed with Bpm. It can be concluded that the addition of $\text{Cu}(\text{acac})_2$ to both iron compounds results in the same type of compound formation. The copper does not react with the backside nitrogens of the bipyrimidine since an analogous reaction is not possible with bipyridyl. The interaction of the copper must be with the macrocyclic portion of the molecule since this is the feature both iron complexes have in common.

The spectral results almost certainly eliminate Figure 2 as the structure of I. An alternative structure should explain all the experimental data. The best possibility is that the copper interacts with one of the hydrazine nitrogens to form a five-coordinative species (Figure 8). This interaction could weaken or totally disrupt one of the iron to hydrazine nitrogen bonds

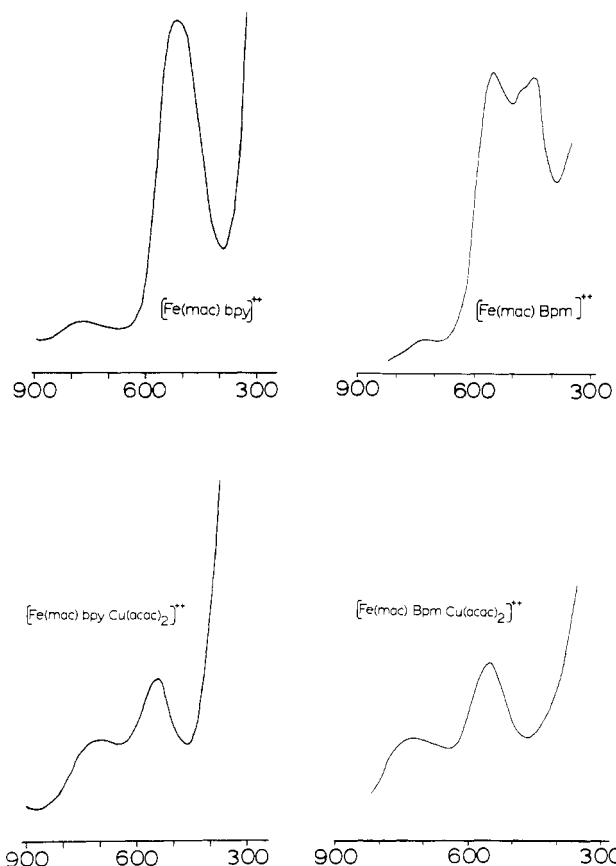


Figure 7. Optical spectra, 300–900-nm region, of the red ions $[\text{Fe}(\text{mac})\text{bpy}]^{2+}$ and $[\text{Fe}(\text{mac})(\text{Bpm})]^{2+}$ ¹³ and their purple $\text{Cu}(\text{acac})_2$ adducts.

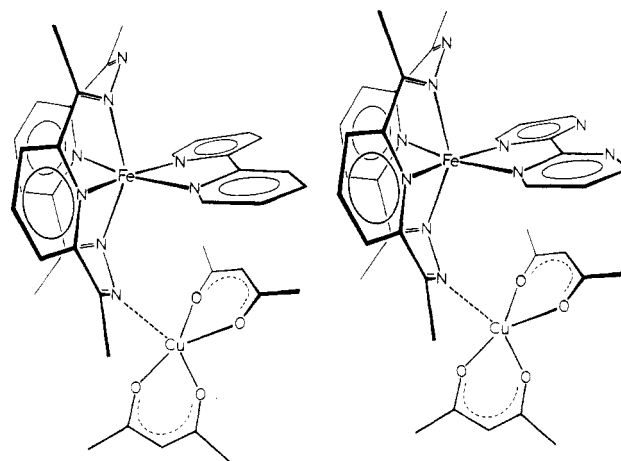


Figure 8. Reasonable structures of $\text{Cu}(\text{acac})_2$ adducts $[\text{Fe}(\text{mac})\text{bpyCu}(\text{acac})_2]^{2+}$ and $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$.

and thereby promote the high-spin state. The observed lack of spin exchange could also be explained since the above pathway would not allow for orbital overlap between the hydrazine nitrogen and the iron. This formulation does explain all the experimental results. This cannot be said for the structure in Figure 2. A crystal structure of either $\text{Cu}(\text{acac})_2$ complex would be useful, but suitable crystals are not yet available.

Electrochemistry. This electrochemical behavior of $[\text{Fe}(\text{mac})(\text{Bpm})\text{Cu}(\text{acac})_2]^{2+}$ is important in assessing any biomimetic value this complex has as a cytochrome oxidase model. It also must be consistent with any structure proposed for the ion. The literature electrochemical characterization¹⁴ for $[\text{Fe}(\text{mac})(\text{Bpm})\text{M}(\text{acac})_2]^{2+}$ ($\text{M} = \text{Cu, Zn}$) must now be

reexamined in view of the evident lack of a Bpm bridge in the (Fe, Cu) or (Fe, Zn) heterobinuclears. The binuclear adducts have a half-wave potential for the Fe(II)/Fe(III) couple $E = 0.60$ V, 700 mV less than that for the mononuclear precursor, which is good evidence that the adducts are discrete entities in solution. The difference in half-wave potentials was attributed to the electronic substituent effect caused by the presence of the $M(\text{acac})_2$.¹³ However, this substituent effect is perhaps larger than we could reasonably expect from a $\text{Cu}(\text{acac})_2$ weakly linked through Bpm, remote from the iron. On the other hand, adduction to a mac N atom adjacent to

the Fe-N bond can and should lead to a greater substituent effect and is therefore more consistent with the electrochemistry.

