

## Bimetallic Reactivity. Investigation of Metal–Metal Interaction in Complexes of a Chiral Macrocyclic Binucleating Ligand Bearing 6- and 4-Coordinate Sites

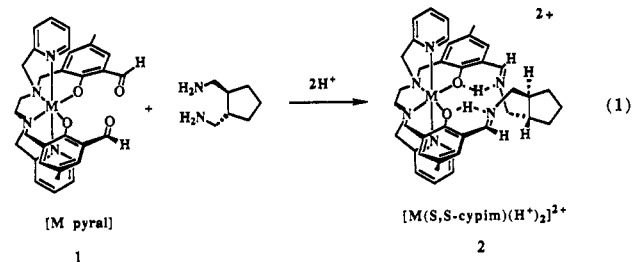
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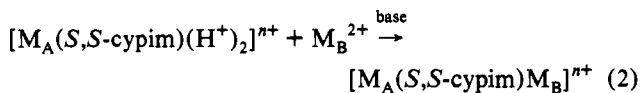
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The cooperative physical properties of a chiral macrocyclic binucleating ligand, *S,S*-cypim, containing 6-coordinate (closed-site) and four coordinate (open-site) compartments bridged by phenolic oxygen atoms have been examined. The chiral (1*S*,2*S*)-*trans*-1,2-bis(aminomethyl)cyclopentane moiety of the *S,S*-cypim ligand forces the monometallic and symmetrical bimetallic complexes to adopt one diastereomer. Solution magnetic moments of the bimetallic complexes containing two paramagnetic metals indicate spin-spin coupling at 20 °C. All of the metals in these complexes, except for Co(III), are spin-free. EPR spectra were recorded for a series of Cu(II) complexes, [Cu(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, [Cu(*S,S*-cypim)ZnCl]<sup>+</sup>, [Cu(*S,S*-cypim)Zn]<sup>2+</sup>, [Cu(*S,S*-cypim)Cu]<sup>2+</sup>, [Zn(*S,S*-cypim)Cu]<sup>2+</sup>, [Ni(*S,S*-cypim)Cu]<sup>2+</sup>, and [Co(*S,S*-cypim)Cu]<sup>3+</sup>, where the closed-site metal is written first. At 77 K in acetonitrile/toluene glasses the EPR spectra indicate that [Cu(*S,S*-cypim)Cu]<sup>2+</sup> may exist as a spin-paired singlet, whereas the spectrum of [Ni(*S,S*-cypim)Cu]<sup>2+</sup> exhibits the spin-interacting doublet state. The EPR spectra were used to monitor both inter- and intramolecular metal site scrambling of these complexes. No scrambling was detected. The electronic absorption spectra for [Co<sup>III</sup>(*S,S*-cypim)M<sup>II</sup>] complexes indicate distorted trigonal bipyramidal open-site metal geometries, whereas the Cu(II) ions in the [M(*S,S*-cypim)Cu]<sup>2+</sup> complexes generally have more planar but distorted four- or five-coordinate structures. Cyclic voltammetry of a series of Cu(II) complexes of the type [M(*S,S*-cypim)Cu]<sup>2+</sup> and of Co(III) complexes of the types [Co(*S,S*-cypim)MCl]<sup>2+</sup> and [Co(*S,S*-cypim)M]<sup>3+</sup> show that the potentials of the invariant metals are dependent on the nature of the neighboring metal. Whereas some of these variations could be due to structural differences in the bimetallic series, metal–metal interaction may also influence the redox properties of the invariant Cu(II) and Co(III) ions in these complexes.

The preceding paper<sup>1</sup> described the synthesis and structural characteristics of complexes derived from the chiral ligand *S,S*-cypim, a binucleating ligand bearing six- and four-coordinate sites. The ligand *S,S*-cypim was prepared from the dialdehyde complex **1**,<sup>2</sup> by condensation with (1*S*,2*S*)-*trans*-1,2-bis(aminomethyl)cyclopentane (eq 1). Monometallic complexes [M(*S,S*-



cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> (**2**), which contain a metal in the six-coordinate site (closed site) and two protons in the four-coordinate site (open site) were isolated for the metals Zn(II), Cu(II), Ni(II), Co(II), and Mn(II). Oxidation of the monometallic Co(II) complex gave the Co(III) complex, [Co(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>3+</sup>. These monometallic complexes provided precursors for the preparation of homo- and heterobimetallic complexes (eq 2). Among the



heterobimetallic complexes prepared were (1) complexes derived from Co(III) in the closed site and the metals Zn(II), Cu(II),

Ni(II), Co(II), and Mn(II) in the open site and (2) complexes with Cu(II) in the open-site and Zn(II), Cu(II), Ni(II), Co(II), and Mn(II) in the closed site. These two series and the other heterobimetallic complexes were prepared in order to investigate systematically the cooperative physical properties of a given metal in a specific site when the metal in the other site is varied.

Crystal structures and <sup>1</sup>H NMR data of representative members of these series indicated that all of the monometallic species and all of the complexes bearing Co(III) in the closed site were C<sub>2</sub> symmetric as illustrated in **2**. When larger, labile metals were present in the closed site, the resulting bimetallic complexes possessed unsymmetrical structures where the pyridine ligands were not *trans* as in **2** but rather were *cis* disposed on the same side of the mean macrocyclic plane. The presence of the chiral diimine enforces a single topological diastereomer of the ligands about the closed-site metal. It appears, however, that the diastereomer selected depends on the radius of the closed-site metal. In particular, the [Mn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> complex has chiral topology opposite to that found for the other monometallic and Co(III)-containing bimetallic complexes.

This paper addresses a number of questions related to the cooperative physical properties which are observed for the bimetallic complexes of the *S,S*-cypim ligand. The determination of some of these properties is a necessary prelude to our ultimate aim of studying cooperative chemical reactivity, particularly in oxidative addition reactions of these types of complexes. One of the issues addressed here relates to electron spin coupling of neighboring metals. In addition, we were interested in determining whether EPR spectroscopy could be used in assessing metal site selectivity and scrambling in heterobimetallic complexes. The effect of neighboring metals on the d–d electronic absorption spectra of bimetallic complexes is also investigated. Finally, we wished to determine whether the reduction potential of a metal in a given site changes as the neighboring metal is varied. Such information is important in assessing (1) the feasibility of employing the reducing power of contiguous metals in the oxidative

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(1) Fraser, C.; Ostander, R.; Rheingold, A. L.; White, C.; Bosnich, B. *Inorg. Chem.*, preceding paper in this issue.

(2) Fraser, C.; Johnston, L.; Rheingold, A. L.; Haggerty, B. S.; Williams, G. K.; Whelan, J.; Bosnich, B. *Inorg. Chem.* 1992, 31, 1835.

**Table 1.** Magnetic Moments for Mono- and Bimetallic *S,S*-cypim Complexes<sup>a,b</sup>

	$\mu_{\text{eff}},^d$ B.M.	$\mu_{\text{s.o.}},^c$ B.M.
[Mn( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	5.9	5.92
[Co( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	4.8	3.87
[Ni( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	3.3	2.45
[Cu( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	1.8	1.73
[Mn( <i>S,S</i> -cypim)MnCl](PF <sub>6</sub> ) <sub>2</sub>	8.4	10.95
[Mn( <i>S,S</i> -cypim)Mn(Cl) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	7.5	9.95
[Ni( <i>S,S</i> -cypim)NiCl](PF <sub>6</sub> ) <sub>2</sub>	4.7	4.90
[Cu( <i>S,S</i> -cypim)ZnCl](PF <sub>6</sub> ) <sub>2</sub>	2.1	1.73
[Mn( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	6.2	6.93
[Co( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	4.5	4.90
[Ni( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	3.3	3.87
[Cu( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	1.8	2.83
[Zn( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	1.8	1.73
[Co( <i>S,S</i> -cypim)MnCl](PF <sub>6</sub> ) <sub>2</sub>	5.8	5.92
[Co( <i>S,S</i> -cypim)CoCl](PF <sub>6</sub> ) <sub>2</sub>	4.4	3.87
[Co( <i>S,S</i> -cypim)NiCl](PF <sub>6</sub> ) <sub>2</sub>	3.4	2.45
[Co( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>3</sub>	1.7	1.73

<sup>a</sup> Magnetic susceptibilities were determined at 20 °C by the Evans NMR method on samples dissolved in CD<sub>3</sub>CN. <sup>b</sup> The magnetic moments are reported per bimetallic dimer. <sup>c</sup> Spin only values are determined for the bimetallic ensemble, (where  $\mu_{\text{s.o.}} = \sqrt{n(n+2)}$  and  $n$  = total number of unpaired spins; e.g. for the Mn(II)-Mn(II) complex  $n = 10$ ). <sup>d</sup> Approximate error =  $\pm 0.1$  B.M.

addition of reactants to the open-site metal and (2) the potential for tuning the reactivity of the open-site metal in these complexes by varying the closed-site metal.

