

Synthesis and Characterization of Monometallic and Bimetallic Mixed-Ligand Complexes of Iron(II) Containing 2,2'-Bipyrimidine or 2,3-Bis(2-pyridyl)pyrazine

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Mono- and bimetallic complexes of the form $\text{Fe}(\text{CN})_4\text{BL}^{2-}$ and $[\text{Fe}(\text{CN})_4]_2(\text{BL})^{4-}$, where BL = 2,2'-bipyrimidine (bpm) or 2,3-bis(2-pyridyl)pyrazine (dpp), have been prepared and characterized by column chromatography, UV-visible spectroscopy, cyclic voltammetry, and coulometry. The complexes are stable in aqueous solution and have electronic spectra dominated by intense metal-to-ligand charge-transfer (MLCT) transitions in the visible region of the spectrum. The maximum for the lowest energy MLCT peak in the monometallic complexes is in the 530–550-nm region while the bimetallic complexes, with an increased stability of the π^* orbitals on BL, show maxima in the 580–660-nm region. The monometallic complexes display one reversible oxidation corresponding to the Fe(III/II) couple, while two reversible oxidations, separated by 140–150 mV, are observed for the bimetallic complexes.

Introduction

In the past there have been several reports concerning the synthesis and characterization of transition-metal complexes of the form $\text{M}(\text{bpm})_{3-n}\text{L}_{2n}$ (where M = Cr,¹ Co,² Mo,³ W,¹ Ru,⁴⁻⁸ Fe,⁹⁻¹¹ or Ni¹² and bpm = 2,2'-bipyrimidine). The 2,2'-bipyrimidine ligand can serve as an effective bridging ligand for the formation of polymeric systems. We have found that in small metal systems such as first-row transition metals which are bridged through bpm the use of sterically bulky ligands (L) causes synthesis of useful polymeric systems to be somewhat difficult. For this reason we have investigated another bridging ligand, 2,3-bis(2-pyridyl)pyrazine (dpp), which separates the metal centers more effectively while still providing good communication between these metal centers.¹³

While there is a large variety of organometallic polyiron systems in the literature, only a few Werner-type complexes with two or more iron centers have been reported. Organometallic complexes such as $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$, and $\text{Fe}_2\text{Cp}_2(\text{CO})_4$ have been known for some time.¹⁴ Several examples of iron-oxygen and iron-sulfur clusters are also present in the literature.¹⁵ Mixed-valence iron complexes are known that include such molecules as Prussian blue, Fe_4S_4 , $\text{K}[\text{Fe}_2\text{F}_6]$, Fe_3O_4 , and $\text{Fe}_2(\text{fulv})_2^{+16}$ (fulv = fulvalene). In addition, several iron bimetallic systems containing porphyrinate ligands are known.¹⁷ Recent interest in bimetallic organometallic complexes of iron(II) has produced several examples of bridged iron species such as $[\text{Fe}(\text{CN})_5]_2(\text{pz})^{6-}$ and $[\text{Fe}(\text{CN})_5]_2(4,4'\text{-bpy})^{6-18}$ (pz = pyrazine, bpy = bipyridine). We report here the synthesis, electronic absorption spectra, infrared spectra, and electrochemistry of two iron(II) bimetallic systems and the corresponding monometallic systems using the chelating bridging ligands bpm and dpp.

Experimental Section

Materials. Water, which was used as the solvent for synthesis and electrochemistry, was redistilled from alkaline permanganate in an all-glass apparatus. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA, and Galbraith Labs, Knoxville, TN. bpm was purchased from Alfa Inorganics, and dpp was prepared according to the procedure described by Goodwin and Lions.¹⁹ All other materials were reagent grade and were used without further purification.

Instrumentation. Cyclic and differential pulse voltammograms and coulometric determinations were recorded on an IBM Instruments Inc. Model EC/225 voltammetric analyzer. A glassy-carbon (IBM) working electrode, a platinum auxiliary electrode, and a saturated KCl/calomel (SCE) reference electrode were used in voltammetric experiments, and a platinum basket was substituted for the working electrode in coulometric determinations. Voltammograms were recorded in aqueous solution with 0.1 M Na_2SO_4 or 2 M KCl as a supporting electrolyte. All electronic absorption spectra were recorded on a Bausch and Lomb Spectronic 2000 using matched quartz cells.

