

## Bimetallic Reactivity. Controlled Synthesis of Monometallic and Homo- and Heterobimetallic Complexes of a Chiral Binucleating Macrocyclic Ligand Bearing 6- and 4-Coordinate Sites

Cassandra Fraser,<sup>†</sup> Robert Ostrander,<sup>†</sup> Arnold L. Rheingold,<sup>\*,‡</sup> Corbet White,<sup>†</sup> and B. Bosnich<sup>\*,†</sup>

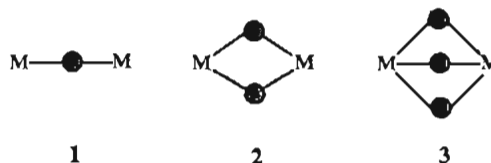
Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, and Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

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A chiral macrocyclic binucleating ligand, *S,S*-cypim, bearing four- and six-coordinate binding sites has been prepared. The macrocyclic framework contains the chiral diamine (1*S*,2*S*)-*trans*-1,2-bis(aminomethyl)cyclopentane, which induces one topological chirality about the six-coordinate site. The macrocyclic closure with the chiral diamine is achieved in good yield by Schiff base condensation of metal dialdehyde complexes. In this way the monometallic complexes  $[M(S,S\text{-cypim})(H^+)_2]^{2+}$ ,  $M = Zn(II), Cu(II), Ni(II), Co(II),$  and  $Mn(II)$ , have been prepared and characterized. These complexes contain a metal in the six-coordinate site and two hydrogen-bonded protons in the four-coordinate site. X-ray crystal structures of the  $Mn(II)$  and  $Zn(II)$  complexes confirm this formulation. Oxidation of the  $Co(II)$  complex gives the stable  $Co(III)$  complex  $[Co(S,S\text{-cypim})(H^+)_2]^{3+}$  from which the heterobimetallic complexes  $[Co(S,S\text{-cypim})MCl]^{2+}$ ,  $M = Zn(II), Ni(II), Co(II),$  and  $Mn(II)$ , and  $[Co(S,S\text{-cypim})Cu]^{3+}$  were prepared and isolated. An X-ray crystal structure of the last complex confirms the expected  $C_2$  symmetric geometry. The  $[M(S,S\text{-cypim})(H^+)_2]^{2+}$  complexes are ideal precursors for mild, kinetically controlled synthesis of heterobimetallic complexes containing labile metals. The complexes  $[M(S,S\text{-cypim})Cu]^{2+}$  where  $M =$  six-coordinate site metals,  $Zn(II), Cu(II), Ni(II), Co(II),$  and  $Mn(II)$ , were prepared, isolated and characterized. The homobimetallic complexes  $[Mn(S,S\text{-cypim})MnCl]^+$  and  $[Ni(S,S\text{-cypim})NiCl]^+$  were also isolated, as well as the mixed-valence complex  $[Mn^{II}(S,S\text{-cypim})Mn^{III}(Cl)_2]^+$ , which is formed by aerial oxidation of the dimanganese(II) complex. The crystal structures of the complexes  $[Mn(EtOH)(S,S\text{-cypim})Cu]^{2+}$  and  $[Cu(S,S\text{-cypim})Cu(CH_3CN)]^{2+}$  are also reported. In the former the  $Mn(II)$  atom is seven-coordinate and a highly distorted ligand structure is observed. The dicopper(II) structure is also distorted, but the copper in the potentially six-coordinate site is only five-coordinate. The incorporation of the chiral diamine in the ligand enforces the formation of a single diastereomer of the  $C_2$  symmetric complexes. This is confirmed by the  $^1H$  NMR spectra of the diamagnetic complexes  $[Zn(S,S\text{-cypim})(H^+)_2]^{2+}$ ,  $[Co(S,S\text{-cypim})(H^+)_2]^{2+}$ , and  $[Co(S,S\text{-cypim})Zn]^{3+}$ . The topological chirality about the closed-site metals in the  $[Zn(S,S\text{-cypim})(H^+)_2]^{2+}$  and  $[Co(S,S\text{-cypim})Cu(CH_3CN)]^{3+}$  complexes was determined to be  $\Delta$  by crystallographic methods, whereas a  $\Lambda$  absolute configuration was found for the  $[Mn(S,S\text{-cypim})(H^+)_2]^{2+}$  complex. This reversal of diastereoselection is believed to arise from the larger radius of the  $Mn(II)$  ions, which causes the ligand to adopt a unique twisted conformation which is considerably different from those observed for  $[Zn(S,S\text{-cypim})(H^+)_2]^{2+}$  and  $[Co(S,S\text{-cypim})Cu(CH_3CN)]^{3+}$ . Circular dichroism associated with the d-d transitions of the  $Co(III)$  complexes indicates that all have the  $\Delta$  configuration whereas that associated with the azomethine chromophores suggests that all of the  $C_2$  symmetric complexes have the same configuration except the  $Mn(II)$  complex.

Inspired by the behavior of multimetallic proteins<sup>1</sup> and propelled by the expectation that metal-metal cooperativity would lead to distinct reactivity patterns,<sup>2</sup> many researchers have prepared numerous and varied multimetallic complexes.<sup>3</sup> Most work has concentrated on bimetallic systems which possess bridging ligands coordinated to two contiguous metals.<sup>3</sup> Other constructions involve tethering two metal complexes by non-coordinating links.<sup>4</sup>

Metals may be linked by one (1),<sup>5</sup> two (2),<sup>6</sup> or three (3)<sup>7</sup> bridging



groups of which the most prevalent is the two-bridge system 2.

<sup>†</sup> The University of Chicago.

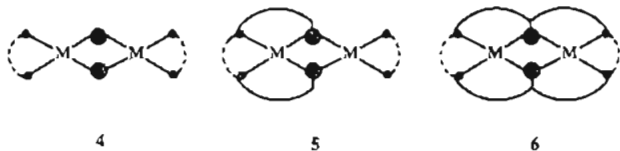
<sup>‡</sup> University of Delaware.

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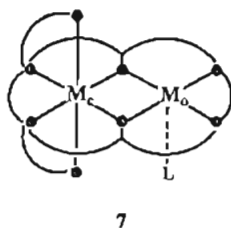
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Such systems can be elaborated in a variety of ways, which include constructions 4–6 where square planar geometries are represented



for illustrative purposes. The dotted lines indicate that a chelate link may or may not be present. On the basis of these three rudimentary structures, an extraordinarily large variety of bimetallic complexes have been synthesized. Of these three structural types, the macrocyclic versions of type 6 are, in a number of respects, the most attractive. The macrocyclic framework lends stability to the system allowing for greater control of the site occupancy of the metals.

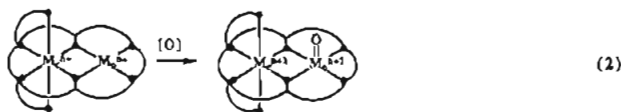
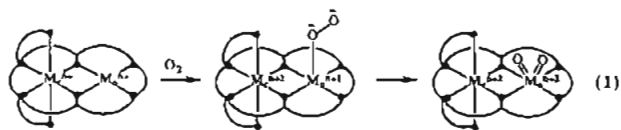
We recently introduced a new type of binucleating ligand, 7, which differs from most systems so far described.<sup>8</sup> Construction 7 provides for one of the metals,  $M_c$ , to be coordinatively saturated



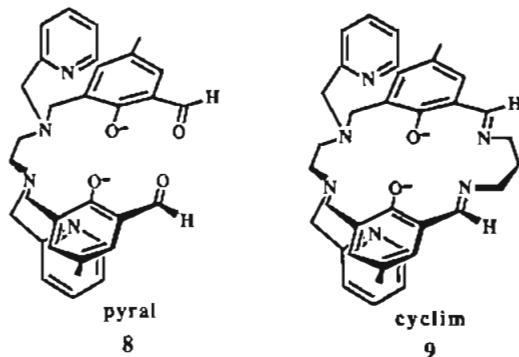
(closed-site) and for the other contiguous metal,  $M_o$ , to occupy

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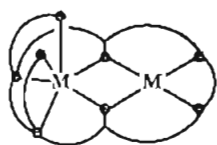
providing electrons for reduction. Equations 1 and 2 are illustrative of the envisioned processes.



In a previous report<sup>8</sup> we described the preparation of the sexadentate ligand pyral (8). Upon complexation of pyral (8) to



a metal and subsequent reaction with 1,3-diaminopropane, the macrocyclic diimine ligand cyclim (9) was produced. Although the pyral ligand formed the expected  $C_2$ -symmetrical structure possessing trans pyridine ligands in monometallic Zn(II) and Co(III) complexes, the bimetallic cyclim complexes gave unsymmetrical species. The pyridine ligands were not trans but were bound on the same side of the mean macrocyclic plane giving the structure illustrated in 10. These unsymmetrical

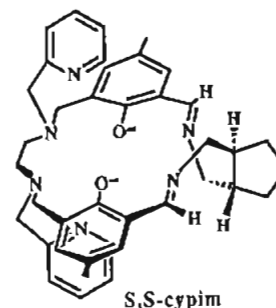


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structures are believed<sup>8</sup> to arise from a number of factors related to chelate ring size and the conformations which the ligand adopts. The ethylenediamine chelate bite angle is less than  $90^\circ$  causing the trans phenoxide-O-M<sub>c</sub>-O-phenoxide angle to expand beyond a value which can accommodate the second contiguous metal. In

order to reduce this O-M<sub>c</sub>-O angle the ligand undergoes conformational rearrangement. This rearrangement, however, is to some extent controlled by the symmetrical chair conformation of the 1,3-diiminopropane link, which causes the phenoxy groups to buckle to the same side of the mean macrocyclic plane. This buckling forces the pyridine ligands to be cis disposed on the other side of the mean macrocyclic plane. Aside from an interest in investigating the factors which influence stereochemistry and topology in bimetallic complexes of multidentate ligands, we require a  $C_2$ -symmetrical structure in order to utilize these complexes as catalysts for asymmetric epoxidation.<sup>11</sup> An identical chiral environment would then exist at both coordination positions of the open-site metal where reactive oxo species would bind and react, thus eliminating stereochemical ambiguity.

One possible solution to obtaining symmetrical bimetallic complexes is to expand the macrocyclic ring at the open site and to provide a twisted linkage joining the diimine portion of the molecule. The ligand chosen for this investigation is *S,S*-cypim (11). Compared to cyclim, the diimines of 11 are spanned by one



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extra carbon atom and a twist is imparted to the link by the presence of the chiral trans cyclopentane fragment. Moreover, the chirality of the trans bis(aminomethyl)cyclopentane link is expected to impart its chirality to the whole molecular framework so that only one diastereomer of the bimetallic complex is formed. This transmission of chirality could provide a simple device for obtaining homochiral complexes and thus provide a variety of systems for asymmetric epoxidation.

The primary aims of this paper are to describe the synthesis of the ligand *S,S*-cypim and to outline routes for the systematic synthesis of a variety of homo- and heterobimetallic complexes of the later first row transition metals. In addition we present the crystal structures of a series of key compounds which illustrate the types of structures that are formed with this ligand. Stereochemical features of *S,S*-cypim complexes are investigated using circular dichroism. The succeeding paper deals with some of the cooperative physical properties which the bimetallic complexes display.

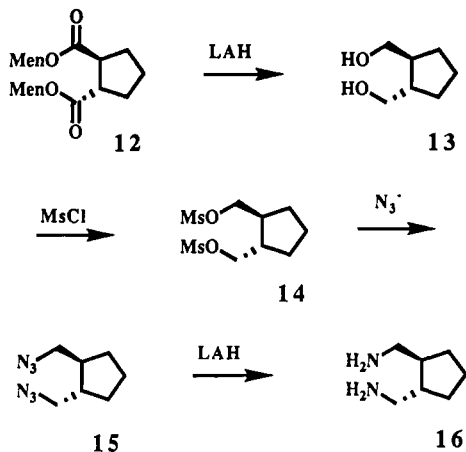
### Ligand Synthesis

The synthesis of the ligand pyralH<sub>2</sub> has been described elsewhere.<sup>8</sup> The preparation of (1*S*,2*S*)-*trans*-1,2-bis(aminomethyl)cyclopentane (16) employed the homochiral starting material di-(1*R*,2*S*,5*R*)-menthyl (1*S*,2*S*)-*trans*-1,2-cyclopentanedicarboxylate (12), which is available from an efficient diastereoselective synthesis.<sup>12</sup> Reduction of 12 and mesylation gave 14.<sup>13</sup> Azide displacement of mesylate 14 followed by reduction gave the desired diamine 16 as a clear liquid. All of these steps proceed in greater than 85% yield. We were unable to prepare the macrocyclic binucleating ligand *S,S*-cypim by condensing

(11) Recent reviews: (a) Shurig, V.; Betschinger, F. *Chem. Rev.* **1992**, *92*, 873. (b) Jorgensen, K. A. *Chem. Rev.* **1989**, *89*, 431. Mn-salen systems: (c) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063. (d) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801. (e) Jacobsen, E. N.; Zhang, W.; Guler, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703. (f) Wei, Z.; Jacobsen, E. N. *J. Org. Chem.* **1990**, *56*, 2296. (g) Lee, N. H.; Jacobsen, E. N. *Tetrahedron Lett.* **1991**, *32*, 6533. (h) Li, D.; Jacobsen, E. N. *J. Org. Chem.* **1992**, *57*, 4320. (i) O'Connor, K. J.; Wey, S. J.; Burrows, C. J. *Tetrahedron Lett.* **1992**, *33*, 1001. Porphyrin systems: (j) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc., Chem. Commun.* **1985**, *105*, 5786. (k) Mansuy, D.; Renand, J. P.; Guerin, P. *J. Am. Chem. Soc., Chem. Commun.* **1985**, 155. (l) O'Malley, S.; Kodadek, T. *J. Am. Chem. Soc.* **1989**, *111*, 9116. (m) Collman, J. P.; Zhang, X.; Hembre, R. T.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 5356. (n) Naruta, Y.; Tani, F.; Ishihara, N.; Marayama, K. *J. Am. Chem. Soc.* **1991**, *113*, 6865. (o) Halterman, R. L.; Ian, S. T. *J. Org. Chem.* **1991**, *56*, 5253. (p) Konishi, K.; Oda, K.; Nishida, K.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1992**, *114*, 1313.

