

## Bimetallic Reactivity. Preparation and Characterization of Symmetrical Bimetallic Complexes of a Binucleating Macrocyclic Ligand, Cytim, Containing 6- and 4-Coordinate Sites

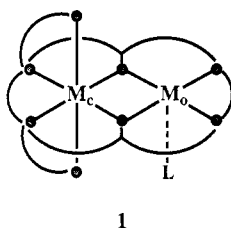
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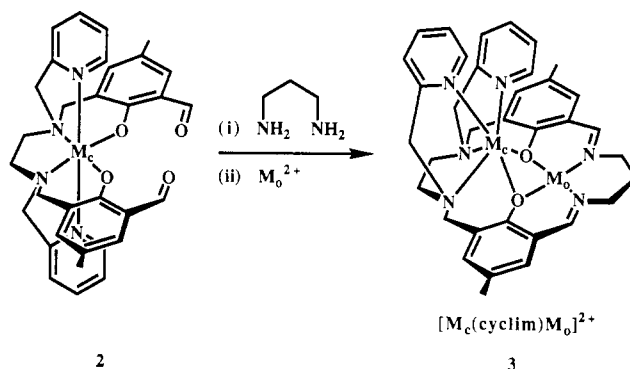
A binucleating macrocyclic ligand, cytim, incorporating 6- and 4-coordinate sites has been prepared. The two metals are bridged by phenolic oxygen ligands, and the 4-coordinate site is completed by a trimethylenediamine link. The 6-coordinate site carries two 2-methylenepyridyl arms and is completed by a trimethylenediamine chelate. This ligand was constructed in order to determine whether the trimethylenediamine chelate in the 6-coordinate site would produce symmetrical complexes where the pyridine ligands lie trans above and below the mean molecular plane. Previous work had shown that the analogous ligand with an ethylenediamine link in this site gave unsymmetrical bimetallic complexes where the pyridines were cis on one side of the mean macrocyclic plane. Synthetic methods for preparing the monometallic complexes,  $[M(\text{cytim})(\text{H}^+)_2]^{2+}$  ( $M = \text{Zn(II)}, \text{Co(II)}$ ), are described. These complexes provide mild methods for introducing a second metal into the 4-coordinate site which is occupied by two protons in the monometallic complexes. The  $^1\text{H}$  NMR spectra of the diamagnetic complexes and X-ray crystal structures of  $[\text{Zn}(\text{cytim})(\text{H}^+)_2](\text{PF}_6)_2$  and of  $[\text{Zn}(\text{cytim})\text{Zn}(\text{OAc})]\text{PF}_6$  demonstrate that the expected trans pyridine symmetric structures are formed. That macrocyclic formation is necessary for obtaining symmetrical structures was demonstrated by the fact that complexes of analogous non-macrocyclic ligands give all possible topological octahedral isomers. Magnetic moments, electronic absorption spectra, and redox couples are reported. Perhaps the most significant observation was that Co(III) in the 6-coordinate site of cytim is unstable. This is attributed to the inability of cytim to adjust to the Co(III) bond lengths.

We recently introduced new binucleating ligands of type 1.<sup>1</sup> Such ligands have two compartments: a closed-site where the metal ( $M_c$ ) is fully coordinated by six ligands and an open-site



where the metal ( $M_o$ ) can be either 4- or 5-coordinate. This construction satisfies a number of objectives, the most notable of which is the expectation that with suitable metal combinations, oxidative addition by substrates at the open-site metal could lead to the oxidative participation of both metals leading to multi-electron reduction of the substrate. For example, it is conceivable that with an Fe(II) ion in the closed-site and a Co(II) in the open-site, dioxygen could bind to the cobalt to form an Fe(III)–Co(III)–peroxy complex as a result of 2-electron reduction, one from each metal.