All anion-exchange columns were DEAE-Sephadex A-25 anion-exchange resin and were eluted with H_2O or varying concentrations of

aqueous KI. Gel filtration columns were Bio-Rad P-2 gel filtration resin or PR Sephadex LH-20 gel filtration resin, and both were eluted with H_2O .

Infrared spectra were recorded on a Nicolet 5DX FT-IR instrument as KBr pellets made with a Wilks minipress.

Syntheses. $\text{K}_4[\text{Fe}(\text{CN})_4(\text{bpm})]$. Preparation of potassium tetracyano(2,2'-bipyrimidine)iron(II) was achieved by a method published earlier.²⁰

$\text{K}_4[\text{Fe}(\text{CN})_4]_2(\text{bpm})$. A mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.796 g, 4.00 mmol) and bpm (0.473 g, 2.85 mmol) was dissolved in 25 mL of H_2O to yield an orange solution. This mixture was heated to boiling and stirred for ca. 30 min under argon. Upon dropwise addition of an aqueous solution of KCN (1.432 g, 21.99 mmol in 15 mL of H_2O) the solution turned deep green-brown. The solution was cooled to room temperature and added to 200 mL of acetone to achieve precipitation. This mixture was filtered to obtain the crude product, which was redissolved in a minimal amount of water and chromatographed on an anion-exchange column. The first band eluted with water was cationic or neutral and discarded. The second band which was brown, was eluted with ca. 5 g of KI/100 mL of water and was found to be $\text{K}_2[\text{Fe}(\text{CN})_4(\text{bpm})]$. The third and final band was eluted with 10 g of KI/100 mL of water. This band was green and was identified as $\text{K}_4[\text{Fe}(\text{CN})_4]_2\text{bpm}$. The excess KI was removed by Soxhlet extraction with acetone.

The elemental analyses were not consistent with the calculated values. In fact, the percentages of carbon and nitrogen varied drastically from one analytical laboratory to another. It has been shown in the past that cyanoferrate complexes often do not give good analyses for percentages

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Table I. Electronic Spectra and Assignments for Fe(II) Complexes^a

| complex | λ_{\max} , nm | $10^{-3}\epsilon_{\max}$, M ⁻¹ cm ⁻¹ | assign |
|--|-----------------------|---|-------------|
| K ₂ [Fe(CN) ₄ (bpm)] | 533 | 1.8 | MLCT |
| | 403 | 4.7 | MLCT |
| | 243 | 20.3 | $\pi-\pi^*$ |
| K ₄ [Fe(CN) ₄] ₂ (bpm) | 660 | 2.2 | MLCT |
| | 600 | 2.3 | MLCT |
| | 425 | 6.9 | MLCT |
| | 250 | 11.0 | $\pi-\pi^*$ |
| | 217 | 21.0 | $\pi-\pi^*$ |
| K ₂ [Fe(CN) ₄ (dpp)] | 548 | 3.0 | MLCT |
| | 363 | 1.8 | MLCT |
| | 310 | 11.0 | $\pi-\pi^*$ |
| | 200 | 24.0 | $\pi-\pi^*$ |
| K ₄ [Fe(CN) ₄] ₂ (dpp) | 577 | 4.9 | MLCT |
| | 326 | 9.7 | MLCT |
| | 219 | 15.0 | $\pi-\pi^*$ |

^a Conditions: aqueous solution; 25 °C.

of carbon and nitrogen.²¹ If a contaminant was present, it must not be electrochemically active from +1.0 to -1.0 V since the cyclic voltammograms were clear of electroactive impurities in the water window. Since the ratio of C to N in the elemental analysis was consistent with theoretical values, these contaminants must either not contain C and N or contain them in the same ratio as the product. The only possible species fitting these requirements would be KCl, which was eliminated by testing with AgNO₃. Our conclusion is that incomplete combustion occurs in the elemental analysis of these systems.