(12) Misumi, A.; Iwanaga, K.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 3343.

(13) Hollis, T. K.; Rbeingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 2812.

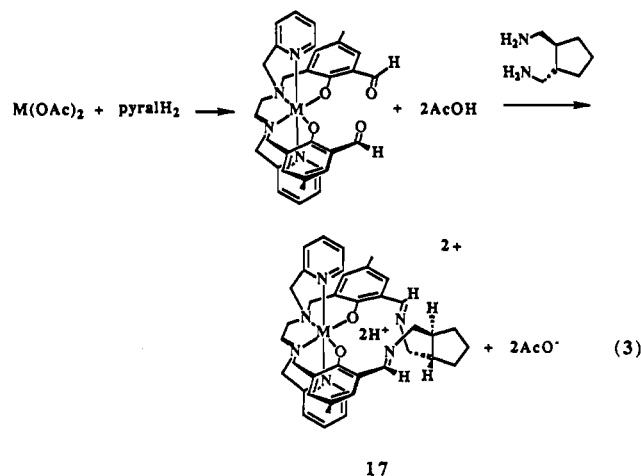


free pyralH<sub>2</sub> with diamine 16. When coordinated to a metal, however, pyral gave the desired *S,S*-cypim ligand generally in high yields.

### Monometallic Complexes

Perhaps the most elegant and controlled route to the synthesis of [M<sub>2</sub>(*S,S*-cypim)M<sub>2</sub>]<sup>n+</sup> complexes is one which allows for the sequential introduction of the metals. (We adopt the convention of writing the closed-site metal first, followed by the binucleating ligand, followed by the open-site metal, followed by the ligand bound to the open-site metal.) For this purpose we investigated methods for synthesizing and isolating monometallic complexes of the type [M<sub>2</sub>(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>n+</sup> in which the metal is in the closed-site and the open-site contains two protons. Such complexes were expected to provide ideal precursors for the preparation of site-specific heterobimetallic compounds. Thus, deprotonation followed by the addition of the second metal should, if the conditions are mild, ensure that the second metal occupies the open site.

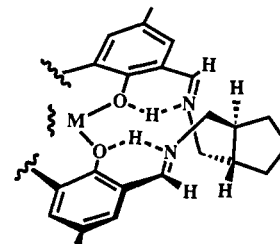
We discovered that when a metal acetate, M(OAc)<sub>2</sub>, was reacted with the pyralH<sub>2</sub> ligand in ethanol solution, the [M(pyral)] complex formed, releasing 2 equiv of acetic acid. Slow addition of the chiral diamine 16 to this mixture gave the desired monometallic products (eq 3), which were isolated as their bis-



(hexafluorophosphate) salts. We note that the acetic acid generated serves to catalyze Schiff base formation and also provides protons for the open site. In this way the monometallic salts [M(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (17), where M = Zn(II), Cu(II), Ni(II), Co(II), and Mn(II), were isolated and characterized. Except for when M = Cu(II), all monometallic complexes were isolated in good yields undoubtedly because the aldehyde functionalities of [M(pyral)] are positioned for cyclization. The

monometallic complex of Cu(II), 17, proved more difficult to prepare in pure form; the bimetallic species [Cu(*S,S*-cypim)-Cu](PF<sub>6</sub>)<sub>2</sub>, and a tarlike side product often formed concomitant with the desired product. Under appropriate conditions formation of the bimetallic dicopper complex could be suppressed. The Co(III) complex [Co(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> was prepared in high yield by oxidation of the Co(II) complex [Co(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> with [Cp<sub>2</sub>Fe]PF<sub>6</sub> (Cp is cyclopentadienyl) in acetonitrile solution. We were unable to oxidize the monometallic Mn(II) complex by this method.

The monometallic complexes of the divalent metals are 2:1 electrolytes in acetonitrile solutions (270–290 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup>)<sup>14</sup> and the Co(III) complex is a 3:1 electrolyte (399 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup>) as expected. The <sup>1</sup>H NMR spectra of the diamagnetic complexes, [Zn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> and [Co(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>3+</sup> indicate that a single diastereomer is formed in each case and that the structures possess C<sub>2</sub> symmetry, where the two pyridine ligands are trans disposed, 17. This C<sub>2</sub> symmetric structure and the presence of a single diastereomer induced by the chiral diamine is also likely to obtain for the other monometallic complexes. The <sup>1</sup>H NMR spectra in CD<sub>3</sub>CN reveal broad signals constituting two protons at 14.45 ppm for the Zn(II) monometallic complex and at 11.91 ppm for the Co(III) complex. These signals are assigned to the open-site protons. Consistently, the imine methine protons are split by coupling to these protons. The methine protons occur at 8.16 ppm (*J* = 13.4 Hz) for the Zn(II) complex and at 8.38 ppm (*J* = 14.9 Hz) for the Co(III) analogue. Addition of D<sub>2</sub>O to these solutions causes rapid proton-deuterium exchange as evidenced by the disappearance of the proton signals and the absence of detectable coupling to the imine methine protons. These observations are consistent with the open-site hydrogen-bonded structure 18. Protonated monometallic complexes of

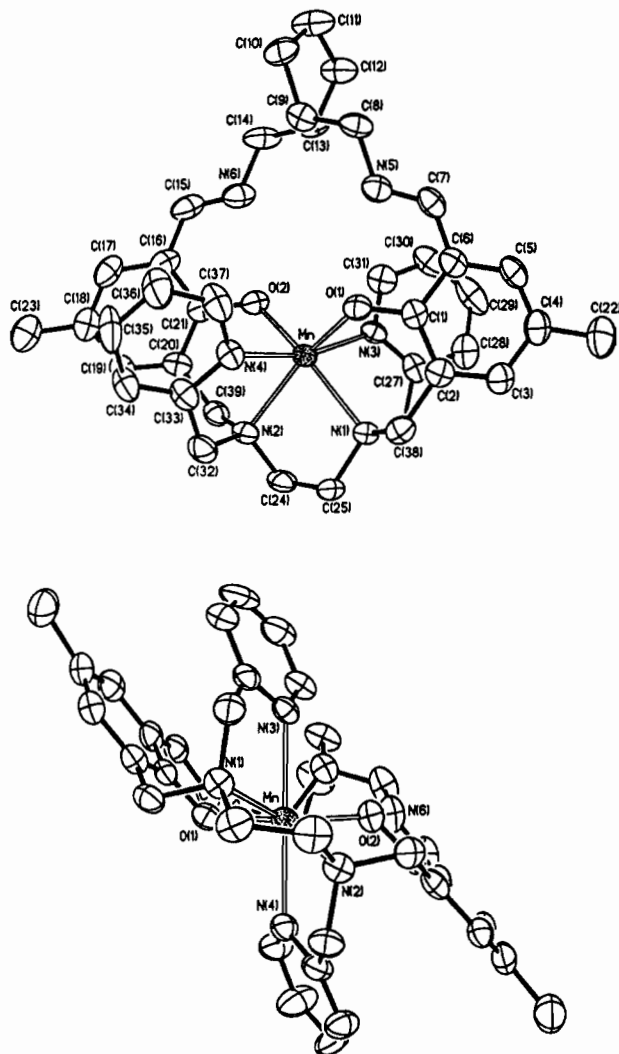


18

macrocyclic binucleating ligands have been reported previously for the mono nickel complex of the Robson ligand<sup>15</sup> and for the triketone Schiff base of Fenton.<sup>16</sup> These complexes, however, were not exploited for, and in some cases were not amenable to, the preparation of site-specific bimetallic complexes. The approach of preparing heterobimetallic complexes by the deprotonation of monometallic precursors has also been used to generate compounds of a clathrochelate ligand.<sup>17</sup>

An X-ray diffraction structure of [Mn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was determined. The hydrogen atoms were not located. Two views of this rather attractive structure are shown in Figure 1, and selected bond distances and angles are collected in Table 2. The crystal, data collection and refinement parameters for this and all subsequent complexes are given in Table 1. This structure reveals two features. First, the Mn(II) ion is in the closed-site. Second, the molecule essentially possesses a C<sub>2</sub> axis. A highly twisted structure is observed in which the phenolic fragments are skewed one above and one below the mean

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 (17) Timken, M. D.; Marrit, W. A.; Hendrickson, D. N.; Gagné, R. A.; Sinn, E. *Inorg. Chem.* **1985**, *24*, 4202.



**Figure 1.** Two perspectives of the structure of  $[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$  shown as 35% probability ORTEP drawings.

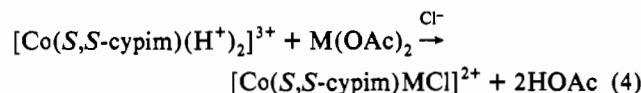
macrocyclic plane. The macrocyclic cavity defined by the two phenolic oxygen atoms and the two imine nitrogen atoms is large. The four potential donor atoms (O(1), O(2), N(5), N(6)) lie essentially in one plane and the diagonal distances O(1)–N(6) and O(2)–N(5) are essentially the same, 4.7 Å. The hydrogen bonding that is assumed to exist for the two protons in this cavity is thought to span O(2) to N(5) and O(2) to N(6). These distances are approximately 2.6 Å. The size of the cavity will depend on the radius of the metal in the closed site and on the conformation of the ligand. In its present conformation the open binding site is probably too large to accommodate a metal ion of the first transition series. As we shall see, however, bimetallic complexes containing a metal with a large radius in the closed site can be prepared. It will be noted that the absolute configuration about the Mn(II) in  $[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$  is  $\Delta$ ,<sup>18</sup> as determined by X-ray crystallographic methods.

The X-ray structure of the complex  $[\text{Zn}(\text{S,S-cypim})(\text{H}^+)_2](\text{PF}_6)_2$  was determined for comparison with the  $[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2](\text{PF}_6)_2$  structure described above. Two views of this structure are given in Figure 2 and selected bond distances and angles appear in Table 3. The Zn(II) ion is also bound in the closed-site of the *S,S*-cypim ligand and the structure is roughly  $C_2$  symmetric, but the topological chirality<sup>18</sup> is  $\Delta$ , opposite to that

found for the Mn(II) complex. In the Zn(II) complex the *S,S*-cypim ligand assumes a less twisted conformation where the phenoxide groups are roughly in the mean macrocyclic plane. This conformation contrasts with that observed for the mono Mn(II) complex in which the phenoxides are tilted above and below the mean macrocyclic plane. The macrocyclic cavity of the mono Zn(II) complexes (O(2)–N(5) = 3.9 Å, O(1)–N(6) = 4.4 Å) is somewhat contracted compared to the Mn(II) structure. Hydrogen bonding is believed to exist across the O(1) and N(5) and O(2) and N(6) atoms; these distances are 2.6 and 2.7 Å, respectively. Three of the atoms defining this cavity, O(1), O(2), and N(6), lie approximately in the macrocyclic plane, whereas the fourth atom, N(5), is projected out of the plane, accounting for the differences in diagonal distances and breaking the  $C_2$  symmetry of the molecule in the crystal. The <sup>1</sup>H NMR spectrum, however, indicates a  $C_2$  symmetric structure, which implies either that a different conformation exists in acetonitrile solution than in the crystal or that the diimine moiety is rapidly oscillating in solution. This difference in diastereoselectivity observed for the Zn(II) and Mn(II) complexes will be discussed presently.

### Bimetallic Complexes of Cobalt(III)

Heterobimetallic complexes containing Co(III) in the closed site are readily prepared by adding an ethanol solution containing the metal acetate and LiCl to an acetonitrile solution of the complex  $[\text{Co}(\text{S,S-cypim})(\text{H}^+)_2](\text{PF}_6)_3$  (eq 4). By this procedure



heterobimetallic complexes containing Zn(II), Ni(II), Co(II), and Mn(II) in the open site were isolated as the chloro complexes,  $[\text{Co}(\text{S,S-cypim})\text{MCl}](\text{PF}_6)_2$ . The corresponding Cu(II) complex,  $[\text{Co}(\text{S,S-cypim})\text{Cu}](\text{PF}_6)_3$ , was isolated without the chloro ligand. It was found that the presence of the chloro ligand, for all of the open-site metals other than Cu(II), resulted in the precipitation of highly crystalline materials from acetonitrile/ethanol solutions. In acetonitrile all of the chloro complexes were found to be 2:1 electrolytes indicating that the chloro ligand is bound to the metal in these solutions. The copper complex was found to be a 3:1 electrolyte in acetonitrile solution.

Since Co(III) forms very stable and stereochemically inert complexes, we expect that all of the heterobimetallic complexes will have the second metal exclusively in the open site and that the  $C_2$  symmetric structure of the original  $[\text{Co}(\text{S,S-cypim})(\text{H}^+)_2]^{3+}$  complex will be preserved in the heterobimetallic complexes. The  $C_2$  symmetry of the diamagnetic  $[\text{Co}(\text{S,S-cypim})\text{Zn}]^{3+}$  complex prepared in acetone by the addition of silver triflate to a solution of  $[\text{Co}(\text{S,S-cypim})\text{ZnCl}]^{2+}$  was confirmed by <sup>1</sup>H NMR (see Experimental Section).