### Magnetic Moments

The gram susceptibilities of all of the paramagnetic complexes were determined in acetonitrile solution at 20 °C by the Evans <sup>1</sup>H NMR method.<sup>3</sup> The derived magnetic moments,  $\mu_{\text{eff}}$ , are accurate to  $\pm 0.1 \mu_{\text{B}}$ . These are collected in Table 1 together with the spin-only values derived from the total spin of the complex. For the monometallic complexes and the bimetallic complexes containing spin-paired Co(III) and Zn(II), the calculated magnetic moments fall within the ranges expected for magnetically dilute complexes containing a single paramagnetic ion.<sup>4</sup> Bimetallic complexes containing two contiguous paramagnetic ions give magnetic moments which are less than the total spin-only values. Presumably the lowering of these magnetic moments is due to antiferromagnetic coupling by superexchange through the phenolic oxygen atoms.<sup>5</sup> We note that the magnetic moments appear to be greater for *S,S*-cypim complexes than were observed for analogous complexes formed with the cyclim ligand.<sup>1</sup> Various postulates have been advanced in order to explain variation in antiferromagnetic coupling in bimetallic complexes. These include emphasis on mutual d-orbital orientation and electron occupancy<sup>6,7</sup> and emphasis on the dispositions of bridging ligand orbitals in relation to metal d orbitals.<sup>8</sup>

### EPR Spectra

EPR studies of selected Cu(II)-containing complexes were conducted for three primary purposes. First, we wished to

- (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791.
- (a) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: New York, 1968. (b) Banci, L.; Bencini, A.; Gatteschi, D.; Zanchini, C. *Struct. Bonding* **1982**, *52*, 37. (c) Sacconi, L.; Mani, F.; Bencini, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 5, Chapter 50, p 54. (d) Hathaway, B. in *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987. Vol. 5, Chapter 53, p 533.
- Boudreaux, E. A.; Mulay, L. N. *Theory and Applications of Molecular Paramagnetism*; John Wiley & Sons: New York, 1976.
- (a) Lambert, S. L.; Spiro, C. L.; Gagné, R. R.; Hendrickson, D. N. *Inorg. Chem.* **1982**, *21*, 68. (b) Lambert, S. L.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2683. (c) Spiro, C. L.; Lambert, S. L.; Smith, T. J.; Duesler, E. N.; Gagné, R. R.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1229.
- Kahn, O. *Struct. Bonding* **1987**, *68*, 89 and references cited therein.

**Table 2.** X-Band EPR Parameters for *S,S*-cypim Complexes<sup>a</sup>

	$g_{\perp}$	$g_{\parallel}$	$10^{-4} A_{\parallel} , \text{cm}^{-1}$
[Cu( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	2.18	2.41	164
[Cu( <i>S,S</i> -cypim)Zn](PF <sub>6</sub> ) <sub>2</sub>	2.12	2.34	174
[Cu( <i>S,S</i> -cypim)ZnCl](PF <sub>6</sub> ) <sub>2</sub>	2.18	2.39	183
[Zn( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	2.11	2.32	187
[Co( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>3</sub>	2.20	2.40	142
[Ni( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	2.31		

<sup>a</sup> EPR spectra were run at 77 K on CH<sub>3</sub>CN-toluene (2:3) frozen glasses.

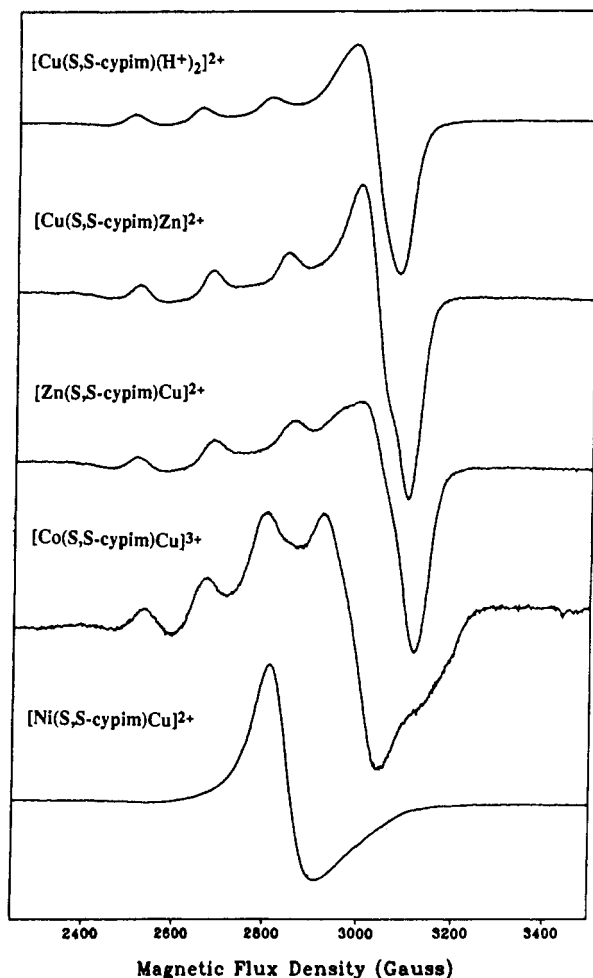
determine whether EPR parameters might be correlated with structural differences in mono- and bimetallic *S,S*-cypim complexes. The second goal was to investigate whether the EPR spectra show evidence of metal-metal interaction. Finally, we wished to determine whether this technique could be used to detect metal site scrambling and thus, to establish the purity of heterobimetallic complexes.

X-Band EPR spectra of the PF<sub>6</sub><sup>-</sup> salts of [Cu(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, [Cu(*S,S*-cypim)ZnCl]<sup>+</sup>, [Cu(*S,S*-cypim)Zn]<sup>2+</sup>, [Zn(*S,S*-cypim)Cu]<sup>2+</sup>, [Co(*S,S*-cypim)Cu]<sup>3+</sup>, and [Ni(*S,S*-cypim)Cu]<sup>2+</sup> were investigated in acetonitrile-toluene (2:3) solutions at 298 K and for the glasses at 77 K. No isotropic spectra were observed at room temperature for any of the complexes studied. Anisotropic spectra were obtained for frozen samples of certain copper-containing complexes. All of the complexes were expected to give rise to rhombic spectra. However, in all cases the high field  $g_1$  and  $g_2$  tensors were poorly resolved and the spectra appear axial with  $g_{\parallel} (g_3) > g_{\perp} (g_2, g_1) > 2$ . Thus the anisotropic  $g$  tensors are approximated as  $g_{\parallel}$  and  $g_{\perp}$ . These parameters and the  $|A_{\parallel}|$  values are listed in Table 2. Selected spectra are shown in Figure 1. While no hyperfine structure is observed for the  $g_{\perp}$  signal,  $g_{\parallel}$  exhibits hyperfine splitting due to the Cu nucleus ( $I = 3/2$ ). For spectra run in CH<sub>3</sub>CN-toluene (2:3), only three of the  $g_{\parallel}$  signals are observed; the fourth high field  $g_{\parallel}$  signal is not clearly resolved from  $g_{\perp}$  at 77 K.

The anisotropic hyperfine splitting constants  $|A_{\parallel}|$  are affected both by the charge on the metal ion and by geometrical perturbations. Among the closed-site Cu(II)-containing complexes, the [Cu(*S,S*-cypim)ZnCl]<sup>+</sup> complex possesses the lowest overall charge and the highest  $|A_{\parallel}|$  value ( $183 \times 10^{-4} \text{cm}^{-1}$ ). When the chloride is removed to give [Cu(*S,S*-cypim)Zn]<sup>2+</sup>, the geometry of the Cu ion is probably little affected, while the charge on the complex increases to 2+. Thus, the  $|A_{\parallel}|$  value drops as is expected. The structural differences between the monometallic complex [Cu(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> and the bimetallic complexes [Cu(*S,S*-cypim)Zn]<sup>2+</sup> and [Cu(*S,S*-cypim)ZnCl]<sup>+</sup> may account for the observed differences in their hyperfine splitting constants  $|A_{\parallel}|$ . In the monometallic complex the ligand is bound in a C<sub>2</sub>-symmetric arrangement, while in both of the bimetallic cases the complexes are likely to exist in non-C<sub>2</sub>-symmetric conformations with the pyridyl groups cis to each other. In addition, the closed-site Cu(II) ions may be five-coordinate in the bimetallic complexes.

There is also a marked difference in the anisotropic hyperfine splitting constants of the two complexes [Co(*S,S*-cypim)Cu]<sup>3+</sup> and [Zn(*S,S*-cypim)Cu]<sup>2+</sup> which contain open-site Cu(II) ions (see Table 2). This may be attributed, in part, to the differences in charge. However, the observed range in  $|A_{\parallel}|$  values is probably also indicative of differences in geometry about the open-site Cu(II) ions in these complexes. It has been shown for the copper protein azurin that smaller  $|A_{\parallel}|$  values correlate with either tetrahedral or trigonal bipyramidal Cu(II) geometries, which

- (a) O'Connor, C. J.; Freyberg, D. P.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 1077. (b) See: Fenton, D. E.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6367 and references cited therein. (c) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884. (d) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173. (e) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.



**Figure 1.** X-Band EPR Spectra of Cu(II)-*S,S*-cypim complexes in acetonitrile-toluene (2:3) glasses at 77 K.

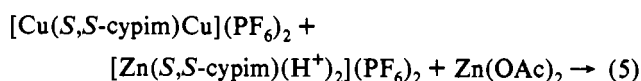
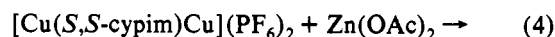
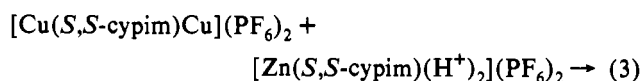
are sometimes difficult to distinguish by EPR.<sup>9</sup> Other geometries such as square planar or square pyramidal typically give rise to considerably higher anisotropic hyperfine splitting constants.<sup>10</sup> In the Co(III)-containing complex the *S,S*-cypim ligand adopts a roughly  $C_2$ -symmetric conformation in which the open site is held in a distorted tetrahedral array. Upon coordination of a molecule of acetonitrile, the open-site Cu(II) assumes a distorted trigonal bipyramidal geometry. This is reflected in a low  $|A_{\parallel}|$  value of  $142 \times 10^{-4} \text{ cm}^{-1}$ . In contrast, the  $[\text{Zn}(\text{S,S-cypim})\text{Cu}]^{2+}$  complex contains a labile metal in the closed site; the *S,S*-cypim ligand can rearrange to generate a structure with a more planar geometry about the open-site copper ion. Thus a larger anisotropic hyperfine splitting constant is observed ( $|A_{\parallel}| = 187 \times 10^{-4} \text{ cm}^{-1}$ ), as is expected for distorted square pyramidal Cu(II) geometries.