K₂[Fe(CN)₄(dpp)]. Preparation of potassium tetracyano(2,3-bis(2-pyridyl)pyrazine)ferrate(II) can be achieved either by the procedure used for preparing K₂[Fe(CN)₄(bpm)], with dpp substituted for bpm, or by isolation as a byproduct in the synthesis of K₄[Fe(CN)₄]₂(dpp).

K₄[Fe(CN)₄]₂(dpp). Preparation of K₄[Fe(CN)₄]₂(dpp) was achieved by a method analogous to that used to prepare K₄[Fe(CN)₄]₂(bpm), with dpp substituted for bpm. The cationic or neutral byproducts from the column were discarded, while the red-violet K₂[Fe(CN)₄(dpp)] and the blue K₄[Fe(CN)₄]₂(dpp) were collected.

Characterization of Bimetallic Complexes. Since elemental analysis was not an effective method for confirming the composition of the products, other methods were necessary. As stated above, cyclic voltammetry confirms only one electroactive species for each of the complexes in the study. A quantitative determination of charge for the two oxidation waves of [Fe(CN)₄]₂(bpm)⁴⁻ shows that the number of electrons by coulometry is 1.95 ± 0.10 , a value consistent with the bimetallic formulation of the complex. When a sample of [Fe(CN)₄]₂(bpm)⁴⁻ or [Fe(CN)₄]₂(dpp)⁴⁻ is doped with Fe(CN)₆⁴⁻, ion-exchange behavior on Sephadex A-25 shows elution at the same time, confirming the 4- charge on the complex. When the bimetallic complexes are doped with the monometallic analogues, gel filtration on LH-20 indicates that the bimetallic complexes are larger since they elute first as a separate band. Our conclusion is that the qualitative results shown by cyclic voltammetry and anion and gel filtration chromatography and the qualitative results obtained by coulometry all are consistent with the formulation of the complexes. Additionally, the shifts in absorption maxima and intensity of peaks (Table I) are similar to the magnitudes observed for analogous mono- and bimetallic ruthenium(II) complexes.^{4,5,7}

Results and Discussion

The preparation of the monometallic mixed-ligand complexes of Fe(II) with cyanide, bpm, and dpp closely paralleled that for the analogous complexes with cyanide and 2,2'-bipyridine. However, the preparation of the bimetallic mixed-ligand complexes, in which there are no bpy analogues, proved more difficult due to the tendency of the reaction to yield a mixture of products. Through the use of ion-exchange chromatography it proved possible to obtain the bimetallic systems bridged by either bpm or dpp with yields of 50% and 25%, respectively. In lieu of ion-exchange chromatography, it also proved possible to separate the mixture by using aqueous gel filtration chromatography, in which the bimetallic fragments passed directly through these gel filtration columns and smaller ions or molecules were retained.

The electronic spectra of these iron complexes are summarized in Table I. The metal-to-ligand charge-transfer (MLCT) bands

Table II. Cyclic Voltammetry of Fe(II) and Ru(II) Complexes of bpm and dpp^a

| complex ion | $E_{1/2}$, V ^b | ΔE , mV ^c | $\Delta E_{1/2}$, mV ^d | ref |
|---|----------------------------|------------------------------|------------------------------------|-----|
| Fe(CN) ₆ ⁴⁻ | 0.17 | 123 | | 20 |
| Fe(CN) ₄ (bpm) ²⁻ | 0.55 | 60 | | e |
| [Fe(CN) ₄] ₂ (bpm) ⁴⁻ | 0.53 | 70 | | |
| | 0.67 | 70 | 140 | e |
| Fe(CN) ₄ (dpp) ²⁻ | 0.45 | 65 | | e |
| [Fe(CN) ₄] ₂ (dpp) ⁴⁻ | 0.41 ^f | 70 | | |
| | 0.56 | 70 | 150 | e |
| Ru(NH ₃) ₄ (bpm) ²⁺ | 0.52 | | | e |
| [Ru(NH ₃) ₄] ₂ (bpm) ⁴⁺ | 0.59 | | | |
| | 0.78 | | 190 | 20 |