The first ligand which we described is cyclim, depicted in 3, which was prepared by the metal-template cyclization of the dialdehyde complex 2. Whereas the complexes, 2, possess  $C_2$



symmetric structures with trans disposed pyridyl ligands, the bimetallic complexes, 3, adopt unsymmetrical structures where the pyridyl ligands are cis disposed and lie on one side of the mean macrocyclic plane.<sup>1a</sup> Although the stereochemistry of the bimetallic complexes of 3 may depend on a variety of stereochemical factors, it is probable that the presence of the small chelate bite-angle of the ethylenediamine unit of the closed-site leads to the unsymmetrical bimetallic structures. We therefore suspected that expansion of this chelate ring by one aliphatic carbon atom might lead to symmetrical bimetallic structures, provided the trimethylenediamine unit adopted a skew (twisted) rather than a chair conformation. One of the purposes of this paper is to test this hypothesis. The ligand we describe is cytim 4 which contains two trimethylenediamine units. Aside from a general interest in determining factors responsible for the stereochemistry of these types of bimetallic complexes, we have a specific reason for achieving symmetrical structures. This relates to our interest in employing these bimetallic complexes in asymmetric epoxidation of olefins via species bearing an oxo group at the open-site metal. Symmetric structures obviate stereochemical ambiguity in the structural features responsible for asymmetric induction since an

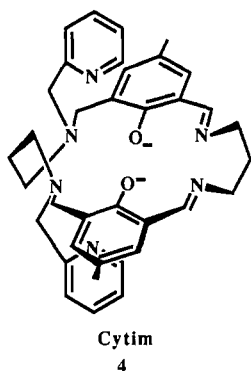
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(1) (a) Fraser, C.; Johnston, L.; Rheingold, A. L.; Haggerty, B. S.; Williams, G. K.; Whelan, J.; Bosnich, B. *Inorg. Chem.* 1992, 31, 1835–44. (b) Fraser, C.; Ostrander, R.; Rheingold, A. L.; White, C.; Bosnich, B. *Inorg. Chem.* 1994, 33, 334. Fraser, C.; Bosnich, B. *Inorg. Chem.* 1994, 33, 338.



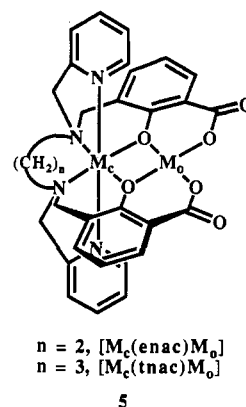
oxo-metal group has identical environments in symmetric complexes. A second interest in the complexes of **4** was to investigate how expansion of the diamine chelate ring of the closed-site affected the redox potentials of metals in this site. Such information is a necessary prelude to establishing which ligands bearing which metals in the closed-site are likely to engage in reduction of a substrate attached to the open-site metal. Finally, we wished to develop secure methods for the synthesis of site-specific heterobimetallic complexes. Before we discuss the synthesis of **4** we describe some related work with non-macrocyclic binucleating ligands which resemble **2**. The purpose of this work was to contrast the stereochemistry and bimetallic stability of related macrocyclic and non-macrocyclic systems.

### 1. Stereochemical Stability

It has been established in stereochemical studies of quadridentate amine complexes that a ligand bearing a sequence of 6-, 5-, and 6-membered chelate rings tends to adopt a planar topology,<sup>2</sup> whereas a ligand containing a succession of three 5-membered chelate rings prefers a *cis-α* disposition.<sup>3</sup> The interplay of interchelate ring interactions<sup>4</sup> in the mononuclear complex **2** therefore implies that the ethylenediamine ring and the contiguous phenolate-bearing chelate rings should be coplanar, whereas the pyridine residues are expected to lie on opposite sides of the molecular plane. The expected  $C_2$  symmetric structure is observed in such complexes.

These stereochemical constraints are relaxed when the ethylenediamine chelate ring is replaced with a trimethylenediamine chelate. In order to achieve 6-coordination with the trimethylenediamine analogue of **2**, the ring must adopt a skew conformation.<sup>5</sup> But, because of the chelate ring bite angle expansion, octahedral complexes of this ligand could assume all three topological isomers, namely, the isomer analogous to **2** with *trans* pyridines and *cis* phenolates, the isomer with *cis* pyridines and *cis* phenolates and the isomer with *cis* pyridines and *trans* phenolates.