In addition to corroborating structural differences of Cu(II) ions observed in the X-ray structures<sup>1</sup> of *S,S*-cypim complexes, the EPR experiment was also effective in demonstrating a metal-metal electronic interaction for two of the complexes studied. The magnetic moment of the  $[\text{Cu}(\text{S,S-cypim})\text{Cu}]^{2+}$  complex exhibited spin-spin coupling at 20 °C (Table 1), but at 77 K no EPR signal was observed. This suggests that the electrons are paired and that a singlet state obtains at low temperatures. The spectrum of the  $[\text{Ni}(\text{S,S-cypim})\text{Cu}]^{2+}$  complex also shows evidence of metal-metal interaction. When there is interaction

between the  $S = 1/2$  state of the Cu(II) ion and the  $S = 1$  state of high spin Ni(II), two states are generated, a doublet and a quartet. While both of these are EPR active in principle, typically only the signal attributable to the doublet state has been observed.<sup>7</sup> (See Figure 1.) The EPR signal for  $[\text{Ni}(\text{S,S-cypim})\text{Cu}]^{2+}$  is similar to what has been previously in the spectra of other bimetallic Ni(II)-Cu(II) complexes with  $g_{\parallel} < g_{\perp}$ ; however, the *S,S*-cypim complex shows no evidence of hyperfine splitting.<sup>6,11</sup> (See Figure 1.) Since the magnetic moment of the  $[\text{Ni}(\text{S,S-cypim})\text{Cu}](\text{PF}_6)_2$  complex is near the spin-only value for the bimetallic system, this indicates that there is extensive population of the quartet state at room temperature.

EPR experiments were also undertaken in order to assess how readily metals scramble in *S,S*-cypim complexes. It is a particular challenge in the preparation of heterobimetallic compounds to ensure that no metal exchange nor site scrambling has occurred and, in their characterization, to determine the homogeneity of the product obtained. If a site-symmetric binucleating ligand is utilized, it is only necessary to determine whether a targeted heterobimetallic complex is contaminated with homobimetallic impurities. When a binucleating ligand contains two different coordination sites, however, in addition to detecting homobimetallic impurities, it is also important to determine whether site scrambling has occurred. For example, a preparation of  $[\text{Zn}(\text{S,S-cypim})\text{Cu}]^{2+}$  could contain  $[\text{Cu}(\text{S,S-cypim})\text{Cu}]^{2+}$  and  $[\text{Zn}(\text{S,S-cypim})\text{Zn}]^{2+}$  homobimetallic impurities or the site-scrambled  $[\text{Cu}(\text{S,S-cypim})\text{Zn}]^{2+}$  heterobimetallic complex if the reaction occurs under thermodynamic control. The two approaches taken to address this issue are described below.

Metal scrambling could occur in heterobimetallic preparations via intermolecular metal ion exchange or by exchange with free metal ions in solution. In order to determine whether such reactions are occurring for *S,S*-cypim complexes, we followed a number of potential scrambling reactions. EPR silent species were combined and, were metal exchange to occur, EPR signals would be observed (eqs 3-5). These reactions were run in 1:1:3



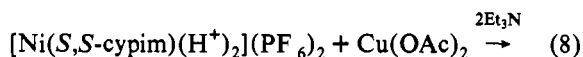
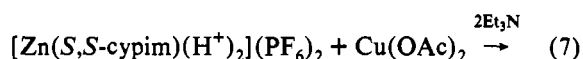
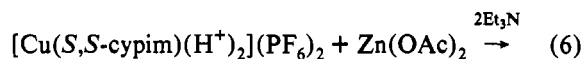
acetonitrile-ethanol-toluene to approximate preparative conditions, with toluene added in order to obtain a glass suitable for EPR. The mixtures were allowed to stand at 298 K and were periodically frozen to 77 K to measure the EPR spectra. No EPR signals were detected in these three samples over a period of 40 h. This suggests, at least for the  $[\text{Cu}(\text{S,S-cypim})\text{Cu}]^{2+}$  complex, that intermolecular exchange with Zn(II) is very slow.

Small-scale preparative reactions were run in order to assess whether intramolecular site scrambling could be detected. The desired heterobimetallic complexes  $[\text{Zn}(\text{S,S-cypim})\text{Cu}]^{2+}$ ,  $[\text{Cu}(\text{S,S-cypim})\text{Zn}]^{2+}$ , and  $[\text{Ni}(\text{S,S-cypim})\text{Cu}]^{2+}$  were prepared from monometallic precursors and the appropriate metal salts in the presence of base (eqs 6-8). These solutions were monitored by EPR spectroscopy over a period of 40 h. The spectra generated were identical to those obtained for purified samples isolated from large-scale preparations (Figure 1), and no changes were detectable in these spectra after allowing the samples to stand in solution for 40 h at 298 K. It should be noted, however that both  $[\text{Cu}(\text{S,S-cypim})\text{Cu}]^{2+}$  and  $[\text{Zn}(\text{S,S-cypim})\text{Zn}]^{2+}$  complexes are

(9) (a) Norris, G. E.; Anderson, B. F.; Baker, E. N. *J. Am. Chem. Soc.* **1986**, *108*, 2784. (b) Solomon, E. I.; Baldwin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, *92*, 521.

(10) (a) Hathaway, B. J. In *Comprehensive Coordination Chemistry*, Wilkinson, G., Ed.; Pergamon Press: New York, 1987. Vol. 5, Chapter 53, pp 663-7. (b) Hathaway, B. J. *Struct. Bonding* **1984**, *57*, 55. (c) Peisach, J.; Blumberg, W. E. *Arch. Biochem. Biophys.* **1974**, *691*.

(11) Morgenstern-Badarau, I.; Rerat, M.; Kahn, O.; Jaud, J.; Galy, J. *Inorg. Chem.* **1982**, *21*, 3050.



EPR silent under these conditions and that, although distinct, the spectra of  $[\text{Zn}(\text{S,S-cypim})\text{Cu}]^{2+}$  and  $[\text{Cu}(\text{S,S-cypim})\text{Zn}]^{2+}$  are similar, making detection of small amounts of site-scrambled impurities difficult. This experiment did confirm that the product generated in the initial reaction is identical to that obtained from large-scale preparations after isolation and purification, and that the heterobimetallic complexes are stable in solution over time. The results of the site-scrambling experiments presented here strongly suggest that on the time scale and under the conditions used for the preparation of heterobimetallic complexes bearing labile metals, little or no scrambling occurs. This conclusion probably also obtains for the other complexes which were described in the preceding paper.

### Electronic Absorption Spectra

The electronic absorption spectra of the monometallic complexes,  $[\text{M}_c(\text{S,S-cypim})(\text{H}^+)_2]^{n+}$  and the bimetallic complexes  $[\text{M}_c(\text{S,S-cypim})\text{M}_c]^{n+}$  were recorded in acetonitrile solutions over the range 275–2000 nm. These regions encompass, to lower energies, the d–d transitions and, to higher energies, some of the metal–ligand charge transfer bands and the  $\pi$ – $\pi^*$  azomethine transitions.<sup>12,13</sup> The purpose of this study was to correlate the d–d transitions with the geometries of the metal ions and to determine whether any intervalence transitions<sup>14</sup> are observed in the bimetallic complexes.

The transitions attributed to the azomethine chromophores in all of the mono- and bimetallic S,S-cypim complexes and their associated circular dichroism spectra were presented and discussed in detail in the preceding paper.<sup>1</sup> In many of the spectra charge transfer bands overlap with some of the d–d bands or with the azomethine  $\pi$ – $\pi^*$  transitions. These charge transfer bands are probably associated with the phenolic ligands bound to Cu(II)<sup>15</sup> and Co(III).<sup>16</sup> In the case of Cu(II), these metal–phenolic transitions are only seen for complexes containing Cu(II) in the open site. It should be noted that in all cases, this charge transfer band appears as a lower energy shoulder on the more intense azomethine transition, which may entirely obscure the metal–phenolic band in closed-site Cu(II) complexes. Table 3 lists the positions and intensities of the azomethine, the d–d, and the charge transfer transitions observed in the spectra of monometallic and bimetallic S,S-cypim complexes. Figure 2 shows the d–d absorption spectra of a series of Cu(II) complexes. All of the transitions are associated with Cu(II); the Co(III) bands occur at higher energies. The monometallic complex  $[\text{Cu}(\text{S,S-cypim})$