^a Conditions: Aqueous solution; 25 °C; 2 M KCl as electrolyte unless otherwise noted. ^b Reported vs. SCE; uncorrected for junction potential. ^c Peak-to-peak separation for cathodic and anodic waves. ^d Separation of (III,II)/(II,II) and (III,III)/(III,II) couples. ^e This work. ^f 0.1 M Na₂SO₄ as electrolyte.

that were observed for all of these Fe(II) complexes in the 400–600-nm range are typical of Fe(II)–bpy or Fe(II)–phen complexes.^{22,23} The formation of a bimetallic system from the monometallic fragment causes the MLCT bands to shift significantly toward lower energy and the internal ligand bands to shift only slightly toward lower energy. This is not surprising since the addition of electron-withdrawing groups on the nitrogen aromatic ring (i.e., remote metal center) typically stabilizes the π system, thus reducing the energy of the π^* orbital on the L and thus lowering the MLCT transition energy.⁶

The cyclic voltammograms of the monometallic complexes of Fe(II) each show one reversible wave. The $E_{1/2}$ values in aqueous solution in 0.1 M Na₂SO₄ are listed in Table II. The $E_{1/2}$ values for the Fe(III)/Fe(II) couple form the following trend: [Fe(CN)₄]₂(dpp)⁴⁻ < Fe(CN)₄(dpp)²⁻ < [Fe(CN)₄]₂(bpm)⁴⁻ < Fe(CN)₄(bpm)²⁻. In the past, workers have stated that Ru(II) ammine complexes are analogous to Fe(II) cyanide complexes.²⁴ The $E_{1/2}$ value of 0.52 V vs. SCE for Ru(NH₃)₄(bpm)²⁺ corresponds very well with that of 0.55 V for the analogous cyanoferrate complex. A correspondence between the bimetallic systems is also observed with the potentials of [Ru(NH₃)₄]₂(bpm)⁴⁺ being $E_{1/2}(1) = 0.59$ V and $E_{1/2}(2) = 0.78$ V compared to the Fe(II) $E_{1/2}(1) = 0.53$ V and $E_{1/2}(2) = 0.67$ V couples.

An interesting observation occurs when we compare the potential of the M(III)/M(II) couple for the monometallic complexes and the first M(III)/M(II) couple for the bimetallic complexes of both Fe(II) and Ru(II). In the case of the iron species, the charge on the monometallic complex decreases from 2- to 1- as the iron goes from Fe(II) to Fe(III), while the bimetallic complex decreases in charge from 4- to 3- as the Fe(II),Fe(II) system goes to Fe(III),Fe(II). Thus, it is not surprising that it is easier to oxidize the bimetallic cyanoferrate complexes because of the greater electrostatic repulsion generated by the larger negative charge. In contrast, the ruthenium system shows less positive potentials for the monometallic (2+ to 3+) than for the bimetallic (4+ to 5+) system. This is consistent with the electrostatic unfavorability of the larger negative or positive charges on the ammineruthenium complexes.

There is an additional factor that is influenced by the charge on the complex ion. In the case of the bimetallic ruthenium complexes, oxidation to the Ru(III),Ru(III) version (6+ charge) leads to decomposition into monometallic fragments.⁴⁻⁶ The cyclic and differential pulse voltammograms of the iron complexes are illustrated in Figure 1. Oxidation of the iron system to the Fe(III),Fe(III) form (2- charge) leads to a reduction in negative charge and a chemically stable product. From Figure 1, it is clear that both redox couples in parts B and C are chemically and electrochemically reversible. The $E_{1/2}$ values for these Fe(II)