The structure of these complexes was elucidated by an X-ray diffraction study of the complex  $[\text{Co}(\text{S,S-cypim})\text{Cu}(\text{CH}_3\text{CN})](\text{PF}_6)_3$ . Two perspectives of the structure are shown in Figure 3, and selected bond distances and angles are given in Table 4. The Co(III) is six-coordinate and has a  $C_2$  symmetric structure with trans-disposed pyridine ligands. Bond distances and angles about cobalt are unexceptional. Analogous to the structure of the  $[\text{Zn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$ , this Co(III) complex has the twisted phenoxide groups lying roughly in the mean macrocyclic plane, and once again one of the imine nitrogens, N(6), is projected out of the macrocyclic plane. The acetonitrile ligand is loosely bound to the open-site Cu(II) ion as judged from the long N(7)–Cu bond length of 2.221 Å and from its disorder in the crystal. This five-coordinate Cu(II) center resembles a trigonal bipyramid where O(2) and N(5) represent the axial ligands. The trigonal bipyramid is distorted because of the constraints imposed by the ligand. Thus, for example, the N(6)–Cu–N(5) angle is 108°,

(18) This assignment is made by the prescriptions outlined in *Inorg. Chem.* 1970, 9, 1, but we have included the pair-wise contributions which arise from the presence of the diimine cyclic chelate. Thus the absolute configuration about the Mn(II) ion in  $[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$  is  $\Delta$ ,  $\Delta$ ,  $\Delta$ ,  $\Delta$ , and, therefore, overall  $\Delta$ .

**Table 1.** Crystallographic Data for  $[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$ ,  $[\text{Zn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$ ,  $[\text{Co}(\text{S,S-cypim})\text{Cu}]^{3+}$ , and  $[\text{Cu}(\text{S,S-cypim})\text{Cu}(\text{CH}_3\text{CN})]^{2+}$ 

	$[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$	$[\text{Zn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$	$[\text{Co}(\text{S,S-cypim})\text{Cu}]^{3+}$	$[\text{Cu}(\text{S,S-cypim})\text{Cu}(\text{CH}_3\text{CN})]^{2+}$
formula	$[\text{Mn}(\text{C}_{39}\text{H}_{44}\text{N}_6\text{O}_2)(\text{H}^+)_2](\text{PF}_6)_2$	$[\text{Zn}(\text{C}_{39}\text{H}_{44}\text{N}_6\text{O}_2)(\text{H}^+)_2](\text{PF}_6)_2$	$[\text{Co}(\text{C}_{39}\text{H}_{44}\text{N}_6\text{O}_2)\text{Cu}(\text{CH}_3\text{CN})](\text{PF}_6)_3 \cdot \text{CH}_3\text{CH}_2\text{OH}$	$[\text{Cu}(\text{C}_{39}\text{H}_{44}\text{N}_6\text{O}_2)\text{Cu}(\text{CH}_3\text{CN})](\text{PF}_6)_2 \cdot \text{CH}_3\text{CH}_2\text{OH}$
fw	975.7	986.1	1273.3	1132.9
cryst syst	monoclinic	trigonal	monoclinic	triclinic
space group	$P2_1$	$P3_1$	$P2_1$	$P\bar{1}$
a, Å	8.462(2)	13.298(3)	12.248(2)	13.404(3)
b, Å	12.218(2)		11.741(2)	13.928(3)
c, Å	21.409(4)	20.836(5)	17.961(4)	15.201(3)
$\alpha$ , deg				72.70(3)
$\beta$ , deg	100.75(3)		94.91(3)	80.50(3)
$\gamma$ , deg				66.92(3)
V, Å <sup>3</sup>	2174.6(7)	3191.5(17)	2573.4(8)	2488.8(9)
Z	2	3	2	2
cryst dimens, mm	0.23 × 0.28 × 0.42	0.04 × 0.36 × 0.40	0.10 × 0.42 × 0.44	0.60 × 0.60 × 0.80
cryst color	orange	green-yellow	dark red	dark green
D(calc), g cm <sup>-3</sup>	1.490	1.540	1.643	1.512
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	4.71	7.48	9.41	10.09
temp, K	298	233	298	253
T(max)/T(min)	a	a	1.298	a
(a) Crystal Parameters				
(b) Data Collection				
diffractometer			Siemens P4	
monochromator			graphite	
radiation			MoK $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )	
2 $\theta$ scan range, deg	4–48	4–44	4–46	4–45
data collected (h, k, l)	$\pm 9, \pm 13, \pm 24$	$\pm 11, \pm 12, \pm 21$	$\pm 13, \pm 12, \pm 19$	$\pm 14, \pm 14, \pm 13$
no. of $\alpha$ reflns colld	3692	2801	7387	6756
no. of indep reflns	3585	2777	7377	6351
R(merg), %	2.03	2.60	3.81	0.61
no. of indep obsd reflns	2925	2139	5051	5009
$F_o \geq 4\sigma(F_o)$				
std. reflns	3 std/197 reflns	3 std/197 reflns	3 std/197 reflns	3 std/197 reflns
var. in stds., %	~5	<1	~9	~4
(c) Refinement				
R(F), %	4.66	6.28	6.95	5.94
R <sub>w</sub> (F), %	5.53	7.84	7.53	9.30
$\Delta/\sigma(\text{max})$	0.001	0.116	2.131	0.240
$\Delta(\rho)$ , e Å <sup>-3</sup>	+0.34	+0.61	+1.43	+0.69
N <sub>o</sub> /N <sub>v</sub>	5.2	6.7	7.4	8.3
GOF	1.35	1.26	1.44	1.30

<sup>a</sup> Not applicable.

**Table 2.** Selected Bond Distances and Angles for  $[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2](\text{PF}_6)_2$ 

Bond Distances (Å)			
Mn–O(1)	2.155(4)	Mn–N(3)	2.285(7)
Mn–O(2)	2.109(5)	Mn–N(4)	2.249(7)
Mn–N(1)	2.285(6)	O(1)–C(1)	1.309(9)
Mn–N(2)	2.316(5)	O(2)–C(21)	1.302(9)
Bond Angles (deg)			
O(1)–Mn–O(2)	115.1(2)	N(2)–Mn–N(3)	117.5(2)
O(1)–Mn–N(1)	88.9(2)	O(1)–Mn–N(4)	86.3(2)
O(2)–Mn–N(1)	148.1(2)	O(2)–Mn–N(4)	87.4(2)
O(1)–Mn–N(2)	149.9(2)	N(1)–Mn–N(4)	116.3(2)
O(2)–Mn–N(2)	87.7(2)	N(2)–Mn–N(4)	74.9(2)
N(1)–Mn–N(2)	79.1(2)	N(3)–Mn–N(4)	165.8(2)
O(1)–Mn–N(3)	85.0(2)	Mn–O(1)–C(1)	119.2(4)
O(2)–Mn–N(3)	86.2(2)	Mn–O(2)–C(21)	123.8(5)
N(1)–Mn–N(3)	74.8(2)		

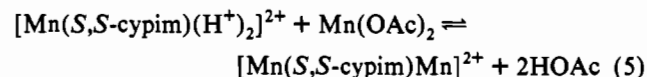
which is probably imposed by the wide bite-angle of the trans bis(iminomethyl)cyclopentane fragment.

The absolute configuration of the molecule was determined by X-ray diffraction and the topological chirality about the Co(III) is  $\Delta$ .<sup>18</sup> This is opposite to what was found for  $[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$  but is the same as was observed for  $[\text{Zn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$  (compare Figures 1–3).

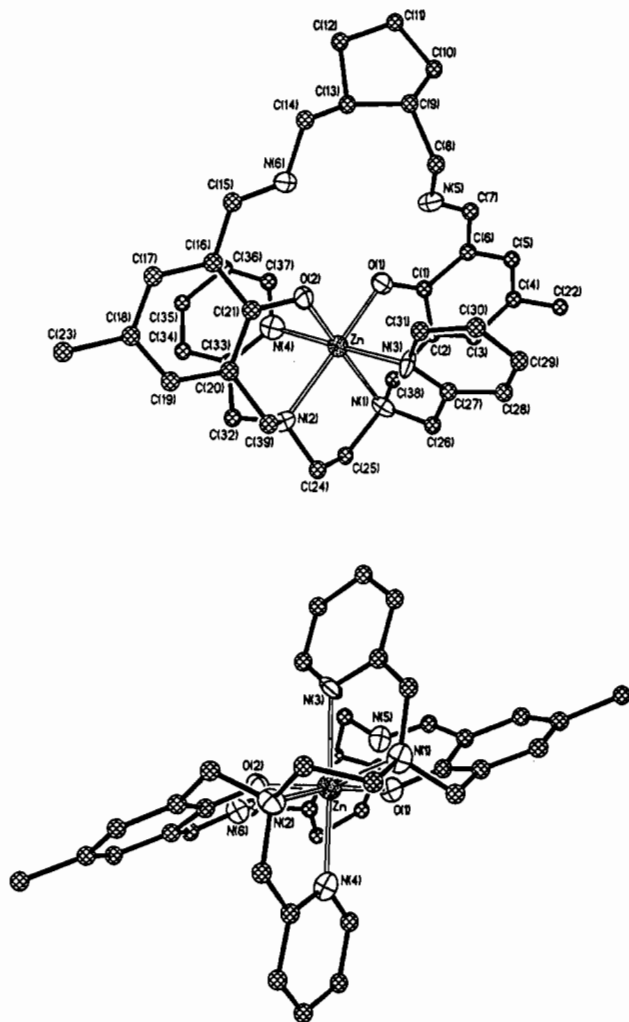
#### Bimetallic Complexes of Labile Divalent Metals

Given the large open-site cavity found in the crystal structure of  $[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$ , it was of interest to determine if a

second metal could be accommodated in this open site. In contrast to the preparation of  $[\text{Co}(\text{S,S-cypim})\text{MnCl}]^{2+}$  complexes, addition of an ethanol solution of  $\text{Mn}(\text{OAc})_2$  to an acetonitrile solution of  $[\text{Mn}(\text{S,S-cypim})(\text{H}^+)_2]^{2+}$  did not result in the formation of the dimanganese complex. Rather, the monometallic starting material was recovered. This suggests that the equilibrium depicted in eq 5 lies to the left. The reaction however, can be



driven to the homobimetallic species  $[\text{Mn}(\text{S,S-cypim})\text{MnCl}]\text{PF}_6$  by the addition of LiCl and 2 equiv of triethylamine. In a similar way the complex  $[\text{Ni}(\text{S,S-cypim})\text{NiCl}]\text{PF}_6$  was prepared. It is probable that the instability of the dimanganese complex in the presence of protons is due to the large open-site cavity which does not accommodate the second metal without considerable rearrangement of the ligand structure. Once isolated as yellow crystals the dimanganese(II) complex is air-stable. Aerated solutions of  $[\text{Mn}(\text{S,S-cypim})\text{MnCl}]^+$ , however, gradually turn green, and after slow evaporation of the solvent, green needles can be isolated. Analytical data and other physical properties indicate that this green product has the formulation  $[\text{Mn}^{\text{II}}(\text{S,S-cypim})\text{Mn}^{\text{III}}(\text{Cl}_2)]\text{PF}_6$ . Although its structure was not determined, it is probable that it is analogous to that found for the  $[\text{Mn}(\text{cyclim})(\mu\text{-Cl})\text{MnCl}]^+$  complex, which was prepared under similar conditions.<sup>8</sup> Having established the conditions for the synthesis of bimetallic complexes containing a large labile metal in the closed-site, we



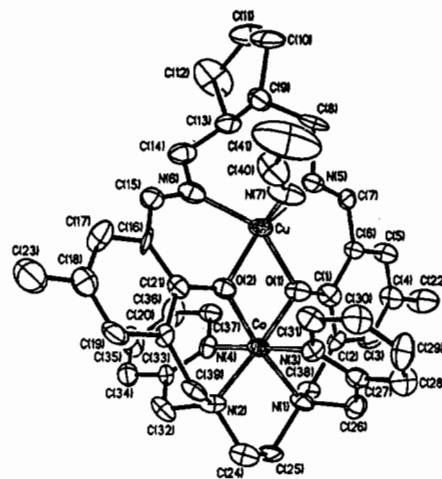
**Figure 2.** Two perspectives of the structure of  $[\text{Zn}(\text{S},\text{S}\text{-cypim})(\text{H}^+)_2]^{2+}$  shown as 35% probability ORTEP drawings.

**Table 3.** Selected Bond Distances and Angles for  $[\text{Zn}(\text{S},\text{S}\text{-cypim})(\text{H}^+)_2](\text{PF}_6)_2$

Bond Distances (Å)			
Zn–O(1)	2.033(9)	Zn–N(3)	2.187(11)
Zn–O(2)	2.087(13)	Zn–N(4)	2.139(12)
Zn–N(1)	2.199(15)	O(1)–C(1)	1.310(25)
Zn–N(2)	2.175(11)	O(2)–C(21)	1.292(20)
Bond Angles (deg)			
O(1)–Zn–O(2)	97.9(4)	N(2)–Zn–N(3)	101.8(4)
O(1)–Zn–N(1)	89.3(5)	O(1)–Zn–N(4)	91.5(4)
O(2)–Zn–N(1)	161.8(4)	O(2)–Zn–N(4)	91.7(5)
O(1)–Zn–N(2)	165.5(4)	N(1)–Zn–N(4)	104.9(5)
O(2)–Zn–N(2)	93.3(5)	N(2)–Zn–N(4)	78.8(4)
N(1)–Zn–N(2)	82.8(5)	N(3)–Zn–N(4)	177.5(6)
O(1)–Zn–N(3)	88.3(4)	Zn–O(1)–C(1)	127.0(9)
O(2)–Zn–N(3)	85.9(5)	Zn–O(2)–C(21)	122.2(8)
N(1)–Zn–N(3)	77.6(5)		

sought methods of preparing heterobimetallic complexes containing labile metal ions.