$(\text{H}^+)_2]^{2+}$  shows a single symmetric band at 710 nm with a weak tail absorption to lower energies.<sup>17,18</sup> In contrast, the corresponding  $[\text{Cu}(\text{S,S-cypim})\text{Zn}]^{2+}$  complex containing spectroscopically neutral Zn(II) in the open site exhibits two bands, one at 652 nm and a broad, weak transition at 1008 nm. This undoubtedly reflects a difference in the coordination geometry and perhaps coordination number of the Cu(II) ion in the respective closed sites. As noted in the preceding paper the Cu(II) in  $[\text{Cu}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$  is probably 6-coordinate and  $C_2$  symmetric whereas the Cu(II) ion in the  $[\text{Cu}(\text{S,S-cypim})\text{Zn}]^{2+}$  complex is probably 5-coordinate and has cis-disposed rather than trans-disposed pyridine ligands, analogous to what was observed in the crystal structure<sup>1</sup> of  $[\text{Cu}(\text{S,S-cypim})\text{Cu}]^{2+}$ . This latter supposition is supported by the addition of the d–d absorption spectra of  $[\text{Cu}(\text{S,S-cypim})\text{Zn}]^{2+}$  and  $[\text{Zn}(\text{S,S-cypim})\text{Cu}]^{2+}$ , which give a composite spectrum with peak positions that match those in the spectrum of  $[\text{Cu}(\text{S,S-cypim})\text{Cu}]^{2+}$  (Figure 3). Addition of the spectra of the  $[\text{Cu}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$  and  $[\text{Zn}(\text{S,S-cypim})\text{Cu}]^{2+}$  complexes does not produce a composite spectrum resembling that of  $[\text{Cu}(\text{S,S-cypim})\text{Cu}]^{2+}$ . This can be seen by inspection of the relevant peak positions of the individual spectra for these complexes shown in Figure 2. The geometries of the open-site Cu(II) ions and, consequently, the d–d absorptions observed are dependent upon the metal ion in the closed site. The crystal structure<sup>1</sup> of  $[\text{Co}(\text{S,S-cypim})\text{Cu}(\text{CH}_3\text{CN})]^{3+}$  indicates that that Cu(II) ion is in a distorted trigonal bipyramidal geometry. On the other hand, the crystal structure of  $[\text{Cu}(\text{S,S-cypim})\text{Cu}]^{2+}$  has the open-site Cu(II) in a distorted square planar geometry. The splittings and low-energy bands observed for these open-site Cu(II) complexes are typical for their respective five- and four-coordinate geometries.<sup>18</sup>

The electronic absorption spectra of Ni(II) complexes are shown in Figure 4. The monometallic  $[\text{Ni}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$  complex shows a broad absorption band at 933 nm which can be ascribed to the lowest energy octahedral Ni(II) d–d transition.<sup>18,19</sup> Four d–d transitions are observed in the spectrum of  $[\text{Co}(\text{S,S-cypim})\text{NiCl}]^{2+}$  which arise from Ni(II) in the open site. Such spectra are characteristic of 5-coordinate spin-free Ni(II) structures.<sup>18–20</sup> It is difficult to distinguish between trigonal bipyramidal and square pyramidal structures for Ni(II) on the basis of absorption spectra. However, the open site of  $[\text{Co}(\text{S,S-cypim})\text{NiCl}]^{2+}$  is probably analogous to what was observed for open-site Cu(II) in the X-ray structure of  $[\text{Co}(\text{S,S-cypim})\text{Cu}(\text{CH}_3\text{CN})]^{3+}$ . The spectrum of  $[\text{Ni}(\text{S,S-cypim})\text{NiCl}]^{2+}$  is very similar to that observed for  $[\text{Co}(\text{S,S-cypim})\text{NiCl}]^{2+}$  and bears little resemblance to the spectrum of  $[\text{Ni}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$ , which is believed to contain an octahedral Ni(II) geometry. Thus, it is possible that the structure of the dinickel(II) complex is similar to that of the dicopper(II) S,S-cypim complex, in which both metal ions adopt five-coordinate structures.

Both  $[\text{Co}(\text{S,S-cypim})\text{CoCl}]^{2+}$  and  $[\text{Co}(\text{S,S-cypim})\text{Co}]^{3+}$  exhibit low-energy spectral bands which may be ascribed to five-coordinate open-site Co(II). Transitions are observed at 773 and 1770 nm in the former and at 830 and 1737 nm in the latter. (Table 3) The lowest energy bands are probably indicative of nearly trigonal bipyramidal open-site geometries for these complexes,<sup>21</sup> with a molecule of acetonitrile binding in the latter. This represents a considerable change in geometry from the previously reported  $[\text{M}(\text{cyclim})\text{CoCl}]^{2+}$  complexes which are

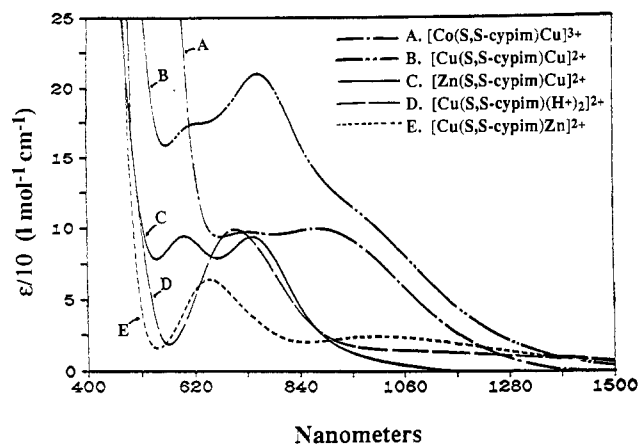
- (12) Bosnich, B. *J. Am. Chem. Soc.* **1968**, *90*, 627.  
 (13) Heinert, D.; Martell, A. E. *J. Am. Chem. Soc.* (a) **1962**, *84*, 3257; (b) **1963**, *85*, 183, 188.  
 (14) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 257. (c) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.  
 (15) (a) Sorrell, T. N. *Tetrahedron* **1989**, *45*, 1 and references therein. (b) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bond.* **1983**, *53*, 1. (c) Gray, H.; Solomon, E. I. In *Copper Proteins*; Spiro, T. G., Ed.; John Wiley & Sons: New York, 1981; Chapter 1. (d) Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121. (e) Sorrell, T. N.; Malachowski, M. R.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 3250. (f) Ainscough, E. W.; Bingham, A. G.; Brodie, A. M.; Husbands, J. M.; Plowman, J. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1701. (g) Amundsen, A. R.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6730.  
 (16) (a) Garbett, K.; Gillard, R. D. *J. Chem. Soc. (A)* **1968**, 979. (b) Yamamoto, Y.; Kudo, H.; Toyota, E. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1051.

- (17) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987. Vol. 5, Chapter 53, p 674.  
 (18) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd. ed.; Elsevier: New York, 1984.  
 (19) Sacconi, L.; Mani, F.; Bencini, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 5, Chapter 50, p 60 ff.  
 (20) (a) Orioli, P. L.; *Coord. Chem. Rev.* **1971**, *6*, 285 and references cited therein. (b) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343 and references cited therein.  
 (21) Lever, A. B. P. Reference 18, pp 487–496 and references therein.

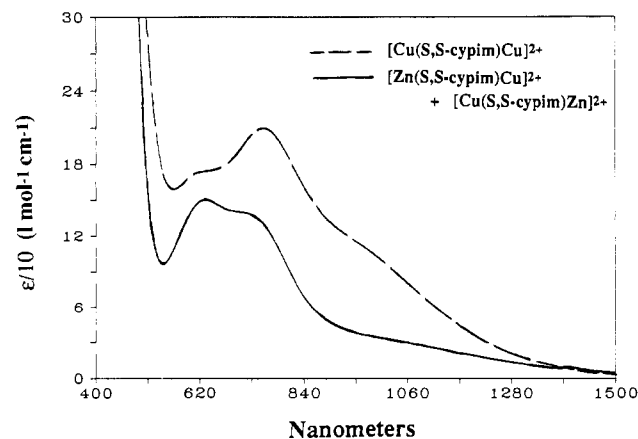
**Table 3.** Electronic Absorption Maxima and Intensities of the Charge Transfer and d-d Transitions for *S,S*-cypim Complexes<sup>a</sup>

		$\lambda_{\text{max}}$ , nm ( $\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup> ) <sup>c</sup>			
[Mn( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	402 (13120)				
[Co( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	406 (11080)			1009 (13)	
[Ni( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	406 (12050)		804 (13)		933 (27)
[Cu( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	404 (10990)		710 (99) <sup>b</sup>		
[Zn( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	399 (11610)				
[Mn( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	365 (9270)	450 (300)	620 (75)	744 (78)	
[Co( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	357 (8200)	456 (890) <sup>b</sup>			
[Ni( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	360 (10190)	464 (674)	646 (131)	791 (97) <sup>b</sup>	
[Cu( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	357 (7920)	387 (6660) <sup>c</sup>	478 (508)	622 (174)	752 (210)
[Zn( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	355 (7070)		457 (352)	601 (95)	742 (94)
[Cu( <i>S,S</i> -cypim)Zn](PF <sub>6</sub> ) <sub>2</sub>	353 (8950)			652 (65)	
[Cu( <i>S,S</i> -cypim)ZnCl]PF <sub>6</sub>	353 (9450)			643 (79)	
[Mn( <i>S,S</i> -cypim)MnCl]PF <sub>6</sub>	357 (8700)				934 (25) <sup>b</sup>
[Ni( <i>S,S</i> -cypim)NiCl]PF <sub>6</sub>	360 (8780)		716 (30)	854 (15)	1336 (20)
[Co( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>3</sub>		395 (12200)	529 (820)		
[Co( <i>S,S</i> -cypim)MnCl](PF <sub>6</sub> ) <sub>2</sub>	342 (6360)	407 (1620)	525 (670)		
[Co( <i>S,S</i> -cypim)CoCl](PF <sub>6</sub> ) <sub>2</sub>	336 (8230)	409 (2000)	561 (410)	773 (25)	1770 (7)
[Co( <i>S,S</i> -cypim)NiCl](PF <sub>6</sub> ) <sub>2</sub>	343 (8100)	403 (2190)	549 (502)	721 (262)	883 (103)
[Co( <i>S,S</i> -cypim)ZnCl](PF <sub>6</sub> ) <sub>2</sub>	345 (5000)	401 (3080)	534 (491)		1191 (158)
[Co( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>3</sub>	344 (6550)	407 (1300)	543 (480)	751 (97)	889 (100)
[Co( <i>S,S</i> -cypim)Co](PF <sub>6</sub> ) <sub>3</sub>	333 (8430)	419 (2750)	551 (601)	830 (10)	1737 (6)
[Co( <i>S,S</i> -cypim)Ni](PF <sub>6</sub> ) <sub>3</sub>	342 (9560)	401 (2917)	550 (607)		1040
					1143 (30)

<sup>a</sup> Spectra were run in CH<sub>3</sub>CN. <sup>b</sup> Tail into near-IR region. <sup>c</sup> Apparent values; uncorrected for underlying absorptions.