Acknowledgment. We are grateful to Dr. Lon J. Wilson for making complex I available and to the Research Corp. and the NSF (Grant CHE83-00516) for support.

Supplementary Material Available: Listings of thermal parameters, interatomic distances and angles, least-squares planes, and observed and calculated structure factors and a packing diagram (12 pages). Ordering information is given on any current masthead page.

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Solvent, Temperature, and Electrolyte Studies on the Electron-Transfer Reaction between Ferrocene and a Cobalt Clathrochelate¹

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The kinetics of the outer-sphere electron-transfer reaction between the clathrochelate $\text{Co}(\text{dmg})_3(\text{BF}_4)^+$ (dmg is the doubly deprotonated ion of dimethylglyoxime) and ferrocene ($\text{Fe}(\text{Cp})_2$) have been studied as a function of the $\text{Fe}(\text{Cp})_2$ concentration, added electrolyte, and temperature in acetonitrile, acetone, nitrobenzene, and ethylene dichloride. The equilibrium constants and their temperature dependences have been determined through electrochemical measurements. The reaction is first order in each reactant, and the second-order rate constants with no added electrolyte are 1.6×10^4 , 8.3×10^3 , 3.8×10^4 , and $1.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in the solvents as listed above. Analysis within the Marcus theory gave self-exchange rate constants for the Co clathrochelate that ranged from $100 \text{ M}^{-1} \text{ s}^{-1}$ in acetone to $2.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in ethylene dichloride. The self-exchange and cross-reaction rate constants corrected for the equilibrium constant varied with the dielectric term $(1/D_{\text{op}} - 1/D_s)$ but did not agree well with the prediction of the Marcus theory. Addition of $n\text{-Bu}_4\text{NBF}_4$ up to 0.5 M lowered the second-order rate constant by a factor of 5 in acetonitrile and acetone, 19 in nitrobenzene, and 27 in ethylene dichloride. A fit to a rate law employing ion-pairing and activity coefficients gave association constants of 17, 200, 53, and 2.9×10^4 in acetonitrile, acetone, nitrobenzene, and ethylene dichloride, respectively. Temperature dependences with no added electrolyte and with 0.1 M $n\text{-Bu}_4\text{NBF}_4$ gave similar activation parameters for a given solvent. Values of ΔH_{12}^\ddagger fell within the range 6–9 kcal mol^{-1} , and ΔS_{12}^\ddagger values were –13 to –7 cal $\text{mol}^{-1} \text{ deg}^{-1}$. Calculated self-exchange activation parameters for the cobalt complex varied considerably from solvent to solvent, with ΔH_{11}^\ddagger ranging from 7.3 to 14.1 kcal mol^{-1} and ΔS_{11}^\ddagger ranging from –26 to 3 cal $\text{mol}^{-1} \text{ deg}^{-1}$, but the ΔG_{11}^\ddagger value varied only 2 kcal mol^{-1} , indicating some compensation. It is concluded that ion pairing decreases electron-transfer reactivity by increasing the electron-transfer distance and by decreasing precursor complex stability, with BF_4^- between the reactants. The transition-state structure is apparently sensitive to the identity of the solvent.

Introduction

The study of the electron-transfer mechanisms employed by transition-metal complexes has been a major field in inorganic chemistry for several decades, but most research has been done on aqueous systems.^{2–5} Recently, several investigators^{6–8} have reported the effects of varying the solvent on the rates of certain electron-transfer reactions. These studies can be expected to reflect the influence of the solvent on the interaction between the reactants, the actual electron-transfer

process, and properties of the reactants such as electrochemical potential and the extent of ion-pair formation. Furthermore, in the case of outer-sphere electron-transfer reactions, reactions in which no bonds are made or broken within the complexes during the reaction, theoretical models are available that make testable predictions about solvent dependences. Within the Marcus theory, one of the more successful and easily applied theories, solvent-dependence data can be used to separate contributions to the total activation energy from the inner-sphere reorganization of the complexes themselves and the outer-sphere reorganization of the solvent.^{4,5,9,10} Previous studies have shown that the predictions of the Marcus theory are sometimes obeyed quite precisely, while other cases are not so well modeled.^{6–8} Since the model treats the solvent as a dielectric continuum, specific solvent effects and dielectric saturation are possible contributors to the observed deviations.

The system presented here is especially appropriate for detailed solvent-dependence studies. The reaction between

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