We chose to prepare the following series of complexes,  $[\text{M}(\text{S},\text{S}\text{-cypim})\text{Cu}]^{2+}$  ( $\text{M} = \text{Zn}(\text{II}), \text{Cu}(\text{II}), \text{Ni}(\text{II}), \text{Co}(\text{II}), \text{Mn}(\text{II})$ ), so as to probe the variation in the physical properties of the  $\text{Cu}(\text{II})$  in the open site when the metal in the closed site was changed. For our EPR studies we also prepared the complex,  $[\text{Cu}(\text{S},\text{S}\text{-cypim})\text{ZnCl}]\text{PF}_6$ . The heterobimetallic complexes,  $[\text{M}(\text{S},\text{S}\text{-cypim})\text{Cu}]^{2+}$  as well as the dicopper complex was prepared by adding a 1,4-dioxane solution of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  to an acetonitrile solution containing  $[\text{M}(\text{S},\text{S}\text{-cypim})(\text{H}^+)_2](\text{PF}_6)_2$  and 2 equiv of triethylamine. The reactions occur upon mixing as witnessed by

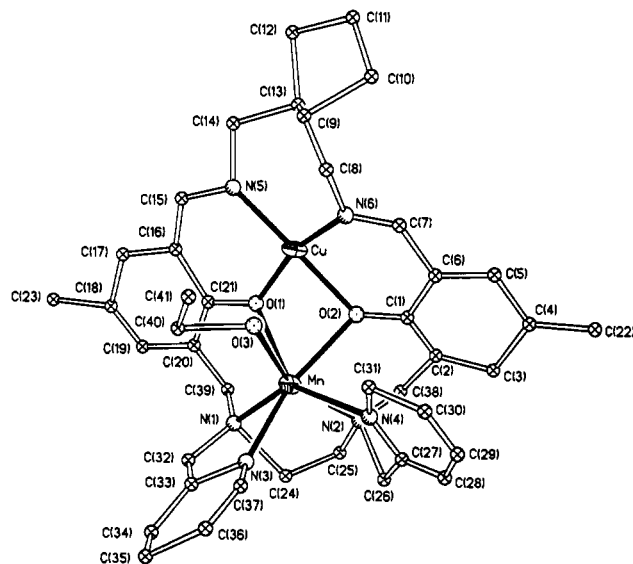


**Figure 3.** Two perspectives of the structure of  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Cu}(\text{CH}_3\text{CN})]^{3+}$  shown as 35% probability ORTEP drawings.

**Table 4.** Selected Bond Distances and Angles for  $[\text{Co}(\text{S},\text{S}\text{-cypim})\text{Cu}(\text{CH}_3\text{CN})](\text{PF}_6)_3$

Bond Distances (Å)			
Co–Cu	2.994(2)	Cu–O(1)	1.999(8)
Co–O(1)	1.898(7)	Cu–O(2)	1.950(7)
Co–O(2)	1.865(8)	Cu–N(5)	1.957(9)
Co–N(1)	1.951(10)	Cu–N(6)	2.004(11)
Co–N(2)	1.951(9)	Cu–N(7)	2.221(11)
Co–N(3)	1.977(10)	O(1)–C(1)	1.366(16)
Co–N(4)	1.945(9)	O(2)–C(21)	1.366(14)
Bond Angles (deg)			
O(1)–Co–O(2)	80.3(3)	O(1)–Cu–N(5)	89.9(4)
O(1)–Co–N(1)	93.6(4)	O(2)–Cu–N(5)	163.8(4)
O(2)–Co–N(1)	172.9(4)	O(1)–Cu–N(6)	140.5(4)
O(1)–Co–N(2)	175.5(4)	O(2)–Cu–N(6)	88.1(4)
O(2)–Co–N(2)	95.6(4)	N(5)–Cu–N(6)	108.0(4)
N(1)–Co–N(2)	90.6(4)	O(1)–Cu–N(7)	116.5(4)
O(1)–Co–N(3)	92.1(4)	N(5)–Cu–N(7)	89.5(4)
O(2)–Co–N(3)	92.1(4)	N(6)–Cu–N(7)	98.8(4)
N(1)–Co–N(3)	84.1(4)	N(6)–Cu–N(7)	98.8(4)
N(2)–Co–N(3)	93.1(4)	Co–O(1)–Cu	100.4(4)
O(1)–Co–N(4)	93.1(4)	Co–O(1)–C(1)	126.9(8)
O(2)–Co–N(4)	87.7(4)	Cu–O(1)–C(1)	129.9(7)
N(1)–Co–N(4)	96.4(4)	Co–O(2)–Cu	103.4(4)
N(2)–Co–N(4)	84.7(4)	Co–O(2)–C(21)	129.6(7)
N(3)–Co–N(4)	177.8(4)	Cu–O(2)–C(21)	126.6(7)
O(1)–Cu–O(2)	75.8(3)		

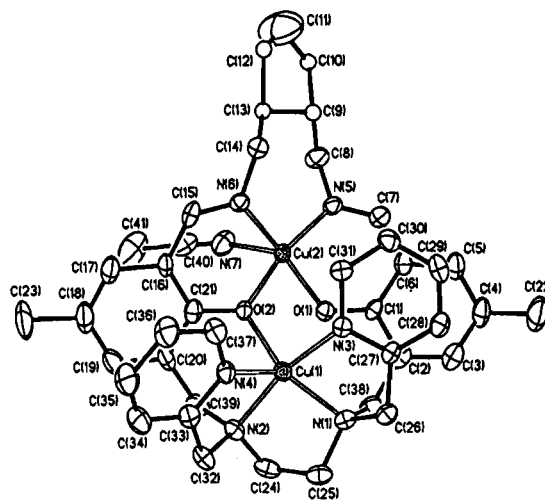
distinct color changes. After removal of the solvents, the residues were redissolved in  $\text{CH}_2\text{Cl}_2$ , and ethanol containing  $\text{NH}_4\text{PF}_6$  was



**Figure 4.** Crystal structure of the  $[\text{Mn}(\text{EtOH})(S,S\text{-cypim})\text{Cu}]^{2+}$  ion. This structure was poorly refined and although the gross structural features are secure, the identity of the seventh unidentate ligand assumed to be EtOH is uncertain (see Experimental Section).

added. Upon slow evaporation of the  $\text{CH}_2\text{Cl}_2$ , the complexes  $[\text{M}(S,S\text{-cypim})\text{Cu}](\text{PF}_6)_2$ , where  $\text{M} = \text{Zn}(\text{II}), \text{Cu}(\text{II}), \text{Ni}(\text{II}), \text{Co}(\text{II}),$  and  $\text{Mn}(\text{II})$ , deposited as crystals. The crystals so obtained were often highly susceptible to solvent effluorescence. Except for when  $\text{M} = \text{Co}(\text{II})$  this method gave the products in good yields and in high analytical purity. The  $[\text{Co}(S,S\text{-cypim})\text{Cu}](\text{PF}_6)_2$  complex is air sensitive in solution, and its preparation required the rigorous exclusion of oxygen. The complex is stable in air as the solid. The air sensitivity of  $[\text{Co}(S,S\text{-cypim})\text{Cu}]^{2+}$  contrasts with the air stability of  $[\text{Co}(S,S\text{-cypim})(\text{H}^+)_2]^{2+}$  in solution. The remaining complex,  $[\text{Cu}(S,S\text{-cypim})\text{ZnCl}]\text{PF}_6$ , was prepared in a manner analogous to that described for the dimanganese complex.

In order to determine the types of structures that the  $S,S\text{-cypim}$  ligand will adopt when two stereochemically labile metals are coordinated, two additional crystal structures were determined, one of the complex  $[\text{Mn}(\text{EtOH})(S,S\text{-cypim})\text{Cu}](\text{PF}_6)_2 \cdot \text{CH}_2\text{Cl}_2$  and the other of  $[\text{Cu}(S,S\text{-cypim})\text{Cu}(\text{CH}_3\text{CN})](\text{PF}_6)_2$ . The Mn–Cu structure proved difficult to refine to an acceptable level,<sup>25</sup> but the gross stereochemical features are secure. Spectroscopic data indicate that only Mn(II) and Cu(II) ions are present, but the analytical data of the crystals are consistent with the presence of an equal mixture of  $[\text{Mn}(\text{EtOH})(S,S\text{-cypim})\text{Cu}](\text{PF}_6)_2$  and  $[\text{Mn}(\text{acetate})(S,S\text{-cypim})\text{Cu}]\text{PF}_6$ . This is consistent with crystallographic data. Two molecules are present in the unit cell which contains only three  $\text{PF}_6$  ions. Both of the Mn(II) ions in the closed site are seven-coordinate. The gross structure of the molecule, which probably contains a coordinated ethanol, is shown in Figure 4. A discussion of the difficulties associated with the refinement of this system is given in the Experimental Section. It will be noted that the ligand adopts an unsymmetrical structure with both of the pyridine ligands coordinating to Mn(II) ion on one side of the mean macrocyclic plane. The seventh ligand coordinates to the Mn(II) adjacent to the two “cis”-disposed pyridine ligands. The larger radius of spin-free Mn(II) presumably allows the metal to achieve seven-coordination.<sup>19</sup> The Cu(II) in this complex is four-coordinate.



**Figure 5.** Two perspectives of the structure of  $[\text{Cu}(S,S\text{-cypim})\text{Cu}(\text{CH}_3\text{CN})]^{2+}$  shown as 35% probability ORTEP drawings.

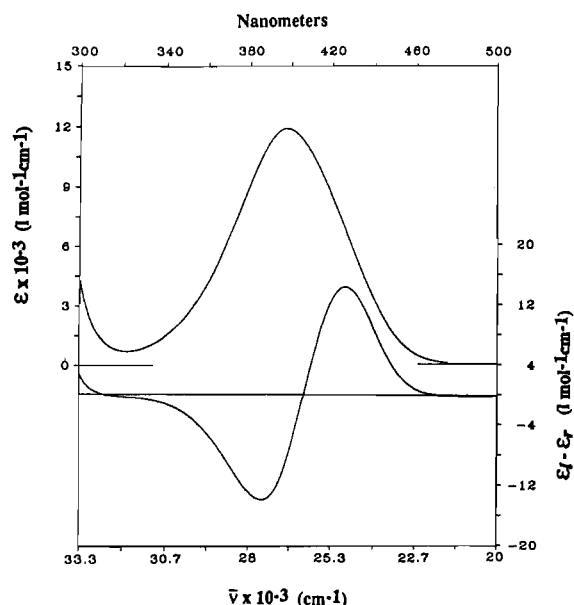
**Table 5.** Selected Bond Distances and Angles for  $[\text{Cu}(S,S\text{-cypim})\text{Cu}(\text{CH}_3\text{CN})](\text{PF}_6)_2$

Bond Distances (Å)			
Cu(1)–O(2)	2.077(5)	Cu(2)–O(2)	1.918(4)
Cu(1)–N(1)	2.068(5)	Cu(2)–N(5)	1.976(5)
Cu(1)–N(2)	2.026(4)	Cu(2)–N(6)	2.037(5)
Cu(1)–N(3)	1.965(5)	Cu(2)–N(7)	2.435(9)
Cu(1)–N(4)	2.115(6)	O(1)–C(1)	1.279(7)
Cu(2)–O(1)	1.938(4)	O(2)–C(21)	1.321(8)
Bond Angles (deg)			
O(2)–Cu(1)–N(1)	130.6(2)	O(2)–Cu(2)–N(5)	169.0(2)
O(2)–Cu(1)–N(2)	93.1(2)	O(1)–Cu(2)–N(6)	160.0(3)
N(1)–Cu(1)–N(2)	87.0(2)	O(2)–Cu(2)–N(6)	87.1(2)
O(2)–Cu(1)–N(3)	99.3(2)	N(5)–Cu(2)–N(6)	102.5(4)
N(1)–Cu(1)–N(3)	83.1(2)	O(1)–Cu(2)–N(7)	106.8(2)
N(2)–Cu(1)–N(3)	167.4(2)	O(2)–Cu(2)–N(7)	92.0(3)
O(2)–Cu(1)–N(4)	92.6(2)	N(5)–Cu(2)–N(7)	93.6(3)
N(1)–Cu(1)–N(4)	136.1(2)	N(6)–Cu(2)–N(7)	88.4(2)
N(2)–Cu(1)–N(4)	82.9(2)	Cu(2)–O(1)–C(1)	122.3(3)
N(3)–Cu(1)–N(4)	98.9(2)	Cu(1)–O(2)–Cu(2)	119.2(2)
O(1)–Cu(2)–O(2)	79.5(2)	Cu(1)–O(2)–C(21)	115.7(4)
O(1)–Cu(2)–N(5)	89.8(2)	Cu(2)–O(2)–C(21)	123.8(4)

Two perspectives of the crystal structure of  $[\text{Cu}(S,S\text{-cypim})\text{Cu}(\text{CH}_3\text{CN})]^{2+}$  are shown in Figure 5 and selected bond distances and angles are given in Table 5. The copper in the open site forms a distorted square pyramidal structure. The metal–nitrogen bond to the acetonitrile ligand is long,  $\text{Cu}(2)\text{–N}(7)$  (2.435 Å), and the ligand is disordered in the crystal. In order to

(19) (a) Stezowski, J. J.; Countryman, R.; Hoard, J. L. *Inorg. Chem.* **1973**, *12*, 1749. (b) Palenik, G. L.; Wester, D. W. *Inorg. Chem.* **1978**, *17*, 864. (c) Gmelin **1982**, D3, 63. (d) Pelizzi, C.; Pelizzi, G.; Predieri, G.; Resola, S. *J. Chem. Soc., Dalton Trans.* **1982**, 1349. (e) Lorenzini, C.; Pelizzi, C.; Pelizzi, G.; Predieri, G. *J. Chem. Soc., Dalton Trans.* **1983**, 721 and references therein.





**Figure 6.** Absorption and circular dichroism spectra of  $\Delta$ -[Zn(*S,S*-cypim)( $H^+$ )<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> in acetonitrile solution.

accommodate both metals, however, the *S,S*-cypim ligand assumes a configuration with the pyridine groups *cis* to each other. The Cu(II) in the closed site (Cu(1)) adopts a five-coordinate distorted square pyramidal geometry by breaking a bond to one of the phenolic oxygen atoms (O(1)). The bond lengths of the closed-site Cu(II) are normal.