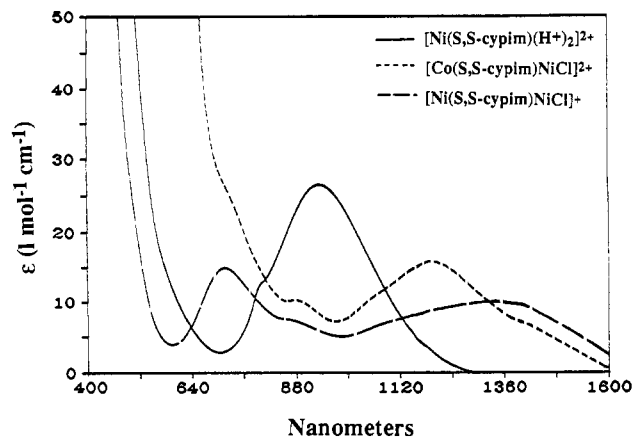


**Figure 2.** Electronic absorption spectra of Cu(II)-*S,S*-cypim complexes in acetonitrile solutions.



**Figure 3.** Composite spectrum of [Zn(*S,S*-cypim)Cu]<sup>2+</sup> and [Cu(*S,S*-cypim)Zn]<sup>2+</sup> for comparison with the absorption spectrum of [Cu(*S,S*-cypim)Cu]<sup>2+</sup>.

square pyramidal in the solid state and in solution.<sup>2</sup> The near-infrared band attributable to the open-site Co(II) shifts 770 nm to the red in [Co(*S,S*-cypim)CoCl]<sup>2+</sup> as compared with [Co(cyclim)CoCl]<sup>+</sup>. It may be noted that whereas trigonal bipyramidal structures are commonly observed for both Ni(II) and



**Figure 4.** Electronic absorption spectra of Ni(II)-*S,S*-cypim complexes in acetonitrile solutions.

Co(II) ions with specially designed tripodal ligands or with sterically bulky chelates,<sup>22</sup> this geometry is unusual for complexes with quadridentate salicylaldimine donor groups.<sup>23</sup> By contrast, the d-d spectrum of the symmetrical monometallic complex [Co(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> shows a weak absorption at 1009, ascribed to Co(II) in an octahedral environment.<sup>1</sup>

In sum, for the monometallic complexes of the type [M(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> all of the physical data, including electronic spectroscopy indicate that C<sub>2</sub>-symmetric octahedral geometries, **2**, obtain. The electronic spectra of the metals in the open site of the Co(III) complexes, [Co(*S,S*-cypim)MCl]<sup>2+</sup> and [Co(*S,S*-cypim)M]<sup>3+</sup> are consistent with nearly trigonal bipyramidal geometries. The remaining bimetallic complexes containing divalent metal ions give rise to spectra which may be ascribed to metal ions in distorted four- and five-coordinate environments. All of the bimetallic complexes show spectra which can be attributed to localized d-d transitions. No intervalence transitions were observed.

- (22) (a) Ciampolini, M.; Speroni, G. P. *Inorg. Chem.* **1966**, *5*, 45. (b) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966**, *5*, 41. (c) Dori, Z.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 1394.  
 (23) Sacconi, L.; Ciampolini, M.; Speroni, G. P. *J. Am. Chem. Soc.* **1965**, *87*, 3102.

**Table 4.** Redox Potentials for the Cu(II)/Cu(I) Couples in *S,S*-cypim Complexes<sup>a,b</sup>

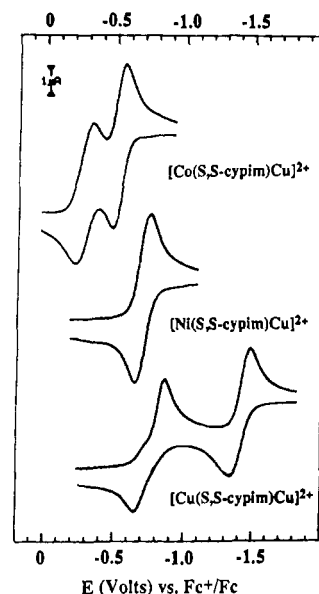
	$E_f$ , V <sup>b</sup>	$E_{pa} - E_{pc}$ , V
[Mn( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	irrev	
[Co( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub> <sup>c</sup>	-0.54 <sup>c</sup>	0.083
[Ni( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	-0.72 <sup>c</sup>	0.086
[Cu( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	-0.72 <sup>d</sup>	0.084
	-1.41 <sup>d</sup>	0.135
[Zn( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>2</sub>	-0.92 <sup>c</sup>	0.089
[Cu( <i>S,S</i> -cypim)Zn](PF <sub>6</sub> ) <sub>2</sub>	irrev	
[Cu( <i>S,S</i> -cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	-0.80 <sup>e</sup>	0.200

<sup>a</sup>  $5 \times 10^{-4}$  M sample, 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>3</sub>CN. Solutions were deaerated with Ar for 10 min prior to each run. <sup>b</sup> Reduction potentials are reported relative to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple. The Fc<sup>+</sup>/Fc couple is +0.43 V vs Ag/AgCl. <sup>c</sup> Scan rate: 100 mV/s. <sup>d</sup> Scan rate: 200 mV/s. <sup>e</sup> Co(III)/Co(II) redox couple at -0.30 V;  $E_{pa} - E_{pc} = 0.11$  V.

### Redox Properties

One of the long term objectives of this work is to develop bimetallic systems in which both metals donate electrons for the oxidative addition of a reactant such as dioxygen to the open-site metal. In order for such a process to occur, both of the metals in their respective open and closed coordination sites must be both kinetically and thermodynamically capable of transferring an electron to the dioxygen molecule. Our present concern has less to do with the values of the formal reduction potentials of the metal ions, but instead, we wished to see whether the redox properties of an invariant metal are affected by variation of the neighboring metal in bimetallic complexes. In order to assess the cooperative effects of one metal on the redox couple of another, we have used cyclic voltammetry to measure the formal potentials,  $E_f$ , of the invariant metal ions in the following series of complexes. The open-site Cu(II)/Cu(I) couple was monitored for the series [M(*S,S*-cypim)Cu]<sup>2+</sup>, where M = Zn(II), Cu(II), Ni(II), Co(II), and Mn(II), while the closed-site Co(III)/Co(II) couple was tracked as a function of the open-site metals in the two series [Co(*S,S*-cypim)MCl]<sup>2+</sup>, where M = Zn(II), Ni(II), Co(II), and Mn(II), and [Co(*S,S*-cypim)M]<sup>3+</sup>, where M = Zn(II), Cu(II), Ni(II), Co(II), and Mn(II). The cyclic voltammograms were measured at 25 °C in acetonitrile solution containing 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> supporting electrolyte. Cyclic voltammograms were recorded using a Ag/AgCl reference electrode; however, all potentials,  $E_f$ , reported or discussed in this paper are adjusted relative to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple, which was used as an internal standard.<sup>24</sup>

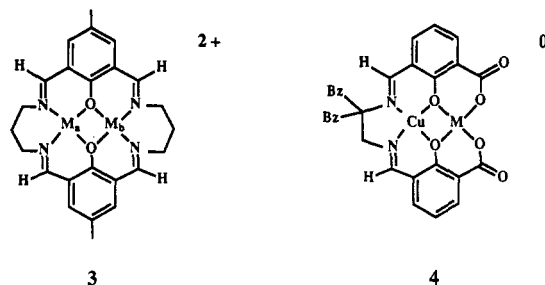
Table 4 lists the redox couples,  $E_f$ , for a series of Cu(II)-*S,S*-cypim complexes. Most of the complexes gave clear quasi-reversible waves, with the anodic and cathodic peak separations,  $E_{pa} - E_{pc}$ , listed. None of the waves in these Cu(II)-*S,S*-cypim complexes possess shoulders which might indicate metal-site-scrambled impurities. The cyclic voltammograms of selected Cu(II) complexes are shown in Figure 5. The Cu(II)/Cu(I) couple of [Cu(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> appears as a broad quasi-reversible wave which loses some current on the anodic sweep. A second weak oxidation is evident at  $\sim -0.43$  V. This may be attributed to the oxidation of free copper ion<sup>25</sup> and suggests that upon reduction, a small percentage of the copper ion dissociates from the *S,S*-cypim ligand. This is confirmed by the fact that a similar peak is present at the same potential in the cyclic voltammogram of Cu(OAc)<sub>2</sub> run under the same conditions. More extensive dissociation occurs upon reduction of the complexes [Mn(*S,S*-cypim)Cu]<sup>2+</sup> and [Cu(*S,S*-cypim)Zn]<sup>2+</sup>, which exhibit complex irreversible processes irrespective of scan rate. In both of these cases, the expected Cu(II) to Cu(I) reduction was observed, but on the reverse sweep, only a strong peak attributable



**Figure 5.** Cyclic voltammograms of selected Cu(II)-*S,S*-cypim complexes in acetonitrile solutions.

to the oxidation of free copper was apparent. The [Co(*S,S*-cypim)Cu]<sup>2+</sup> complex shows two redox couples. We ascribe the wave at -0.30 V to the Co(III)/Co(II) couple and that at -0.54 V to the Cu(II)/Cu(I) couple. Although these assignments are not known with certainty, we show presently that the Co(III)/Co(II) couples generally occur near the ascribed potential. The voltammogram of the dicopper complex also contains two waves due to two separate Cu(II)/Cu(I) couples. The wave at -0.72 V is ascribed to open-site copper, while that at -1.41 V is assigned to the copper ion in the closed site. This assignment is consistent with the voltammograms of the [Ni(*S,S*-cypim)Cu]<sup>2+</sup> and [Zn(*S,S*-cypim)Cu]<sup>2+</sup> complexes which show waves due only to the open-site copper ions at -0.72 and -0.92 V, respectively.