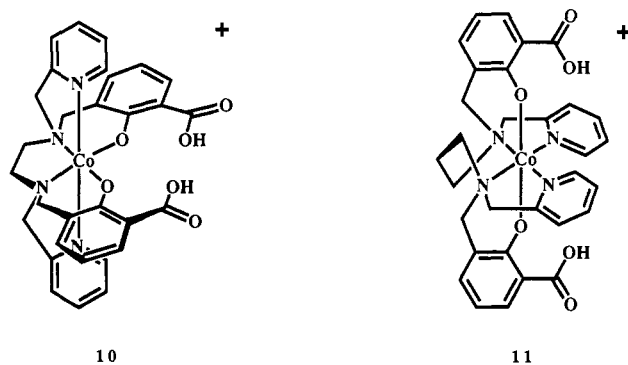
These considerations raise a number of questions related to the design of binucleating ligands of type **1**. First, what topologies do octahedral complexes similar to type **2** adopt when the ethylenediamine is replaced by a trimethylenediamine unit? Second, if a variety of topologies form with stereochemically labile octahedral complexes, will macrocyclic closure as depicted by **2** → **3** lead to the topology depicted in **1**? Third, is macrocyclic closure necessary to obtain stable bimetallic complexes? Specifically, were the aldehyde groups of **2** replaced by carboxylate functionalities would bimetallic complexes of the type **5** form?



### 2. Acyclic Complexes

Two dicarboxylate complexes, **9a** ( $enacH_4$ ) and **9b** ( $tnacH_4$ ) were prepared by the methods outlined in Scheme 1.<sup>6</sup> Monometallic complexes of the type  $[M(enacH_2)]$  and  $[M(tnacH_2)]$ , where the divalent first-row transition metal is probably in the closed-site, are almost completely insoluble in common solvents. The insolubility of these complexes precluded attempts to synthesize bimetallic species.

Both of the insoluble complexes  $[Co(enacH_2)]$  and  $[Co(tnacH_2)]$  were prepared in DMSO solutions by mixing cobaltous acetate with the respective ligands. Each of these pink Co(II) species was suspended in acetonitrile solution and oxidized with ferrocenium hexafluorophosphate. The  $[Co(enacH_2)]PF_6$  complex was isolated as maroon plates, and  $[Co(tnacH_2)]PF_6$  formed dark green needles. Both of these cationic Co(III) complexes are soluble in common polar organic solvents. The  $^1H$  NMR spectra of these two complexes indicates that both are  $C_2$  symmetric and that the product obtained from oxidation consisted of a single topological isomer in both cases. The visible absorption spectra in the  $^1A_{1g} \rightarrow ^1T_{1g}$  transition region, however, suggests that the complexes adopt different topologies. The maroon  $[Co(enacH_2)]^+$  ions has a lowest energy absorption maximum at 531 nm whereas the green  $[Co(tnacH_2)]^+$  species shows a lowest energy absorption maximum at 650 nm. These data clearly indicate that the Co(III) in  $[Co(enacH_2)]^+$  exists in a rhombic environment whereas the Co(III) in  $[Co(tnacH_2)]^+$  is in a tetragonal crystal field.<sup>7</sup> Together, the  $^1H$  NMR and absorption spectra indicate that the complexes  $[Co(enacH_2)]^+$  and  $[Co(tnacH_2)]^+$  have the structures **10**<sup>8</sup> and **11**, respectively. Given