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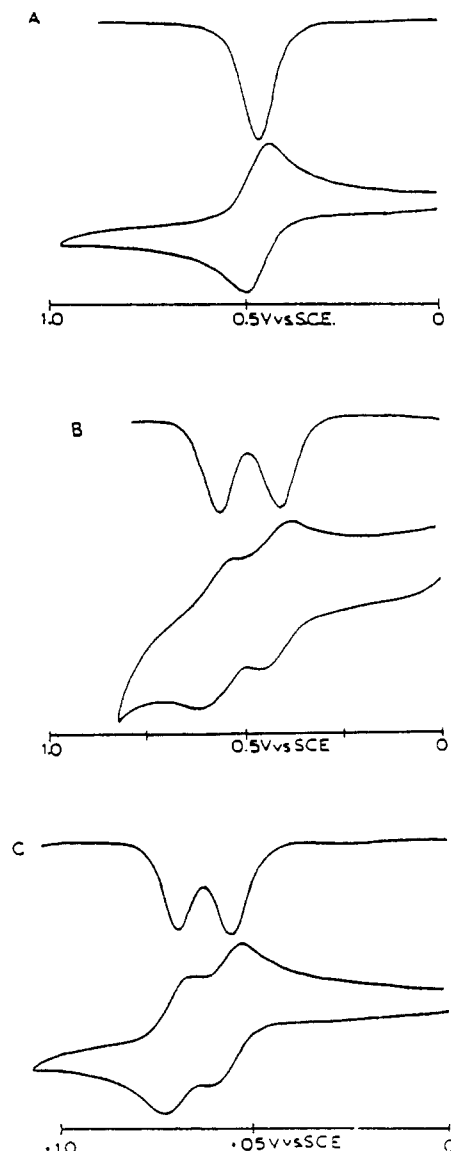
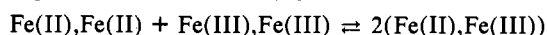


Figure 1. Cyclic and differential voltammograms: (A) $K_2[Fe(CN)_4(dpp)]$; (B) $K_4[Fe(CN)_4]_2(dpp)$; (C) $K_4[Fe(CN)_4]_2(bpm)$. The electrolyte in (A) and (C) is 2 M KCl and in (B) is 0.1 M Na_2SO_4 .

compounds have been found to be very dependent on both the type of electrolyte and the concentration of the electrolyte used. Further investigation into this phenomenon is in progress.²⁵

From the $E_{1/2}$ values in Table II, it is possible to calculate the comproportionation constants (K_c) for the reaction²⁶



$$K_c = \frac{[Fe(II), Fe(III)]^2}{[Fe(II), Fe(II)][Fe(III), Fe(III)]} = \exp(\Delta E_{1/2}/25.69)$$

where $\Delta E_{1/2}$ is given in millivolts and $T = 25^\circ C$. From this, K_c values of 233 and 343 were calculated for $[Fe(CN)_4]_2(bpm)$ and $[Fe(CN)_4]_2(dpp)$, respectively. These values are consistent with the two metal centers being slightly coupled, although the unique electrostatic situation existing in these systems requires a more rigorous theoretical treatment in order to separate the contributions to the stability of the mixed-valence state.

The overall stability of the mixed-valence complex with respect to the isovalent forms (i.e., $Fe(II), Fe(II) + Fe(III), Fe(III)$) is given²⁷ by $\Delta G_{MV} = 0.5RT \ln(K_c/4)$, which shows that the dpp-bridged system is 120 cal/mol more stable than the bpm-bridged

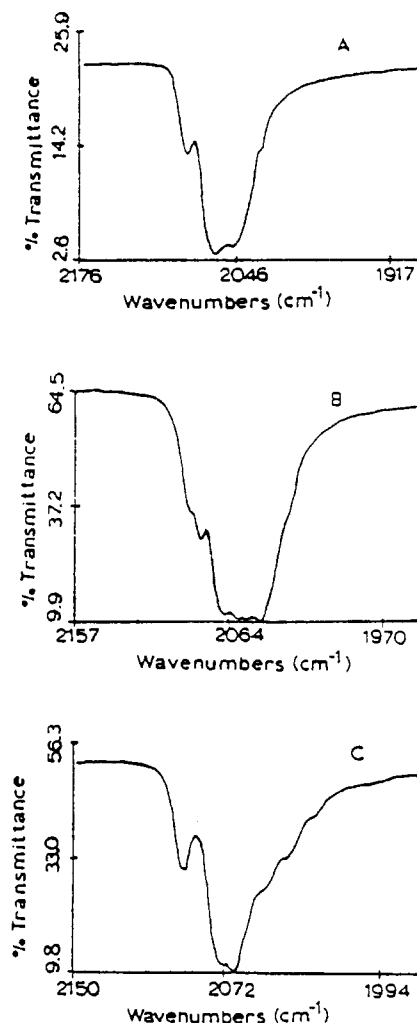


Figure 2. Infrared spectra in the cyanide stretching region (KBr pellets): (A) $K_2[Fe(CN)_4(dpp)]$; (B) $K_4[Fe(CN)_4]_2(dpp)$; (C) $K_4[Fe(CN)_4]_2(bpm)$.