It is of interest to compare the redox behavior of *S,S*-cypim complexes containing open-site Cu(II) ions with those reported for analogous ligands. In particular, we compare the variations of Cu(II)/Cu(I) couples when the metal in the other site is varied and we consider the value of the Cu(II)/Cu(I) couple when the copper ion is in a nonplanar geometry. Copper redox couples have been reported for a series of M(II)-Cu(II) complexes of the Okawa-Robson ligand,<sup>26-28</sup> where M(II) = Mn(II), Fe(II), Co-



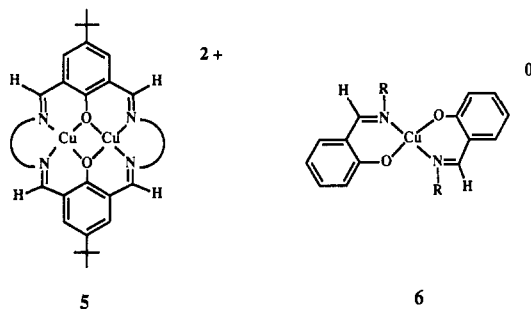
(II), Ni(II), Cu(II), and Zn(II). A similar series of M(II)-Cu(II) heterobimetallic complexes of the Okawa diacid ligand

(24) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. chem.* **1980**, *19*, 2855.  
 (25) Zanello, P.; Tamburini, S.; Vigato, P. A.; Mazzocchin, G. A. *Coord. Chem. Rev.* **1987**, *77*, 165.

(26) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225.  
 (27) (a) Okawa, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3019. (b) Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1759.  
 (28) (a) Gagné, R. R.; Spiro, C. L.; Smith, T. J.; Hamann, C. A.; Thies, W. R.; Shiemke, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 4073. (b) Gagné, R. R.; Spiro, C. L. *J. Am. Chem. Soc.* **1980**, *102*, 1443. (c) Gagné, R. R.; Koval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571. (d) Gagné, R. R.; Koval, C. A.; Smith, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 8367.

4 were studied,<sup>29</sup> where M(II) = Co(II), Ni(II), Cu(II), and Zn(II). For the dicopper complex of the site-symmetric ligand 3 there were observed two well-separated Cu(II)/Cu(I) redox waves indicating cooperative interaction of the two copper ions in this homobimetallic complex. However, the Cu(II)/Cu(I) reduction potentials of the transition metal heterobimetallic complexes of 3 and 4 were essentially invariant to the nature of the neighboring transition metal. By contrast, the data in Table 4 show that the Cu(II)/Cu(I) couples for [M(S,S-cypim)Cu]<sup>2+</sup> complexes exhibit considerable variation at the closed-site metal ion, M, is varied. Potentials,  $E_f$ , range from -0.54 V for [Co(S,S-cypim)Cu]<sup>2+</sup> to -0.92 V for [Zn(S,S-cypim)Cu]<sup>2+</sup>.

The second issue to be addressed is the relation of the copper reduction potentials to the coordination geometry of the copper ions. The redox couples of 5 were investigated as a function of



chelate ring size and with respect to the twist imparted by various diimine links.<sup>30</sup> The electrochemical properties of a series of neutral Cu(II) Schiff base complexes<sup>31</sup> 6 were studied as a function of the nonplanar twist that is imparted by the presence or absence of bulky R groups. For complexes of the ligands 5 and 6, the redox potentials correlated with the degree of tetrahedral distortion of the copper coordination environments. More tetrahedral geometries correspond to more positive redox potentials for the Cu(II)/Cu(I) couples, whereas more planar geometries give rise to more negative potentials. For the essentially planar dicopper complex 5 containing 1,3-diiminopropane links, for example,  $E_f = -0.93$  V for the Cu(II)-Cu(II)/Cu(II)-Cu(I) couple whereas for the dicopper complex 5 in which the diimines were prepared from 2,2'-biphenylenediamine,  $E_f = -0.63$  V. This latter complex is believed to contain copper ions in tetrahedrally distorted geometries. A similar trend is observed with the monometallic copper(II) Schiff base complexes 6. A range of 0.24 V is spanned as the Cu(II) complexes 6 vary from planar to more tetrahedrally distorted coordination environments. Both the crystal structure data and the d-d spectra of the [M(S,S-cypim)Cu]<sup>2+</sup> complexes indicate that the Cu(II) ions adopt nonplanar geometries. Thus, we would expect that the Cu(II)/Cu(I) couples should be more positive than is observed for the essentially planar system 3. This is borne out for all of the [M(S,S-cypim)Cu]<sup>2+</sup> complexes as compared with the analogous bimetallic complexes of 3. The origins of the observed variations in the Cu(II)/Cu(I) couples of the S,S-cypim complexes may arise from structural differences, from metal-metal communication, or from both, but it is difficult to disentangle these factors. It is probable that all of the bimetallic complexes listed in Table 4 adopt unsymmetrical S,S-cypim structures where the pyridine ligands are cis disposed as was established in the crystal structures of [Mn(S,S-cypim)Cu]<sup>2+</sup> and [Cu(S,S-cypim)Cu]<sup>2+</sup>. Different metal-metal pairs may adapt in different ways to the binding sites of the S,S-cypim ligand, depending upon the preferred geometries of the open-site copper ion and of the closed-site metal. It is not clear, however,

**Table 5.** Redox Potentials for the Co(III)/Co(II) Couples in S,S-cypim Complexes<sup>a,b</sup>

	$E_f$ , V <sup>b</sup>	$E_{pa} - E_{pc}$ , V
[Co(S,S-cypim)MnCl](PF <sub>6</sub> ) <sub>2</sub> <sup>c</sup>	-0.32	0.057
[Co(S,S-cypim)CoCl](PF <sub>6</sub> ) <sub>2</sub>	-0.38	0.114
	-1.82	0.164
[Co(S,S-cypim)NiCl](PF <sub>6</sub> ) <sub>2</sub> <sup>d</sup>	-0.37	0.076
[Co(S,S-cypim)ZnCl](PF <sub>6</sub> ) <sub>2</sub>	-0.43	0.072
[Co(S,S-cypim)Mn](PF <sub>6</sub> ) <sub>3</sub> <sup>e</sup>	-0.36	0.115
[Co(S,S-cypim)Co](PF <sub>6</sub> ) <sub>3</sub> <sup>e</sup>	-0.33	0.180
[Co(S,S-cypim)Ni](PF <sub>6</sub> ) <sub>3</sub> <sup>e,f</sup>	-0.38	0.113
[Co(S,S-cypim)Cu](PF <sub>6</sub> ) <sub>3</sub> <sup>g</sup>	-0.27	0.123
[Co(S,S-cypim)Zn](PF <sub>6</sub> ) <sub>3</sub> <sup>e</sup>	-0.44	0.126
[Co(S,S-cypim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>3</sub>	-0.24	0.182

<sup>a</sup>  $5 \times 10^{-4}$  sample, 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>3</sub>CN. Scan rate: 100 mV/s. Solutions were deaerated with Ar for 10 min prior to each run.

<sup>b</sup> Reduction potentials are reported relative to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple. The Fc<sup>+</sup>/Fc couple is 0.43 V vs Ag/AgCl. <sup>c</sup> Mn(III)/Mn(II) couple at +0.91 V;  $E_{pa} - E_{pc} = 0.079$ . <sup>d</sup> Broad Ni(II)/Ni(I) redox couple at -1.25 V;  $E_{pa} - E_{pc} = 0.163$  V. <sup>e</sup> Tris(hexafluorophosphate) salts were prepared from the chloro bis(hexafluorophosphate) complexes with AgPF<sub>6</sub>. <sup>f</sup> Ni(II)/Ni(I) redox couple at -1.25 V;  $E_{pa} - E_{pc} = 0.115$  V. <sup>g</sup> Cu(II)/Cu(I) redox couple at -0.54 V;  $E_{pa} - E_{pc} = 0.081$  V.

what possible structural variations of the S,S-cypim ligand from one complex to another could lead to such a large range in the potentials of the open-site Cu(II)/Cu(I) couples observed for the [M(S,S-cypim)Cu]<sup>2+</sup> complexes. Thus, it is probable that both structural and electronic interactions play a role in the observed differences.