Thus, in these two structures, accommodation of a square planar or square pyramidal Cu(II) ion in the open site leads to extensive configurational changes in the ligand and coordination number changes at the closed-site metal. In both cases *cis*-disposed pyridine ligands obtain, and the coordination number changes reflect the known tendencies of the closed-site metals, namely, the formation of a five-coordinate Cu(II) and a seven-coordinate Mn(II) ion.

### Circular Dichroism and Diastereoselection

Information about the diastereoselection of the *S,S*-cypim ligand has been obtained from X-ray crystallography and from <sup>1</sup>H NMR and circular dichroism spectra. The fact that the [Mn(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>2+</sup> and the [Co(*S,S*-cypim)Cu]<sup>3+</sup> complexes form diastereomers with opposite configurations about the closed-site metals raised a number of questions regarding the diastereoselection of the *S,S*-cypim ligand. Is the Mn(II) complex unique among monometallic *S,S*-cypim complexes by virtue of its large size, or do all monometallic *S,S*-cypim complexes assume a  $\Delta$  topological chirality which somehow isomerizes upon oxidation of Co(II) to Co(III) or upon coordination of a second metal to the open-site cavity? These questions prompted the determination of an additional structure of a monometallic complex of smaller ionic radius, namely [Zn(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>2+</sup>, as well as circular dichroism studies in order to correlate a spectroscopic property with the stereochemistry observed crystallographically.

From <sup>1</sup>H NMR studies it is known that the diamagnetic complexes [Zn(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>2+</sup>, [Co(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>3+</sup>, and [Co(*S,S*-cypim)Zn]<sup>3+</sup> all display spectra which indicate that a single diastereomer exists in solution within the accuracy of the <sup>1</sup>H NMR experiment (3%). Although NMR does not indicate which diastereomer is preferred, these results imply that the ligand is strongly diastereoselective. No useful <sup>1</sup>H NMR spectra were obtained for the paramagnetic complexes.

When the chiral (1*S*,2*S*)-*trans*-1,2-bis(aminomethyl)cyclopentane undergoes a double Schiff base condensation to form the macrocyclic framework of the *S,S*-cypim ligand, we expect that the two resultant azomethine groups will adopt a chiral confor-

**Table 6.** Linear Absorption and Circular Dichroism Wavelengths and Intensities for C<sub>2</sub> Symmetric *S,S*-cypim Complexes

complex	absorption		circular dichroism			
	$\lambda^a$	$\epsilon^b$	$\lambda^a$	$\epsilon_1 - \epsilon_2^b$	$\lambda^a$	$\epsilon_1 - \epsilon_2^b$
[Mn( <i>S,S</i> -cypim)( $H^+$ ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	402	13120	422	+12.76		
[Co( <i>S,S</i> -cypim)( $H^+$ ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	406	11080	437	+12.26	395	-7.73
[Ni( <i>S,S</i> -cypim)( $H^+$ ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	406	12050	438	+15.97	396	-13.86
[Cu( <i>S,S</i> -cypim)( $H^+$ ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	404	10990	437	+14.44	395	-16.86
[Zn( <i>S,S</i> -cypim)( $H^+$ ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	399	11610	428	+14.17	387	-14.05
[Co( <i>S,S</i> -cypim)( $H^+$ ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>3</sub>	395	12200	423	+25.83	384	-13.38
[Co( <i>S,S</i> -cypim)MnCl](PF <sub>6</sub> ) <sub>2</sub>	342	6360	364	+12.60	328	-3.32
[Co( <i>S,S</i> -cypim)CoCl](PF <sub>6</sub> ) <sub>2</sub>	336	8230	369	+8.11	330	+1.75
[Co( <i>S,S</i> -cypim)NiCl](PF <sub>6</sub> ) <sub>2</sub>	343	8100	365	+13.03	335	-2.37
[Co( <i>S,S</i> -cypim)Cu](PF <sub>6</sub> ) <sub>3</sub>	344	6550	363	+30.62	334	-8.92
[Co( <i>S,S</i> -cypim)ZnCl](PF <sub>6</sub> ) <sub>2</sub>	345	5000	363	+10.48	331	-0.06

<sup>a</sup>  $\lambda$  in nm. <sup>b</sup>  $\epsilon$  and  $\epsilon_1 - \epsilon_2$  in L mol<sup>-1</sup> cm<sup>-1</sup>.

mation when metal complexes are formed. If this is so then the electric transition dipole moments of the individual azomethine  $\pi \rightarrow \pi^*$  transitions will couple to generate a (+, -) circular dichroism couplet under the azomethine  $\pi \rightarrow \pi^*$  absorption manifold.<sup>20,21</sup> According to exciton theory the coupled azomethine  $\pi \rightarrow \pi^*$  transition will split into two components according to the dipole-dipole interaction of the two electric transition dipole vectors. Whether the symmetric and antisymmetric coupling modes appear at lower or higher energies will depend on the overall directions of the two dipole vectors, but whatever the sense of the splitting, the circular dichroism should appear as an equal but opposite couplet. In Figure 6 we show the absorption and circular dichroism spectra associated with the  $\pi \rightarrow \pi^*$  azomethine absorption of [Zn(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>2+</sup>. Although the expected splitting of the linear absorption is not resolved, the circular dichroism shows a classical couplet probably because the  $\pi \rightarrow \pi^*$  azomethine transitions are well separated from other transitions that could couple and because no other transitions overlap in these regions. Listed in Table 6 are the linear absorption and circular dichroism wavelength maxima, minima, and intensities for the  $\pi \rightarrow \pi^*$  transitions of the azomethine chromophores for the monometallic and bimetallic Co(III) complexes. For the Co(III) complexes the azomethine  $\pi \rightarrow \pi^*$  transition is partially coincident with other transitions so that the expected circular dichroism couplet is distorted by overlap. Even so, the (+, -) couplet is resolved in all cases except for the Co(III)-Co(II) complex where the negative component does not become negative because of overlap. However the general contour of the circular dichroism clearly indicates its presence. Except for the Mn(II) complex, all of the monometallic complexes show the expected couplet (Table 6). The [Mn(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>2+</sup> complex only displays a positive circular dichroism band, and there are no overlapping bands in this region.

Evidence that the Co(III)-containing complexes possess the same absolute configuration is found upon examination of the circular dichroism associated with the Co(III) chromophore. The monometallic complex, [Co(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>3+</sup>, for example, shows a magnetic dipole allowed d-d transition at 530 nm. The lowest energy circular dichroism absorption associated with this transition is observed at 573 nm and carries negative absorption (Figure 7). Although other circular dichroism absorption overlaps with this d-d transition in [Co<sup>III</sup>(*S,S*-cypim)M<sup>II</sup>] bimetallic complexes, they too show negative dichroism at lower energies of the magnetic dipole transition manifold. Circular dichroism data for the Co(III) chromophore in Co(III)-containing complexes are collected in Table 7. These results provide further proof that all of these complexes possess the same  $\Delta$  topological chirality<sup>18</sup> about the Co(III) ion,<sup>22</sup> as was observed in the X-ray crystal structure of the [Co(*S,S*-cypim)Cu]<sup>3+</sup> complex.

(20) Bosnich, B. *Acc. Chem. Res.* **1969**, *2*, 266.

(21) Bosnich, B. *J. Am. Chem. Soc.* **1968**, *90*, 627.

(22) Hawkins, C. J. *Absolute Configuration of Metal Complexes*; Wiley Interscience: New York, 1971.

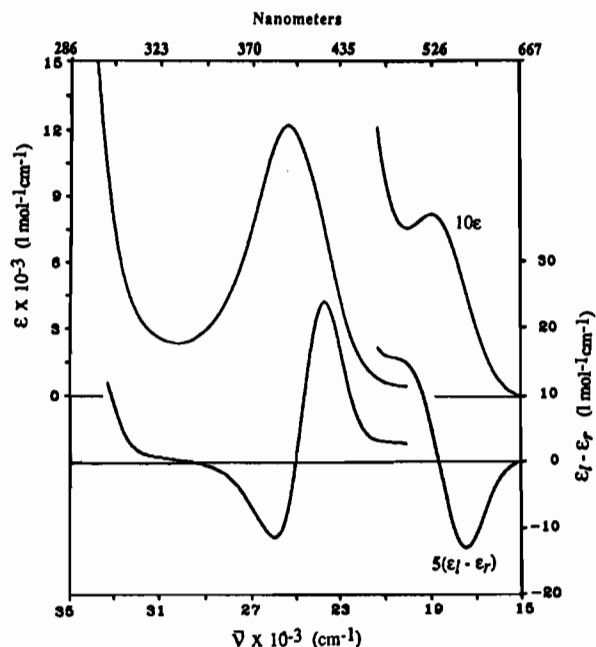


Figure 7. Absorption and circular dichroism spectra of  $\Delta$ -[Co(*S,S*-cypim)-( $H^+$ )<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> in acetonitrile solution.

Table 7. Wavelength and Circular Dichroism Intensity of the Lowest Energy Co(III) d-d Transition of Mono- and Bimetallic Co(III) Complexes

complex	$\lambda$ , nm	$\epsilon_1 - \epsilon_r$ , L mol <sup>-1</sup> cm <sup>-1</sup>
[Co( <i>S,S</i> -cypim)( $H^+$ ) <sub>2</sub> ] <sup>3+</sup>	573	-2.67
[Co( <i>S,S</i> -cypim)ZnCl] <sup>2+</sup>	555	-3.92
[Co( <i>S,S</i> -cypim)Cu] <sup>3+</sup>	538	-7.68
[Co( <i>S,S</i> -cypim)NiCl] <sup>2+</sup>	561	-7.93
[Co( <i>S,S</i> -cypim)CoCl] <sup>2+</sup>	565	-3.95
[Co( <i>S,S</i> -cypim)MnCl] <sup>2+</sup>	559	-5.59

## Discussion

This work had three principle objectives. The first was to develop precursors for kinetically controlled synthesis of heterobimetallic complexes. The second goal was to design a binucleating macrocyclic ligand which would generate  $C_2$ -symmetric complexes. Finally, the *S,S*-cypim ligand was prepared in order to investigate whether a chiral moiety in the open site of the ligand could influence, or even control the topological stereochemistry about the neighboring closed-site metal.

Kinetically controlled synthesis of heterobimetallic complexes has been demonstrated with the *S,S*-cypim ligand. The observation that cyclized monometallic complexes may be readily prepared in highly crystalline form as their PF<sub>6</sub><sup>-</sup> salts represents an important discovery for the synthesis of heterobimetallic complexes using ligands of this type. Such monometallic complexes allow for incorporation of a second metal ion into the open site under very mild conditions. The desired heterobimetallic products form essentially upon mixing when a monometallic precursor is combined with a second metal salt, a base, and in some cases a Cl<sup>-</sup> ligand. A similar strategy of combining a metal salt with a precyclized monometallic precursor was employed previously by Okawa and Gagné with a related ligand. In these cases however, neutral unprotonated precursors were utilized.<sup>23,24</sup> Whereas the monometallic complexes described are ideal precursors, there remains the challenge of demonstrating that pure site-specific heterobimetallic compounds have been obtained with labile metal ions. Taken as a whole the physical methods that we utilized suggest that the labile metal heterobimetallic com-

plexes are at least 90% pure. We have found no physical methods which can unequivocally establish purity to higher precision. The *S,S*-cypim ligand, which preferentially binds a metal ion in the sexadentate site in monometallic precursors, and the mild preparative methods used, however, provide a persuasive case for assuming that pure compounds were isolated. Physical characterization of these heterobimetallic complexes in support of this assertion is detailed in the succeeding paper.

The second objective of generating  $C_2$ -symmetric complexes was partially successful. Replacing the trimethylenediamine link of the cyclim ligand **9<sup>b</sup>** by the (1*S*,2*S*)-*trans*-1,2-bis(aminomethyl)cyclopentane moiety to produce the present *S,S*-cypim ligand served to add an extra carbon atom to this link and imparted a chiral twist to the molecule. The larger chelate ring size was expected to provide greater conformational flexibility to the coordinated *S,S*-cypim ligand, and it was expected that the twist of the diimine would be transmitted through the whole conformational framework of the coordinated ligand so that the pyridine ligands would naturally adopt a *trans* topology. The twist imparted by the chiral diimine does indeed ensure that topologically chiral  $C_2$ -symmetric complexes are formed but only for the monometallic species and for bimetallic complexes bearing the smaller radius Co(III) ion in the closed site. Bimetallic complexes of stereochemically labile divalent ions, however, generate highly non- $C_2$ -symmetric structures.