system. This result is paralleled in the $[Ru(bpy)_2]_2(BL)$ system, where $\Delta G_{MV}(dpp) = 1.66$ kcal/mol and $\Delta G_{MV}(bpm) = 1.43$ kcal/mol, which suggests that dpp not only preserves the features that permit highly luminescent, long-lived excited states in the bpy analogues¹³ but also couples the two metals effectively.

It was initially expected that the bpm-bridged systems would be more stable, given the shorter estimated metal-metal separation for bpm (5.20 Å) vs. that for dpp (6.90 Å).²⁸ Richardson and Taube²⁹ delineated several factors likely to be responsible for the stability of the mixed-valence state, the most important of which are increased π acidity, electrostatic interaction, and electronic delocalization. Each of these features will be discussed below.

A significant portion of the stabilization of the mixed-valence state is attributed to the inductive effect of the M(III) metal center on the bridging ligand. This is based on the lowering of the energy of the π^* orbital of the bridging ligand by the electron-withdrawing M(III) center, which increases the affinity of the ligand for the M(II) π -donor center. This can be shown by comparing $Ru(II), M(III) \rightarrow Ru(III), M(III)$ ($M = Ru$ or Rh) and $Fe(II), M(III) \rightarrow Fe(III), M(III)$ ($M = Fe$ or Co) redox potentials.^{18,30} We have found essentially no difference between the $Fe(II), Co(III)/Fe(III), Co(III)$ and $Fe(II), Fe(III)/Fe(III), Fe(III)$ redox potentials in the $[(CN)_5Fe(pz)M^{III}(CN)_3]$ system, which suggests that this is a weakly coupled system, with virtually all of the stabilization of the mixed-valence state coming from the inductive effect of

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M(III). The inductive effect is a major contributor even in significantly delocalized systems like the Creutz-Taube ion,^{27,30} so it is expected to be important in less delocalized systems as well.

There is also a stabilization to the mixed-valence state due to simple electrostatic repulsion of the two metal centers, which for the pentaammineruthenium systems gives a slight advantage to the mixed-valence vs. isovalent forms. A calculation based on the Fuoss approach to ion pairing³²⁻³⁴

$$\Delta G_A = \frac{z_1 z_2 e_0^2}{D_S^d} \frac{1}{1 + \kappa d} - RT \ln \frac{4Nd^3}{300}$$

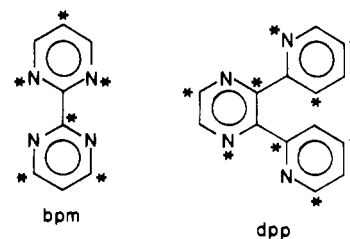
where z_1, z_2 = charge on monometallic fragments, $e_0^2 = 3.318 \times 10^{-3}$ cal cm/mol, D_S = dielectric constant (80 for 0.1 M ionic strength H_2O at 23 °C),³² d = intermetallic separation, κ = Debye inverse length ($(0.329 \times 10^8)^{1/2} J^{1/2} \text{ cm}^{-1}$ for H_2O at 23 °C), N = Avogadro's number, and $R = 1.987$ cal/(mol K), and Hess's law

$$\Delta G_{MV} = 2G_A(\text{Fe(II),Fe(III)}) - [G_A(\text{Fe(II),Fe(II)}) + \Delta G_A(\text{Fe(III),Fe(III)})]$$

yields $\Delta G_{MV}(\text{bpm}) = -294$ cal/mol and $\Delta G_{MV}(\text{dpp}) = -184$ cal/mol. While the simplistic nature of this model underestimated ΔG_{MV} ,²⁷ the result is consistent with the expectation that the smaller metal-metal separation should yield a greater electrostatic stabilization of the mixed-valence form. The fact that the electrostatic stabilization for bpm is greater than for dpp, in spite of the fact that overall the mixed-valence-state dpp-bridged system is more stable than the bpm-bridged complex, focuses attention on the remaining contribution to mixed-valence stabilization, electronic delocalization.