Complexes of the types [Co(S,S-cypim)MCl]<sup>2+</sup> and [Co(S,S-cypim)M]<sup>3+</sup> were also prepared in order to assess the role of metal-metal interaction on the redox properties in S,S-cypim complexes. Unlike the copper series just discussed, all of these complexes are expected to have C<sub>2</sub>-symmetric structures where the Co(III) ions have trans disposed pyridine ligands as in 2.<sup>1</sup> Whereas there may be some slight structural differences in the closed-site Co(III) ion as the open-site metal is varied, the differences in redox potentials ascribed to the Co(III)/Co(II) couple (Table 5) can be traced primarily to metal-metal interactions within a particular charge type. A representative collection of cyclic voltammograms are given in Figure 6. In addition to the waves ascribed to the Co(III)/Co(II) couple, which will be discussed presently, there were also observed redox couples arising from the open-site metal ions in a number of the [Co<sup>III</sup>(S,S-cypim)M<sup>II</sup>] complexes. The [Co(S,S-cypim)NiCl]<sup>2+</sup> complex shows a quasi-reversible wave at -1.25 V which we ascribe to the open-site Ni(II)/Ni(I) couple. A redox couple was observed at a similar potential for the dinickel complex [Ni(S,S-cypim)-NiCl]<sup>+</sup>. The absence of waves in this region of the cyclic voltammogram of [Ni(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> probably reflects the greater difficulty of reducing the Ni(II) ion in the octahedral sites of the mono- and dinickel complexes, as compared with the five-coordinate Ni(II) in the open sites of S,S-cypim complexes.<sup>32</sup> The [Co(S,S-cypim)CoCl]<sup>2+</sup> complex also shows two waves in the voltammogram, including one at -1.82 V attributable to the Co(II)/Co(I) couple of open-site cobalt.<sup>33</sup> The same redox process for [Co(S,S-cypim)Co]<sup>3+</sup> was found to be irreversible. Finally, a nearly reversible wave was observed for [Co(S,S-cypim)MnCl]<sup>2+</sup> at +0.91 V which is ascribed to the open-site Mn(III)/Mn(II) couple.<sup>34</sup>

Although the range observed in the Co(III)/Co(II) couples for these two series of complexes, [Co(S,S-cypim)MCl]<sup>2+</sup> and

(29) Kanda, W.; Nakamura, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 471.

(30) Long, R. C.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1983**, *105*, 1513.

(31) Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257 and references cited therein.

(32) Bond, A. M.; Haga, M.; Creece, I. S.; Robson, R.; Wilson, J. C. *Inorg. Chem.* **1988**, *27*, 712.

(33) Kitaura, E.; Nishida, Y.; Okawa, H.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1987**, 3055.

(34) (a) Lawrence, G. D.; Sawyer, D. T. *Coord. Chem. Rev.* **1978**, *27*, 173. (b) Buchanan, R. M.; Mashuta, M. S.; Richardson, J. F.; Oberhausen, K. J.; Hendrickson, D. N.; Webb, R. J.; Nanny, M. A. *Inorg. Chem.* **1990**, *29*, 1301.



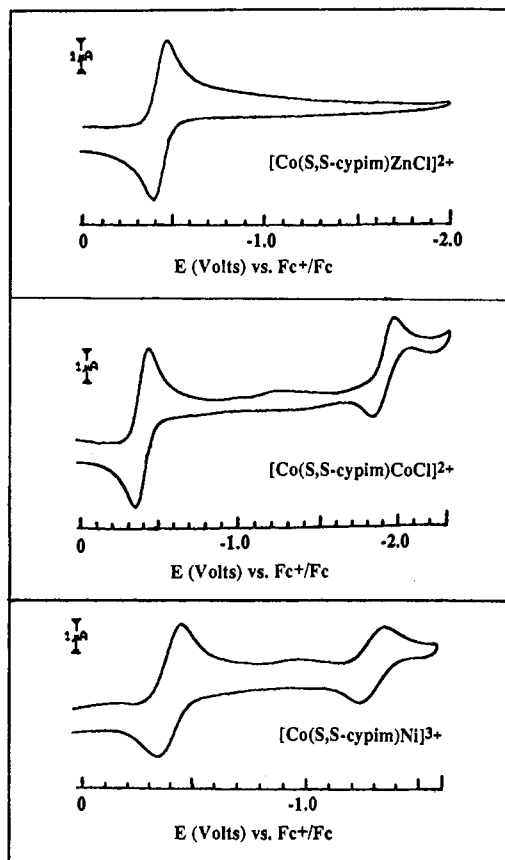


Figure 6. Cyclic voltammograms of selected Co(III)-*S,S*-cypim complexes in acetonitrile solutions.

$[\text{Co}(\text{S},\text{S}\text{-cypim})\text{M}]^{3+}$ , is smaller than that seen for the  $[\text{M}(\text{S},\text{S}\text{-cypim})\text{Cu}]^{2+}$  series, differences are apparent. The Co(III)/Co(II) couple of the dicationic complexes  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{MCl}]^{2+}$  range from  $-0.32$  to  $-0.43$  V for the closed-site metal and the tricationic complexes  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{M}]^{3+}$  vary from  $-0.27$  to  $-0.44$  V (Table 5). The monometallic complex  $[\text{Co}(\text{S},\text{S}\text{-cypim})(\text{H}^+)_2]^{2+}$  has the most positive couple at  $-0.24$  V. The differences between the di- and tricationic series probably reflect, in part, the charge differences on the complexes.

One of the possible reasons for the variations in the Co(III)/Co(II) couple is related to the preferred structure of the metal in the open site. For example, with Co(III) in the closed site, the open binding site of the *S,S*-cypim ligand adopts a distorted tetrahedral geometry. If the preferences of Cu(II) and Zn(II) for square planar and tetrahedral four-coordinate geometries, respectively, are in some way communicated to the closed-site cobalt ions, this could account for the differences in the potentials observed for  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Cu}]^{3+}$  and  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Zn}]^{3+}$ . Reduction of the Co(III) ion in  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Cu}]^{2+}$  to the stereochemically flexible Co(II) may result in a flatter open binding site, and thus, a more planar geometry which is preferred by Cu(II). In contrast, the same flattening could have an unfavorable effect on the open-site Zn(II) ion in  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Zn}]^{3+}$ . If this is so, we expect  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Cu}]^{3+}$  to be more readily reduced than  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Zn}]^{3+}$ , as is observed. It is not clear how this structural argument could be convincingly pursued for the other  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{M}]^{3+}$  complexes, however.

Although the Co(II) oxidation state is expected to be more stereochemically labile than Co(III), it seems unlikely that the ligand coordination rearranges from the original  $C_2$ -symmetric structure of  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{MCl}]^{2+}$  and  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{M}]^{3+}$  to the unsymmetrical structure with cis-disposed pyridyl ligands on the time scale of the electrochemical experiment. Such extensive rearrangement, were it to occur, is unlikely to give the almost reversible waves that are observed. Further, in the

symmetrical Co(III) complexes the tertiary nitrogen atoms bearing  $\alpha$ -pyridyl groups are of the same absolute configuration, whereas in the unsymmetrical structures in which the pyridyl groups are cis disposed, the tertiary nitrogens are meso. Thus, in order to transform from the symmetrical to the unsymmetrical structures, one of the tertiary nitrogen atoms would have to invert its absolute configuration. Since tertiary nitrogen atoms bound to metals are stable with respect to inversion,<sup>35</sup> the only way for nitrogen inversion to occur is for the cobalt to dissociate from all or part of the closed site of the *S,S*-cypim ligand. This we consider unlikely on the time scale of the electrochemical experiment since no waves corresponding to the Co(III)/Co(II) couple of free Co(II) ions were detected by cyclic voltammetry.

Whatever the cause of the redox variations observed for the  $[\text{M}(\text{S},\text{S}\text{-cypim})\text{Cu}]^{2+}$ ,  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{MCl}]^{2+}$ , and  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{M}]^{3+}$  series, it is likely that oxidative addition of a reactant to the open-site metal of a bimetallic *S,S*-cypim complex will be affected by the nature of the neighboring closed-site metal.

## Discussion

The physical properties of *S,S*-cypim complexes were investigated for three primary reasons. First, we wanted see whether the unusual structural features of these complexes could be correlated with spectroscopic and physical properties. The second issue was the question of site scrambling and the purity of heterobimetallic complexes containing labile metal ions. Finally, we were interested in investigating whether any of the *S,S*-cypim complexes showed evidence of metal-metal cooperativity.

Complexes of the binucleating *S,S*-cypim ligand possess structural features which give rise to unusual spectroscopic properties. The *S,S*-cypim ligand, with its large distorted open binding site, imposes unique geometrical constraints upon the open-site metal ion. Perhaps the clearest example of open-site distortion is found with the bimetallic Co(III) complex  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Cu}(\text{CH}_3\text{CN})]^{3+}$ . The metal in the open site of this complex adopts a distorted trigonal bipyramidal geometry. As a consequence the open-site Cu(II) ion gives rise to red-shifted d-d transitions, a reduced  $|A_1|$  hyperfine constant, and a more positive redox couple compared to square planar Cu(II) geometries. The other Co(III)-M(II) (M = Mn, Co, Ni, Zn) *S,S*-cypim complexes were obtained as chlorides, and these too appear to have five-coordinate nearly trigonal bipyramidal open-site metal ions. The electronic absorption spectra of the Ni(II)- and Co(II)-containing complexes exhibit low-energy bands in the near-IR region consistent with such an open-site structure. This geometry is unusual for both mono- and bimetallic complexes with similar ligand donor groups, and is believed to originate in the constraints imposed by the rigid closed-site metal-ligand moiety and in the preferred nonplanar orientation of the chiral cyclopentane diimine unit.

These structural and spectroscopic features are less pronounced in the case of  $[\text{M}^{\text{II}}(\text{S},\text{S}\text{-cypim})\text{M}^{\text{II}}]$  complexes. Complexes of *S,S*-cypim which contain a labile metal in the closed site rearrange to adopt non- $C_2$ -symmetric structures with the pyridyl ligands in a cis arrangement about the closed-site metal. With larger divalent metal ions in the closed site, the open-site binding cavities are also enlarged. Whereas the *S,S*-cypim ligand is sufficiently flexible to adjust the dimensions of the binding cavities to accommodate various first row transition metals, these adjustments result in somewhat distorted, more planar open-site geometries as compared with the open-site structures in Co(III)-M(II) complexes. This is confirmed by both crystallographic and spectroscopic data. For example, the EPR hyperfine splitting constant for  $[\text{Zn}(\text{S},\text{S}\text{-cypim})\text{Cu}]^{2+}$  is larger than was observed for  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Cu}]^{3+}$ , indicative of a more planar Cu(II) geometry in the former complex.