These distorted structures probably originate in a number of features inherent in the *S,S*-cypim ligand. The first of these is the bite angle of the ethylenediamine link in the closed site. The N-M-N angle of this link is less than 90° when M is a divalent metal, and it becomes progressively smaller as the radius of the closed-site metal increases. The N-M-N angles are found to be 79, 83, and 91° for the [Mn(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>2+</sup>, [Zn(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>2+</sup>, and [Co(*S,S*-cypim)Cu(CH<sub>3</sub>CN)]<sup>3+</sup> complexes, respectively. A smaller N-M-N angle, however results in a larger *trans* O-M-O phenoxide-metal angle and, hence, in a larger open-site cavity in monometallic complexes. Thus we find that the O-M-O angles for [Mn(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>2+</sup> and for [Zn(*S,S*-cypim)( $H^+$ )<sub>2</sub>]<sup>2+</sup> are 115 and 98°, respectively. In bimetallic complexes containing two phenoxide bridges the O-M-O angles are small, generally about 80°, as is observed for the O-Co-O angle in the [Co(*S,S*-cypim)Cu(CH<sub>3</sub>CN)]<sup>3+</sup> complex. Thus, in order to accommodate a metal in the open site, this O-M-O angle must undergo considerable contraction, which is constrained by the *trans* N-M-N angle of the ethylenediamine link. In order to accommodate the second metal, either a small radius metal such as Co(III) is required in the closed site or, when a larger metal is present, the ligand undergoes considerable conformational and topological rearrangement. These rearrangements can take a number of forms; in the case of [Mn(*S,S*-cypim)Cu]<sup>2+</sup>, the Mn(II) ion becomes 7-coordinate, and in the case of [Cu(*S,S*-cypim)Cu]<sup>2+</sup>, the closed-site Cu(II) becomes 5-coordinate. In each of these cases it appears that *cis* disposed pyridine ligands are preferred. Thus in summary, the *S,S*-cypim ligand has two principal characteristics which conspire to generate unsymmetrical bimetallic complexes of stereochemically labile divalent metals, the tight bite angle of the ethylenediamine link and the wide bite angle of the *trans*-1,2-bis(aminomethyl)cyclopentane chelate. One possible method of circumventing these problems is to replace both the ethylenediamine and the *trans*-1,2-bis(aminomethyl) links by trimethylenediamine. But in order to obtain  $C_2$ -symmetric bimetallic complexes the trimethylenediamine link of the closed site would have to adopt a chiral skew (twist) conformation. We shall report shortly on the complexes of this ligand.

The radius of the closed-site metal also appears to determine which diastereomer is preferred. X-ray, <sup>1</sup>H NMR, and circular dichroism data suggest that a single diastereomer is formed for all of the  $C_2$  symmetric complexes, and except for the [Mn(*S,S*-

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cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> complex, the *S,S*-cypim ligand gives the  $\Delta$  absolute configuration about the closed-site metal. The synthesis of the *S,S*-cypim ligand from the racemic [M(pyral)] complex is a highly diastereoselective process and relies on the ability of [M(pyral)] to racemize during Schiff base condensation in order to achieve the >50% yields observed for most preparations.

It is unusual, if no unprecedented, for a chiral ligand to generate opposite topological chirality depending on the incorporated metal. As we have noted, the larger radius Mn(II) ion in the [Mn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> complex causes the macrocyclic framework to develop a pronounced twist, whereas in the smaller radius Zn(II) complex, [Zn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, only slight twisting is observed (Figures 1 and 2). A similar, more planar conformation is observed for the [Co(*S,S*-cypim)Cu]<sup>3+</sup> complex. We suspect that the interligand interactions that ensue from the highly twisted geometry of [Mn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> lead to a preference for the  $\Delta$  absolute configuration in this complex. The precise nature of these interactions must await molecular mechanics calculations which may be able to correlate the size of the metal radius with the diastereomeric preference. The evidence suggests, however, that only for the Mn(II) complex is the diastereoselection reversed.

These results obtained for the *S,S*-cypim complexes demonstrate a new way of controlling stereochemistry in bimetallic complexes. The presence of a remote chiral ligand or fragment coordinated to one metal can influence or, as has been shown for *S,S*-cypim, even stereospecific the chirality about a proximal metal center in suitable bimetallic systems. This strategy could find wide application in inorganic and organometallic synthesis as more bimetallic complexes are found to be effective catalysts for transition metal mediated reactions.

### Experimental Section

<sup>1</sup>H NMR spectra were recorded either on a General Electric QE 300 or a Chicago-built 500 Fourier transform spectrometer. Conductance measurements were made at 25 °C with a YSI Model 35 conductance meter on 0.001 M CH<sub>3</sub>CN solutions of the complexes. Elemental analyses were performed by Desert Analytics, Tucson, AZ, and Huffman Laboratories, Inc., Golden, CO. Solvents used in preparative reactions were dried over CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>), K (THF), or LiAlH<sub>4</sub> (diethyl ether, 1,4-dioxane). All complexes which are air sensitive in solution were prepared under Ar using deaerated solvents and standard Schlenk techniques. All samples were dried to constant weight under high vacuum (0.25 mm) for at least 5 h prior to characterization and elemental analysis. Due to solvent effluorescence, crystals of [Mn(*S,S*-cypim)Cu](PF<sub>6</sub>)<sub>2</sub> and [Cu(*S,S*-cypim)Cu](PF<sub>6</sub>)<sub>2</sub> were stored in the mother liquor as long as possible prior to X-ray structural analysis. Crystals of [Mn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, [Co(*S,S*-cypim)Cu](PF<sub>6</sub>)<sub>2</sub>·CH<sub>3</sub>CN and [Zn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> were dried in the air before structure determination. The UV/vis spectra were obtained on a Varian (Cary) 2400 Spectrophotometer using spectral grade CH<sub>3</sub>CN. Circular dichroism spectra were recorded using a Jasco J-600 instrument.

**Cyclopentane Diamine Synthesis.** (1*S*,2*S*)-*trans*-1,2-Bis(hydroxymethyl)cyclopentane (13). A dry ether solution (60 mL) of di-(1*R*,2*S*,5*R*)-menthyl (1*S*,2*S*)-*trans*-1,2-cyclopentanedicarboxylate<sup>12</sup> (17.39 g, 0.04 mol) was added slowly dropwise under N<sub>2</sub> to a stirred LiAlH<sub>4</sub> suspension (3.04 g, 0.08 mol) in ether (230 mL). The reaction was stirred for 20 h and then was quenched using the usual N:N:3N procedure (3 mL of H<sub>2</sub>O; 3 mL of 15% NaOH; 9 mL of H<sub>2</sub>O). (The reaction mixture was cooled in an ice bath during addition of the initial 1.5 mL of H<sub>2</sub>O. The cooling was then removed.) The resultant white solid was filtered and then was extracted with boiling water (2 × 200 mL). The combined ether fractions were dried over Na<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>CO<sub>3</sub>, were filtered, and were concentrated under reduced pressure. The menthol byproduct was removed by heating at 100 °C under high vacuum (0.25 mm) for 5 h. The remaining oily residue was then distilled to yield pure (1*S*,2*S*)-*trans*-1,2-bis(hydroxymethyl)cyclopentane (13), as a viscous colorless oil: 4.58 g, 88%. bp<sub>2.4</sub>: 124–127 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.26 (m, 2H), 1.58 (m, 2H), 1.82 (m, 4H), 3.35 (m, 2H), 3.74 (dd, *J* = 10.2 Hz, *J* = 3.2 Hz, 2H), 3.97 (s, 2H).

(1*S*,2*S*)-*trans*-1,2-Bis(aminomethyl)cyclopentane (16). Methanesulfonyl chloride (5.99 mL, 0.077 mol) in dry CH<sub>2</sub>Cl<sub>2</sub> (8 mL) was added slowly dropwise under N<sub>2</sub> to a stirred dry CH<sub>2</sub>Cl<sub>2</sub> mixture of diol 13 (4.58

g, 0.035 mol) and Et<sub>3</sub>N (14.71 mL, 0.105 mol) maintained at –35 °C under N<sub>2</sub>. The pale yellow heterogeneous reaction mixture was stirred at –35 °C for 30 min and at 0 °C for 30 min and then was quenched by pouring the mixture into ice water (150 mL). The CH<sub>2</sub>Cl<sub>2</sub> layer was washed successively with ice cold solutions of 10% HCl (2 × 100 mL), saturated aqueous brine (1 × 150 mL), saturated aqueous NaHCO<sub>3</sub> (2 × 100 mL), and H<sub>2</sub>O (1 × 100 mL) and then was dried over MgSO<sub>4</sub>. Upon filtration and concentration under reduced pressure, dimethylate 14 was obtained as a very pale yellow oil in essentially quantitative yield.<sup>13</sup> The dimethylate was combined with NaN<sub>3</sub> (9.14 g, 0.141 mol) in diethylene glycol (100 mL). The suspension was heated at 100 °C for 3 h and then was poured into H<sub>2</sub>O (500 mL). The diazide intermediate 15, was extracted with ether (2 × 300 mL). (*Caution!*) The combined ether fractions were washed with water (3 × 400 mL), shaken with saturated aqueous brine (400 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the ether solution was concentrated to a volume of ~40 mL and was transferred to an addition funnel with additional dry ether (~80 mL total volume). This diazide solution was added slowly dropwise to a dry ether suspension (150 mL) of LiAlH<sub>4</sub> (4 g, 0.105 mol) under N<sub>2</sub> such that a steady reflux was maintained. Once all of the diazide had been added, a gray solid aggregated and deposited on the walls of the reaction vessel. When gas evolution ceased, the reaction was refluxed for 1.5 h using a 50 °C water bath. The reaction was cooled in an ice bath and then quenched by the usual N:N:3N procedure (4 mL of H<sub>2</sub>O; 4 mL of 15% NaOH; 12 mL of H<sub>2</sub>O). After the initial vigorous reaction the ice bath was removed and the reaction was allowed to reflux. The heterogeneous reaction mixture was stirred for 2–3 h until all of the gray solid disappeared and only a fluffy white solid remained suspended in solution. The ether solution was filtered and the white solid was extracted with additional refluxing ether (2 × 100 mL). The combined ether fractions were concentrated *in vacuo*. The resultant chiral diamine, 16, was purified by distillation to yield a viscous colorless oil: yield 3.90 g, 87% (based on 13). bp<sub>2.4</sub>: 74–76 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.15 (br s, 4H), 1.30 (m, 2H), 1.56 (m, 4H), 1.81 (m, 2H), 2.55 (m, 2H), 2.72 (m, 2H). Anal. Calcd for C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>: C, 65.57; H, 12.58; N, 21.85. Found: C, 65.77; H, 12.38; N, 22.14.

**Monometallic Complexes.** All [M(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> complexes were prepared according to the general procedure described below for [Mn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. Any variations from this method are indicated for the respective complexes. Standard Schlenk techniques were followed only in the preparation of Mn(II) and Co(II) complexes to prevent slow aerial oxidation in solution. All complexes including those containing Mn(II) and Co(II) are air-stable as solids. Yields are reported after recrystallization and are based upon [Zn(pyral)] unless otherwise indicated.

[Mn(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. The pyral ligand (8) was liberated from [Zn(pyral)] (0.5 g, 0.83 mmol) by passing H<sub>2</sub>S (g) through a CH<sub>2</sub>Cl<sub>2</sub>/EtOH solution of the complex as previously described.<sup>8</sup> To the pyral ligand dissolved in EtOH (15 mL) under Ar were added sequentially Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.2 g, 0.83 mmol) and glacial acetic acid (96  $\mu$ L, 1.66 mmol). The resultant orange solution was stirred and heated to 70 °C, followed by slow dropwise addition of diamine 16 (0.106 g, 0.83 mmol) in EtOH (5 mL). After 1 h, the reaction mixture was filtered to remove any insoluble solid, and the product was precipitated with NH<sub>4</sub>PF<sub>6</sub> (0.68 g, 4.15 mmol) dissolved in EtOH (10 mL). The resultant mixture was refluxed for 15 min and then was cooled to room temperature with stirring. An air-stable orange solid was collected by filtration and was washed with EtOH, ether, and pentane. The solid was recrystallized twice from CH<sub>3</sub>CN/EtOH and washed as above to give red-orange blocks: yield 0.49 g, 60%. Crystals suitable for X-ray structure determination were grown by vapor diffusion of ether into a CH<sub>3</sub>CN solution of the complex.  $\Delta_M = 289 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Mn: C, 48.01; H, 4.75; N, 8.61; Mn, 5.63. Found: C, 48.23; H, 4.62; N, 8.53; Mn, 5.64.

[Co(*S,S*-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. The Co(II) complex was prepared under Ar by the standard procedure. The product was recrystallized by dissolution in a minimal amount of CH<sub>3</sub>CN followed by an equal amount of EtOH. The solution was warmed to ~50 °C and then was filtered to remove any insoluble powdery solid. The solution was allowed to cool to room temperature, and additional EtOH was added until crystallization commenced. Crystals were collected and washed as described above. Upon a second recrystallization, brown needles were obtained: yield 43%.  $\Delta_M = 277 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Co: C, 47.81; H, 4.73; N, 8.58; Co, 6.02. Found: C, 48.07; H, 4.67; N, 8.71; Co, 6.65.

**[Ni(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.** The Ni(II) complex was obtained as an ochre microcrystalline solid after preparation and recrystallization by the standard procedures: yield 70%.  $\Delta_M = 269 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Ni: C, 47.82; H, 4.73; N, 8.58; Ni, 5.99. Found: C, 47.52; H, 4.70; N, 8.28; Ni, 6.22.

**[Cu(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.** The Cu(II) complex was purified and recrystallized as follows. The fluffy ochre reaction product obtained after cyclization was redissolved in twice the minimal amount of CH<sub>3</sub>CN, and a large volume of EtOH was added until an orange-brown oily material coated the walls of the flask. The mixture was allowed to stand for at least 2 h, and then the solution was filtered and concentrated. This procedure was repeated up to five times until no orange-brown residue nor orange-yellow solid deposited prior to crystallization of the product. (The CH<sub>3</sub>CN/EtOH recrystallization solution changed color from orange-brown to yellow-green as a result of these repeated filtrations.) The yellow-green filtrate was then concentrated. The resultant residue was dissolved in a minimal amount of CH<sub>3</sub>CN and excess EtOH was added until the solution became cloudy. This solution was allowed to stand for 3–5 days, after which time olive green crystals coprecipitated with a golden yellow powder. The filtrate was separated from the green crystals, and any remaining yellow powder was decanted off with EtOH washes. The green crystals were recrystallized twice more to yield greenish-gold needles: yield 38%.  $\Delta_M = 279 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Cu: C, 47.59; H, 4.71; N, 8.54; Cu, 6.46. Found: C, 47.99; H, 4.74; N, 8.38; Cu, 6.99.