Richardson and Taube²⁹ have noted that if a metal is bound to a starred position of an alternating hydrocarbon, the strongest metal-metal interaction is observed if the second metal is bound to an unstarred position. This is based on general observation of the transmission of electronic effects through conjugated bond systems, as well as by mechanistic theories.²⁹ If the star formalism

is applied to bpm and dpp, the following results:



This suggests that the electronic distribution for dpp (a 1,4-coordination on the pyrazine ring) is more favorable for metal-metal interaction than in bpm (a 1,3-coordination on each pyrimidine ring). A more quantitative estimate of the extent of electronic interaction can be made from intervalence transfer band data, which are currently under investigation.²⁵

Conclusion

From the $E_{1/2}$ values we can see that dpp functions well as a bridging ligand and provides excellent communication between the two metal centers. The dpp ligand provides a means to separate the metal centers, thereby reducing steric crowding.

These bimetallic systems show that we can bridge two first-row transition-metal centers using either bpm or dpp as the bridging ligand. The electrochemical data seem to indicate a large amount of communication between the metal centers, supporting our idea of possible energy transfer across the bridging ligand. The results presented here indicate that dpp may yield more promising results than bpm in the preparation of mixed-metal bimetallic complexes since it significantly lowers the steric crowding without reducing the communication between the metal centers.

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Registry No. $K_2[\text{Fe}(\text{CN})_4(\text{bpm})]$, 92787-94-5; $K_4[\text{Fe}(\text{CN})_4]_2(\text{bpm})$, 109765-39-1; $K_2[\text{Fe}(\text{CN})_4(\text{dpp})]$, 109765-40-4; $K_4[\text{Fe}(\text{CN})_4]_2(\text{dpp})$, 109765-41-5; $\text{Fe}(\text{CN})_4(\text{bpm})^-$, 109765-42-6; $[\text{Fe}(\text{CN})_4]_2(\text{bpm})^{3-}$, 109765-43-7; $[\text{Fe}(\text{CN})_4]_2(\text{bpm})^{2-}$, 97823-73-9; $\text{Fe}(\text{CN})_4(\text{dpp})^-$, 109765-44-8; $[\text{Fe}(\text{CN})_4]_2(\text{dpp})^{3-}$, 109765-45-9; $[\text{Fe}(\text{CN})_4]_2(\text{dpp})^{2-}$, 109765-46-0.

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Preparation, Structure, and Magnetic Properties of a New Form of Chromium Orthoarsenate: β -CrAsO₄

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A new (β) form of CrAsO_4 has been prepared at 700 °C under 3-kbar hydrothermal pressure, and a single-crystal X-ray study shows that β - CrAsO_4 adopts the ZnSO_4 structure ($a = 8.995$ (2) Å, $b = 6.237$ (3) Å, $c = 4.755$ (1) Å, $Z = 4$, space group $Pnma$). The ordered magnetic structure at 5 K has been determined from a powder neutron diffraction experiment and consists of Cr^{3+} moments of 2.38 (4) μ_B parallel to c , antiferromagnetically ordered both in the ac plane and along b . Variable-field magnetic susceptibility measurements are consistent with antiferromagnetic behavior in the high-temperature Curie-Weiss limit but reveal ferromagnetic behavior below the Néel temperature of 10 ± 2 K. This is consistent with magnetic symmetry arguments that show that a weak field-induced ferromagnetic component parallel to b is allowed. This magnetic behavior is compared with that of other ZnSO_4 type materials.

Introduction

Crystalline salts of the first-row transition metals have been of interest for many years in the study of the magnetic behavior of the various $3d^n$ electronic configurations and the interactions

between the magnetic ions. As part of this effort, the low-temperature magnetic properties and ordered magnetic structures of many salts with the CrVO_4 ³ or the related ZnSO_4 ⁴ structure have been studied. Both of these orthorhombic structures consist of infinite chains of trans edge-sharing MO_6 octahedra, with XO_4 tetrahedra linking the chains. Strong ferromagnetic or antifer-

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