(35) Halpern, B.; Sargeson, A. M.; Turnbull, K. R. *J. Am. Chem. Soc.* 1966, 88, 4630.



The *S,S*-cypim ligand provides many of the characteristics that we sought to embody in its original design. It provides ready access to the monometallic species,  $[M(S,S\text{-cypim})(H^+)_2]^{2+}$  which are ideal precursors for the synthesis of site-specific heterobimetallic complexes. All of the physical properties strongly suggest that pure heterobimetallic complexes were prepared. In cyclic voltammetry, none of the waves possess shoulders or additional features which would indicate the presence of site-scrambled homo- or heterobimetallic impurities. EPR experiments designed to detect whether inter- or intramolecular metal exchange is occurring show no evidence of scrambling over a 40-h period. Although it was difficult to quantify precisely the extent of intramolecular scrambling, the preparative reactions monitored by EPR confirm that the products are identical to those obtained from large-scale preparation after isolation and purification.

Finally, we were interested in detecting evidence of metal-metal interaction in these bimetallic systems. No intervalence transitions were observed in the electronic absorption spectra of *S,S*-cypim complexes; spectra of bimetallic complexes could be interpreted by the superposition of the transitions expected for the respective metal chromophores. The EPR spectra of  $[Cu(S,S\text{-cypim})Cu]^{2+}$  and  $[Ni(S,S\text{-cypim})Cu]^{2+}$ , however, did show evidence of electronic interaction. The dicopper complex is EPR silent, and a spin-interacting doublet state is observed in the spectrum of the Ni(II)-Cu(II) complex. The most dramatic evidence of metal-metal cooperativity is observed in the electrochemistry of *S,S*-cypim complexes. In the  $[M(S,S\text{-cypim})Cu]^{2+}$  series the Cu(II)/Cu(I) redox couple is strongly dependent on the neighboring metal M. This dependence may be due, in part, to the varying ability of the closed-site metals to accommodate the deformations and rearrangement of the binucleating *S,S*-cypim ligand which occur upon oxidation or reduction. Whereas structural differences undoubtedly play a role, other forms of metal-metal communication may also be operating in these *S,S*-cypim complexes. This is supported by the results obtained for the more structurally defined  $[Co(S,S\text{-cypim})M]^{2+}$  series where the Co(III)/Co(II) couple generally varies with the nature of M. Although there may be structural components to the Co(III)/Co(II) redox variations, metal-metal interaction seems to play a role. Whatever the origin of these variations, the practical result is that oxidative additions to the open-site metal are likely to be affected by the nature of the metal in the closed site.

The results described here and in the previous papers<sup>1,2</sup> are important in defining the future course toward our ultimate objective of investigating redox cooperativity in the oxidative addition reactions of bimetallic complexes. This work has suggested possible modifications in ligand design in order to obtain  $C_2$ -symmetric complexes, it has provided synthetic routes to pure site specific heterobimetallic complexes, and it has defined the types of metal-metal cooperativity that might influence oxidative addition reactions. Refinements in the ligand design and the associated cooperative chemical behavior are the subjects of future papers.

### Experimental Section

UV spectra were obtained on a Varian (Cary) 2400 spectrophotometer using spectral grade solvents. Magnetic susceptibilities were measured on  $CD_3CN$  solutions at 20 °C according to the Evans NMR method<sup>3</sup> using coaxial NMR tube inserts and a constant field GE QE 300 NMR instrument. Diamagnetic corrections were made using Pascal's constants.<sup>4e</sup> X-Band EPR spectra were recorded on both room temperature and frozen samples in quartz tubes using a Varian E-9 EPR spectrometer equipped with a Bruker ER048R microwave bridge and a Hewlett Packard 5255A frequency counter.  $CH_3CN$ -toluene (2:3) or  $CH_3CN$ -EtOH-toluene

(1:1:3) EPR solutions were typically  $\sim 2.5 \times 10^{-4}$  M in complex and were prepared under Ar. Typical instrument settings were as follows: gain = 10 or 12.5; modulation amplitude = 32 G; microwave power = 1.99 mW; attenuation = 20 dB; time constant = 0.3 s. Cyclic voltammograms were recorded using a Bioanalytical Systems BAS 100 electrochemical analyzer on deaerated  $CH_3CN$  solutions which were 0.1 M in *n*-Bu<sub>4</sub>-NBF<sub>4</sub> supporting electrolyte and  $5 \times 10^{-4}$  M in sample. Redox potentials were measured using a Pt-button working electrode, an Ag/AgCl reference electrode, and a Pt-wire auxiliary electrode and are tabulated versus a ferrocene internal standard.<sup>24</sup> Acetonitrile used in electrochemical experiments was distilled from CaH<sub>2</sub>; 1,4-dioxane was distilled from LiAlH<sub>4</sub>.

**Dechlorination of  $[M(S,S\text{-cypim})MCl](PF_6)_n$  Complexes.** With the exception of  $[Co(S,S\text{-cypim})Cu](PF_6)_3$ ,<sup>1</sup>  $[Co(S,S\text{-cypim})M](PF_6)_3$ , and  $[Cu(S,S\text{-cypim})Zn](PF_6)_2$ , complexes were prepared for electrochemical experiments by the following general procedure. The  $[M(S,S\text{-cypim})MCl](PF_6)_n$  complex (5  $\mu$ mol) was dissolved in acetone (3 mL), and a stoichiometric amount of AgPF<sub>6</sub> dissolved in  $CH_3CN$  (100  $\mu$ L) was added to precipitate the chloride ion. The resultant cloudy solutions were filtered through Celite and concentrated. The residues were resuspended in acetone, filtered through Celite again, and then were reconcentrated. The glassy solid so obtained was dissolved in 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> in  $CH_3CN$  (10 mL), and cyclic voltammograms were recorded. The same procedure was followed on the appropriate scale for the preparation of samples for electronic absorption spectroscopy and EPR. The glassy solids obtained after dechlorination and repeated filtration was dissolved in the required solvents.

**EPR Spectroscopy.** Standard spectra were recorded on  $\sim 2.5 \times 10^{-4}$  M solutions of the metal complex in acetonitrile-toluene (2:3) solution. The solutions were placed under Ar; spectra were run at room temperature and then were frozen slowly in liquid nitrogen before spectra were recorded at 77 K. All *g* tensors were calculated using the expression  $g = h\nu/BH$ , where  $\nu$  is read from the microwave frequency counter for each sample, the magnetic flux density or field strength, *H*, is obtained from the recorded spectra, and the other constants have their usual meanings. For  $g_{\perp}$ , the field strength was determined from the position on the high field signal where the first derivative spectrum equals zero. The  $g_{\parallel}$  values were determined from the magnetic field strength, *H*, at the midpoint of the lower field Cu hyperfine lines.  $|A_{\perp}|$  was determined using the expression  $A = g\beta\Delta H$ , where  $\Delta H$  is the average peak separation in Gauss of the copper hyperfine lines. Since the signal of  $A_{\parallel}$  is not readily apparent, the hyperfine splitting constants are represented as  $|A_{\parallel}|$  and are given in units of  $cm^{-1} \times 10^4$ .

**A. Scrambling Experiment.** The di-copper complex  $[Cu(S,S\text{-cypim})Cu](PF_6)_2$  was weighed into three separate quartz EPR tubes. Stock solutions of  $[Zn(S,S\text{-cypim})(H^+)_2](PF_6)_2$  in  $CH_3CN$  and Zn(OAc)<sub>2</sub> in EtOH were prepared. To tubes 1 and 2 was added 1 equiv of the stock  $[Zn(S,S\text{-cypim})(H^+)_2](PF_6)_2$  solution. To tubes 2 and 3 was added 1 equiv of stock Zn(OAc)<sub>2</sub> solution. The volumes of  $CH_3CN$  and EtOH were adjusted, then toluene was added such that the final ratio was 1:1:3  $CH_3CN$ -EtOH-toluene, and the overall concentration of each reagent was  $2.5 \times 10^{-4}$  M. The solutions were kept at room temperature except when spectra were recorded at 77 K. The samples were monitored over a 40-h period.

**B. Preparative Experiments.** A typical preparative experiment was conducted as follows.  $[M(S,S\text{-cypim})(H^+)_2](PF_6)_2$  was weighed into a quartz EPR tube and was then dissolved in  $CH_3CN$ . The appropriate M(OAc)<sub>2</sub> was dissolved in EtOH and 1 equiv was added to the  $[M(S,S\text{-cypim})(H^+)_2](PF_6)_2$  solution. Et<sub>3</sub>N ( $\sim 1 \mu$ L) was added. The mixture was capped and shaken. The intense color attributable to the diimine chromophore faded at once, indicating complexation. The volumes of EtOH and  $CH_3CN$  were adjusted and toluene was added such that the solvent ratio was 1:1:3  $CH_3CN$ -EtOH-toluene and the overall concentrations of  $[M(S,S\text{-cypim})(H^+)_2](PF_6)_2$  and M(OAc)<sub>2</sub> were each  $2.5 \times 10^{-4}$  M. The solutions were deaerated with Ar and were frozen slowly in liquid nitrogen to 77 K, and spectra were recorded.

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