**[Zn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.** The Zn(II) complex was prepared by the standard method with the following exception. Glacial acetic acid (2 equiv) and the diamine ligand **16** (1 equiv) were added to an EtOH suspension of the [Zn(pyral)] complex. After recrystallization from CH<sub>3</sub>CN/EtOH, yellow needles were obtained: yield 81%. Crystals suitable for X-ray structure determination were grown by vapor diffusion of EtOH into a CH<sub>3</sub>CN/EtOH solution of the complex.  $\Delta_M = 278 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Zn: C, 47.50; H, 4.70; N, 8.52; Zn, 6.63. Found: C, 47.45; H, 4.67; N, 8.41; Zn, 6.84. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  1.44 (m, 2 H), 1.70 (m, 2 H), 2.07 (m, 2 H), 2.19 (s, 6 H), 2.89 (m, 4 H), 3.65 (d,  $J = 12.6$  Hz, 2 H), 3.79 (m, 4 H), 4.03 (m, 6 H), 7.03 (s, 2 H), 7.09 (d,  $J = 7.9$  Hz, 2 H), 7.29 (m, 4 H), 7.77 (m, 2 H), 8.16 (d,  $J = 13.4$  Hz, 2 H), 8.64 (d,  $J = 5.0$  Hz, 2 H), 14.45 (br s, 2 H).

**[Co(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>·CH<sub>3</sub>CN.** To a stirred deaerated CH<sub>3</sub>CN solution (~2 mL) of [Co(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (118 mg, 0.120 mmol) under Ar was added [Cp<sub>2</sub>Fe](PF<sub>6</sub>) (43.8 mg, 0.132 mmol) in deaerated CH<sub>3</sub>CN (~2 mL). The dark solution was stirred under Ar for 15 min and then was concentrated *in vacuo*. The maroon residue was extracted with ether (~5 × 5 mL) and then was recrystallized from CH<sub>3</sub>CN/EtOH. The product was collected and washed with EtOH, ether, and pentane. Maroon needles were obtained: yield 0.082 g, 98% (based on [Co(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>).  $\Delta_M = 399 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>41</sub>H<sub>49</sub>N<sub>7</sub>O<sub>2</sub>P<sub>3</sub>F<sub>18</sub>Co: C, 42.24; H, 4.24; N, 8.41; Co, 5.06. Found: C, 41.77; H, 4.22; N, 8.28; Co, 5.26. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  1.43 (m, 2 H), 1.70 (m, 2 H), 1.88 (m, 2 H), 2.18 (m, 2 H), 2.26 (s, 6 H), 3.31 (br s, 4 H), 3.57 (m, 6 H), 3.86 (d,  $J = 13.8$  Hz, 2 H), 4.50, 4.62 (system AB,  $J_{AB} = 19.0$  Hz, 4 H), 7.27 (s, 2 H), 7.33 (s, 2 H), 7.41 (d,  $J = 8.0$  Hz, 2 H), 7.49 (t,  $J = 6.5$  Hz, 2 H), 8.00 (t,  $J = 7.7$  Hz, 2 H), 8.20 (d,  $J = 6.0$  Hz, 2 H), 8.38 (d,  $J = 14.9$  Hz, 2 H), 11.91 (br s, 2 H).

**Bimetallic Complexes.** The air-sensitive dimanganese(II) and Co(II)–Cu(II) complexes were prepared under Ar using standard Schlenk techniques. Reported yields are based on the [M(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>n+</sup> starting material unless otherwise indicated. All complexes are air stable as solids.

**I. Homobimetallic Complexes.** **[Mn(S,S-cypim)MnCl](PF<sub>6</sub>)<sub>2</sub>.** [Mn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (0.27 g, 0.28 mmol), Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.068 g, 0.28 mmol), and LiCl (0.024 g, 0.56 mmol) were dissolved under Ar in a deaerated CH<sub>3</sub>CN/EtOH mixture (5 mL/10 mL) to give an orange solution. Et<sub>3</sub>N (0.078 mL, 0.56 mmol) was added, and the orange reaction solution turned yellow. The product was precipitated by partial concentration of the reaction solution. The resultant yellow solid was recrystallized from CH<sub>3</sub>CN/EtOH to give golden yellow needles: yield 0.13 g, 50%.  $\Delta_M = 118 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>ClPF<sub>6</sub>Mn<sub>2</sub>: C, 50.97; H, 4.83; N, 9.14; Cl, 3.86; Mn, 11.95. Found: C, 50.64; H, 4.78; N, 9.01; Cl, 3.99; Mn, 12.57.

**[Mn(S,S-cypim)Mn(Cl)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·H<sub>2</sub>O.** [Mn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (0.14 g, 0.15 mmol), Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.035 g, 0.15 mmol), and LiCl (0.012 g, 0.30 mmol) were dissolved in CH<sub>3</sub>CN/EtOH (2 mL/10 mL) under Ar. Then Et<sub>3</sub>N (41  $\mu$ L, 0.30 mmol) was added. The yellow solution was stirred under Ar for ~15 min and then was uncapped and exposed

to air. Over time, the solution turned emerald green, and upon slow evaporation, grass green needles precipitated. After recrystallization from CH<sub>3</sub>CN/EtOH, the product was obtained as grass green plates: yield 0.11 g, 73%.  $\Delta_M = 124 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>46</sub>N<sub>6</sub>O<sub>3</sub>Cl<sub>2</sub>PF<sub>6</sub>Mn<sub>2</sub>: C, 48.16; H, 4.97; N, 8.64; Cl, 7.29; Mn, 11.30. Found: C, 48.29; H, 4.82; N, 8.29; Cl, 6.87; Mn, 10.63.

**[Ni(S,S-cypim)NiCl](PF<sub>6</sub>)<sub>2</sub>·H<sub>2</sub>O.** [Ni(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (0.15 g, 0.15 mmol) was dissolved in CH<sub>3</sub>CN (5 mL), and Et<sub>3</sub>N (42  $\mu$ L, 0.29 mmol) was added. Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.037 g, 0.015 mmol) in EtOH (15 mL) and LiCl (0.006 g, 0.045 mmol) in EtOH (5 mL) were added sequentially. The resultant golden solution was concentrated *in vacuo* and then was recrystallized from CH<sub>3</sub>CN/EtOH. An ochre microcrystalline solid was obtained: yield 0.11 g, 80%.  $\Delta_M = 152 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>46</sub>N<sub>6</sub>O<sub>3</sub>ClPF<sub>6</sub>Ni<sub>2</sub>: C, 49.59; H, 4.91; N, 8.90; Cl, 3.75; Ni, 12.43. Found: C, 49.46; H, 4.97; N, 8.97; Cl, 3.30; Ni, 12.17.

**II. Heterobimetallic Complexes.** **[Cu(S,S-cypim)ZnCl](PF<sub>6</sub>)<sub>2</sub>.** [Cu(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (0.10 g, 0.11 mmol) was dissolved in CH<sub>3</sub>CN (2 mL), and then Et<sub>3</sub>N (29  $\mu$ L, 0.21 mmol) was added. To the stirred dark green solution was added Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.023 g, 0.11 mmol) in EtOH (5 mL), followed by LiCl (0.013 g, 0.32 mmol) in EtOH (5 mL). The resultant yellow-green solution was stirred for 15 min and then was concentrated *in vacuo* at 30 °C to ~2 mL of total volume. A lime-green solid was collected and was washed with EtOH (2 × 2 mL), Et<sub>2</sub>O (3 × 2 mL), and pentane (3 × 2 mL). A second crop was obtained by the addition of Et<sub>2</sub>O (~6 mL) to the filtrate fraction. A fluffy lime-green solid was collected and washed with Et<sub>2</sub>O (3 × 2 mL) and pentane (3 × 2 mL). Both fractions were recrystallized from CH<sub>3</sub>CN/EtOH to give green blocks: yield 0.085 g. Combined yield: 86%.  $\Delta_M = 127 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>46</sub>N<sub>6</sub>O<sub>3</sub>ClPF<sub>6</sub>CuZn: C, 49.93; H, 4.73; N, 8.96; Cl, 3.78; Cu, 6.77; Zn, 6.97. Found: C, 49.56; H, 4.82; N, 8.88; Cl, 2.13; Cu, 8.23; Zn, 7.36.

**A. [Co<sup>III</sup>(S,S-cypim)M<sup>III</sup>] Complexes.** All [Co<sup>III</sup>(S,S-cypim)M<sup>III</sup>] complexes were prepared by the general procedure described for [Co(S,S-cypim)CoCl](PF<sub>6</sub>)<sub>2</sub>. Variations from this method are indicated for the respective metal complexes.

**[Co(S,S-cypim)CoCl](PF<sub>6</sub>)<sub>2</sub>.** To a CH<sub>3</sub>CN solution (5 mL) of [Co(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>·CH<sub>3</sub>CN (178 mg, 0.153 mmol) was added Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (40 mg, 0.161 mmol) in EtOH (7 mL) followed by LiCl (19 mg, 0.458 mmol) in EtOH (7 mL). The reaction was stirred under N<sub>2</sub> for 15 min and then was concentrated *in vacuo*. The dark red-brown residue was dissolved in CH<sub>3</sub>CN/EtOAc (1 mL/1 mL), was filtered through Celite, and then was reconcentrated. The resultant brown solid was recrystallized from CH<sub>3</sub>CN/EtOH (~0.5 mL/25 mL) to give dark maroon rectangular blocks: yield 0.097 g, 59%.  $\Delta_M = 245 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>ClP<sub>2</sub>F<sub>12</sub>Co<sub>2</sub>: C, 43.69; H, 4.14; N, 7.84; Cl, 3.31; Co, 10.99. Found: C, 43.51; H, 4.02; N, 7.59; Cl, 3.40; Co, 10.97.

**[Co(S,S-cypim)MnCl](PF<sub>6</sub>)<sub>2</sub>.** This was obtained as dark maroon rectangular blocks: yield 93%.  $\Delta_M = 257 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>ClP<sub>2</sub>F<sub>12</sub>CoMn: C, 43.86; H, 4.15; N, 7.87; Cl, 3.32; Co, 5.52; Mn, 5.14. Found: C, 43.77; H, 4.45; N, 7.95; Cl, 3.63; Co, 5.22; Mn, 4.79.

**[Co(S,S-cypim)NiCl](PF<sub>6</sub>)<sub>2</sub>.** This was obtained as red-brown plates: yield 59%.  $\Delta_M = 260 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>ClP<sub>2</sub>F<sub>12</sub>CoNi: C, 43.70; H, 4.14; N, 7.84; Cl, 3.31; Co, 5.50; Ni, 5.48. Found: C, 43.43; H, 4.08; N, 7.69; Cl, 3.49; Co, 5.23; Ni, 5.21.

**[Co(S,S-cypim)Cu](PF<sub>6</sub>)<sub>3</sub>.** [Co(S,S-cypim)Cu](PF<sub>6</sub>)<sub>3</sub> was prepared by the method described for [Co(S,S-cypim)CoCl](PF<sub>6</sub>)<sub>2</sub>, but without the addition of LiCl. For recrystallization, the compound was dissolved in a minimal amount of CH<sub>3</sub>CN and then was precipitated with EtOH containing additional NH<sub>4</sub>PF<sub>6</sub> (3 equiv). Dark maroon needles were obtained: yield 98%. Crystals suitable for X-ray structure determination were grown by vapor diffusion of EtOH into a CH<sub>3</sub>CN/EtOH solution of the complex.  $\Delta_M = 378 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>P<sub>3</sub>F<sub>18</sub>CoCu: C, 39.49; H, 3.74; N, 7.08; Co, 5.36; Cu, 4.97. Found: C, 39.58; H, 3.94; N, 7.43; Co, 5.47; Cu, 4.97.

**[Co(S,S-cypim)ZnCl](PF<sub>6</sub>)<sub>2</sub>.** Maroon plates were obtained: yield 64%.  $\Delta_M = 260 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>ClP<sub>2</sub>F<sub>12</sub>CoZn: C, 43.43; H, 4.11; N, 7.79; Cl, 3.29; Co, 5.46; Zn, 6.06. Found: C, 43.00; H, 3.98; N, 7.79; Cl, 2.83; Co, 5.14; Zn, 5.82. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  1.39 (m, 2 H), 1.65 (m, 2 H), 1.82 (m, 2 H), 2.23 (s, 3 H), 2.30 (s, 3 H), 3.01 (m, 1 H), 3.17 (m, 1 H), 3.38 (m, 2 H), 3.97 (d,  $J = 14.3$  Hz, 1 H), 4.24 (m, 7 H), 4.81 (m, 2 H), 5.19 (m, 2 H), 7.23 (d,  $J = 1.6$

H<sub>z</sub>, 1 H), 7.31 (d,  $J = 1.6$  Hz, 1 H), 7.40 (m, 3 H), 7.54 (m, 1 H), 7.73 (m, 2 H), 7.97 (m, 1 H), 8.25 (m, 1 H), 8.62 (d,  $J = 3.4$  Hz, 1 H), 9.34 (d,  $J = 6.1$  Hz, 1 H). (A resonance at  $\sim 2$  ppm which represents 2H is obscured by the solvent resonance.)

**[Co(S,S-cypim)Zn](OTf)(PF<sub>6</sub>)<sub>2</sub>.** [Co(S,S-cypim)ZnCl](PF<sub>6</sub>)<sub>2</sub> (10 mg, 9.27  $\mu$ mol) was weighed into an NMR tube and was dissolved in CD<sub>3</sub>COCD<sub>3</sub> (0.5 mL). Solid AgOTf (4.6 mg, 18.5  $\mu$ mol) was added. The red solution became cloudy immediately upon addition and over time a solid precipitated. After 30 min a spectrum was recorded. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  1.40 (m, 2 H), 1.64 (m, 2 H), 1.85 (m, 2 H), 2.28 (s, 6 H), 2.48 (m, 2 H), 3.44 (m, 2 H), 3.78 (s, 4 H), 4.20 (m, 6 H), 5.07 (s, 4 H), 7.38 (d,  $J = 1.7$  Hz, 2 H), 7.44 (d,  $J = 1.8$  Hz, 2 H), 7.59 (d,  $J = 7.9$  Hz, 2 H), 7.65 (m, 2 H), 8.13 (m, 2 H), 8.49 (s, 2 H), 8.64 (d,  $J = 6.0$  Hz, 2 H).

**B. [M(S,S-cypim)Cu](PF<sub>6</sub>)<sub>2</sub> Complexes.** All [M(S,S-cypim)Cu](PF<sub>6</sub>)<sub>2</sub> complexes were prepared by the general method described for [Mn(S,S-cypim)Cu](PF<sub>6</sub>)<sub>2</sub> from the appropriate starting material. Variations from this general method are indicated for the respective complexes.

**[Mn(EtOH)(S,S-cypim)Cu](PF<sub>6</sub>)<sub>2</sub>·[Mn(CH<sub>3</sub>CO<sub>2</sub>)(S,S-cypim)Cu](PF<sub>6</sub>)<sub>2</sub>.** [Mn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (0.258 g, 0.265 mmol) was dissolved in CH<sub>3</sub>CN (5 mL), and Et<sub>3</sub>N (74  $\mu$ L, 0.530 mmol) was added. Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.053 g, 0.265 mmol) was dissolved in 1,4-dioxane (10 mL) and then was added to the above solution. The green solution was stirred for 10 min and then was concentrated at 30 °C *in vacuo*. The residue was redissolved in CH<sub>3</sub>CN (5 mL) and then was reconcentrated. The dark green residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 mL); then the solution was filtered through Celite. NH<sub>4</sub>PF<sub>6</sub> (0.170 g, 1.06 mmol) dissolved in EtOH (6 mL) was added. The dark green solution was left loosely capped and was allowed to evaporate for  $\sim 1$  day. Large green-black crystals suitable for X-ray structure determination were collected. Since these crystals turned opaque over time after isolation, they were dried to constant weight under high vacuum at 60 °C for 8 h prior to characterization. An olive solid was obtained: yield 0.20 g, 74%.  $\Delta_M = 246 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>82</sub>H<sub>99</sub>N<sub>12</sub>O<sub>7</sub>P<sub>2</sub>F<sub>18</sub>Mn<sub>2</sub>Cu<sub>2</sub>: C, 48.41; H, 4.81; N, 8.26; Mn, 5.40; Cu, 6.25. Found: C, 47.89; H, 4.71; N, 8.20; Mn, 5.42; Cu, 6.89.

**[Co(S,S-cypim)Cu](PF<sub>6</sub>)<sub>2</sub>.** The Co(II)–Cu(II) complex was prepared as above, but all solvents were deaerated and standard Schlenk techniques were utilized. The initial reaction solution was concentrated under high vacuum (0.25 mm). The resultant brown residue was dissolved in a minimal amount of CH<sub>3</sub>CN ( $\sim 1$  mL), and then EtOH ( $\sim 20$  mL) was added to precipitate a brown solid. The brown solid was collected, was washed with EtOH, and was then recrystallized from CH<sub>3</sub>CN/EtOH to give an air-stable brown powder: yield 70%.  $\Delta_M = 259 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>CoCu: C, 44.99; H, 4.26; N, 8.07; Co, 5.66; Cu, 6.10. Found: C, 45.11; H, 4.01; N, 7.82; Co, 5.97; Cu, 5.82.

**[Ni(S,S-cypim)Cu](PF<sub>6</sub>)<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub>.** The Ni(II)–Cu(II) complex was prepared by the general method described above for Mn(II)–Cu(II) with the following changes. For recrystallization, the CH<sub>2</sub>Cl<sub>2</sub>/EtOH solution was placed in a small pear-shaped flask, which was then put in a jar containing EtOH ( $\sim 25$  mL). This jar was capped to allow for slow evaporation of the CH<sub>2</sub>Cl<sub>2</sub>. After  $\sim 24$  h orange-brown needles were collected and were washed and dried as above: yield 64%.  $\Delta_M = 264 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>ClNiCu: C, 43.79; H, 4.19; N, 7.76; Ni, 5.42; Cu, 5.86. Found: C, 43.92; H, 4.28; N, 7.86; Ni, 5.86; Cu, 6.38.

**[Cu(S,S-cypim)Cu](PF<sub>6</sub>)<sub>2</sub>.** The dicopper(II) complex was prepared according to the standard method described for Mn(II)–Cu(II) but was recrystallized from CH<sub>3</sub>CN/EtOH rather than from CH<sub>2</sub>Cl<sub>2</sub>/EtOH. Dark green crystals were obtained, which were suitable for X-ray structure determination. Crystals of this complex turned opaque and slightly brown after drying under high vacuum (0.25 mm) prior to characterization. Yield: 57%.  $\Delta_M = 266 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Cu<sub>2</sub>: C, 44.79; H, 4.24; N, 8.04; Cu, 12.15. Found: C, 44.99; H, 4.27; N, 7.86; Cu, 12.37.

**[Zn(S,S-cypim)Cu](PF<sub>6</sub>)<sub>2</sub>.** The Zn(II)–Cu(II) complex was prepared according to the standard procedure described for the Mn(II)–Cu(II) complex and was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/EtOH by the slow-evaporation method outlined for the Ni(II)–Cu(II) complex. The dark green crystals so obtained were very sensitive to solvent effluorescence. After these crystals were dried under high vacuum (0.25 mm) for 8 h, a pale brown-green solid was obtained: yield 65%.  $\Delta_M = 268 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ . Anal. Calcd for C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>ZnCu: C, 44.71; H, 4.23; N, 8.02; Zn, 6.24; Cu, 6.06. Found: C, 44.67; H, 4.24; N, 8.32; Zn, 6.04; Cu, 6.91.

**X-ray Structure Determinations.** Crystals of the monometallic [Mn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> and [Zn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> and the bimetallic [Co(S,S-cypim)Cu(CH<sub>3</sub>CN)](PF<sub>6</sub>)<sub>2</sub>·EtOH, [Cu(S,S-cypim)Cu(CH<sub>3</sub>CN)](PF<sub>6</sub>)<sub>2</sub>·EtOH, and [Mn(EtOH)(S,S-cypim)Cu](PF<sub>6</sub>)<sub>1.5</sub>·CH<sub>2</sub>Cl<sub>2</sub> compounds were analyzed by X-ray diffraction. Crystallographic data for [Mn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, [Zn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, [Co(S,S-cypim)Cu]<sup>3+</sup>, and [Cu(S,S-cypim)Cu]<sup>2+</sup> are collected in Table 1, and data for [Mn(EtOH)(S,S-cypim)Cu]<sup>2+</sup> has been submitted as supplementary material. All specimens were mounted on glass fibers with epoxy. Photographic analysis revealed 2/*m* Laue symmetry for [Mn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> and [Co(S,S-cypim)Cu]<sup>3+</sup>,  $\bar{3}$  or  $\bar{3}/m$  symmetry for [Zn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, and  $\bar{1}$  symmetry for [Cu(S,S-cypim)Cu]<sup>2+</sup> and [Mn(EtOH)(S,S-cypim)Cu]<sup>2+</sup>. For both compounds with 2/*m* Laue symmetry, systematic absences in the diffraction data were consistent with either of the space groups P<sub>2</sub><sub>1</sub> or P<sub>2</sub><sub>1</sub>/*m* and for [Zn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> systematic absences indicated choices of P<sub>3</sub><sub>1</sub>, P<sub>3</sub><sub>1</sub>2, or P<sub>3</sub><sub>1</sub>2. The noncentrosymmetric space groups P<sub>2</sub><sub>1</sub> for [Mn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> and [Co(S,S-cypim)Cu]<sup>3+</sup> and P<sub>3</sub><sub>1</sub> for [Zn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> were initially chosen based on the statistical distribution of the normalized structure factors and the appropriateness of these choices for the expected chiral complexes. However, in both of the triclinic cases, the *E*-value statistics indicated the centrosymmetric choice of the space group, P $\bar{1}$ . Racemic mixtures were assumed, and the triclinic compounds were solved in the centrosymmetric space group. However, due to the presumed chirality of these complexes, refinement was also carried out in the noncentrosymmetric group P<sub>1</sub>. The second, presumably independent, molecule (as well as all counter ions and solvents of crystallization) could be located in the noncentrosymmetric group, but the positions and chirality at the six-coordinate site indicated that an inversion point symmetry operation existed in the unit cell; however, the expected *S,S* chirality of the cyclopentane moiety was observed in the two "independent" molecules. The chemical sensibility was lost; that is, internal consistency of chemically similar bond lengths and angles was poor in P<sub>1</sub> for both structures, but the discrepancy between P<sub>1</sub> and P $\bar{1}$  was greatest in the [Cu(S,S-cypim)Cu]<sup>2+</sup> structure. Because the crystal used for the [Cu(S,S-cypim)Cu]<sup>2+</sup> structure was fairly large, an empirical absorption correction was successfully applied. All other crystals were small with small linear absorption coefficients, and therefore no absorption corrections were applied in the remaining structures.

All structures were solved by direct methods, which located the metal atom(s), and completed by difference Fourier synthesis. For [Mn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, all non-hydrogen atoms were refined anisotropically and the hydrogen atoms were treated as idealized, updated isotropic contributions. The absolute configuration was established by a Rogers test where  $\eta$  refined to a value of 1.26(16). For [Zn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, the Zn atom and all nitrogen and oxygen atoms of the *S,S*-cypim molecule were refined anisotropically; all other non-hydrogen atoms were refined isotropically; the hydrogen atoms were treated as idealized, updated isotropic contributions, and the (PF<sub>6</sub>)<sup>−</sup> counter ions were refined as fixed octahedra, with  $d(\text{P-F}) = 1.586(3)$  Å. A Rogers test indicated that the absolute configuration was correct:  $\eta = 1.00(6)$ . For [Co(S,S-cypim)Cu]<sup>3+</sup>, all non-hydrogen atoms were refined anisotropically with the exception of the EtOH solvent molecule oxygen and carbon atoms which were refined isotropically, hydrogen atoms were treated as idealized, updated isotropic contributions, and the (PF<sub>6</sub>)<sup>−</sup> counterions were refined as fixed octahedra, with  $d(\text{P-F}) = 1.522(3)$  Å. The absolute configuration was checked by a Rogers test,  $\eta = 1.02(8)$ . For [Cu(S,S-cypim)Cu]<sup>2+</sup>, with the exception of the EtOH solvent molecule oxygen and carbon atoms and four disordered atoms (C(9), C(10), C(12), and C(13) plus their mates C(9'), C(10'), C(12'), and C(13')), all at one-half occupancies) of the cyclopentane ring moiety which were refined isotropically, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized, updated isotropic contributions and the (PF<sub>6</sub>)<sup>−</sup> counterions were refined as fixed octahedra, with  $d(\text{P-F}) = 1.552(2)$  Å. Computations were made with the SHELXTL PLUS (4.27) program library (G. Sheldrick, Siemens, Madison, WI). Selected bond distances and angles for [Mn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, [Zn(S,S-cypim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, [Co(S,S-cypim)Cu]<sup>3+</sup> and [Cu(S,S-cypim)Cu]<sup>2+</sup> are given in Tables 2–5, respectively.

For the three compounds refined in noncentrosymmetric space groups, the chemically sensible results indicate that the initial space group choices were appropriate. For [Cu(S,S-cypim)Cu]<sup>2+</sup>, the criterion of chemical reasonableness indicates that P $\bar{1}$  is the more appropriate choice of space group. Because of the similarities between the [Cu(S,S-cypim)Cu]<sup>2+</sup> and the [Mn(EtOH)(S,S-cypim)Cu]<sup>2+</sup> structures, we suggest that P $\bar{1}$  is the more appropriate choice for the latter structure, too. One of the

(PF<sub>6</sub>)<sup>-</sup> counterions in the [Mn(EtOH)(S,S-cypim)Cu]<sup>2+</sup> structure resides on a center of inversion in *P* $\bar{1}$ , giving a total count of three negative charges in the unit cell (in *P*1, three independent (PF<sub>6</sub>)<sup>-</sup> ions are found). These results may be interpreted in terms of two independent molecules, one with EtOH coordinated to the Mn and the second with a coordinated acetate or EtO<sup>-</sup> group to account for the fourth negative charge. A second explanation involving mixed valence of the metals was considered less likely, on the basis of spectroscopic evidence. Since the refinement statistics<sup>25</sup> for the [Mn(EtOH)(S,S-cypim)Cu]<sup>2+</sup> structure were less

(25) Crystal data for [Mn(C<sub>2</sub>H<sub>5</sub>OH)(C<sub>39</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>)Cu](PF<sub>6</sub>)<sub>1.5</sub>·CH<sub>2</sub>Cl<sub>2</sub>: fw 1089.8, triclinic *P* $\bar{1}$  *a* = 12.374(2) Å, *b* = 13.453(3) Å, *c* = 16.682(3) Å, *a* = 83.64(3)°, *β* = 81.33(3)°, *γ* = 64.66(3)°, *V* = 2078.6(1) Å<sup>3</sup>, *Z* = 2, *R*(*F*) = 11.49%, *R*<sub>w</sub>(*F*) = 13.93%, GOF = 1.60.

satisfactory, it was decided to submit material for this compound as supplementary material only and to make only a few observations based on the gross structure.

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**Supplementary Material Available:** Detailed crystallographic data for all structures including tables of atomic coordinates, bond lengths, bond angles, anisotropic displacements, and (except for the Mn/Cu compound) hydrogen atom parameters and tables of crystal data and a structure diagram for [Mn(EtOH)(S,S-cypim)Cu](PF<sub>6</sub>)<sub>1.5</sub>·CH<sub>2</sub>Cl<sub>2</sub> (49 pages). Ordering information is given on any current masthead page.