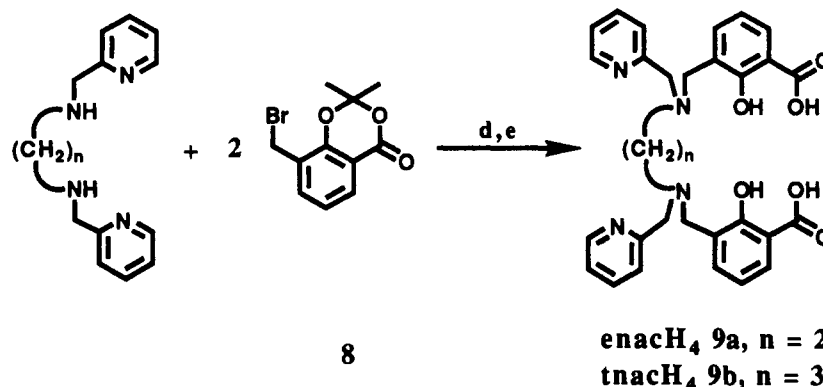
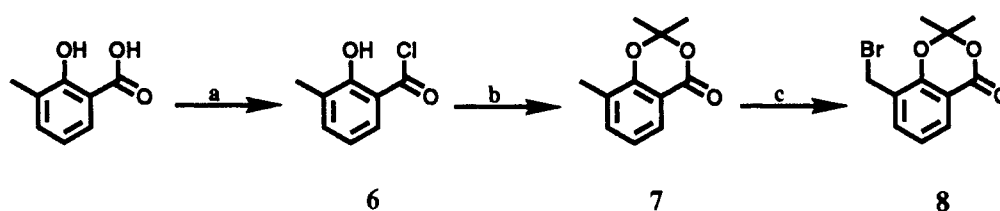


structure **11**, we would not expect that bimetallic complexes would

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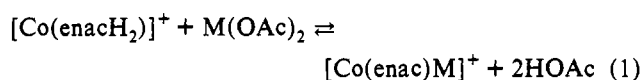
Scheme 1



a.  $\text{SOCl}_2$ , cat. pyridine, hexanes, 90% b. acetone, reflux, 63% c. NBS, AIBN,  $\text{CCl}_4$ , reflux, 48% d.  $\text{Na}_2\text{CO}_3$ , THF,  $65^\circ\text{C}$ , 85% e. NaOH, methanol-water,  $75^\circ\text{C}$ , 91%

be formed, and indeed, our attempts to make them failed. Structure 10, however, appears ideal for forming bimetallic species.

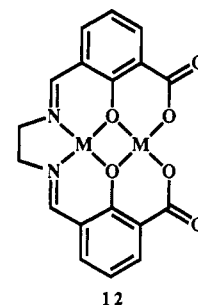
Perhaps surprisingly, the reaction of  $[\text{Co}(\text{enacH}_2)]^+$  (10) with  $\text{M}(\text{OAc})_2$  ( $\text{M} = \text{Cu}(\text{II}), \text{Ni}(\text{II}), \text{Co}(\text{II}), \text{Mn}(\text{II})$ ; OAc = acetate) in the presence of triethylamine and in a variety of solvents gave evidence for the formation of the expected heterobimetallic species, but attempts to isolate the pure compounds failed. In all cases the material isolated contained varying amounts of the second labile metal. The qualitative evidence suggests that the equilibrium depicted in eq 1 obtains and that the equilibrium cannot



be driven completely in favor of the bimetallic complexes even in the presence of added base. (The convention we adopt for the designation of bimetallic complexes is to write the closed-site metal first, followed by the ligand, followed by the open-site metal, followed by ligands coordinated exclusively to the open-site metal.)

The instability of the  $[\text{Co}(\text{enac})\text{M}]^+$  complexes probably arises from the small chelate bite angle of the ethylenediamine link which has the effect opening the O—Co—O angle to give a coordination cavity, defined by the four donor oxygen atoms, which is too large to accommodate the second metal. This cavity size expansion cannot be the only effect which leads to bimetallic

instability because bimetallic complexes of the type 12, for



example, appear to be stable.<sup>9</sup> It is possible that whereas the complexes 12 are essentially planar, in  $[\text{Co}(\text{enacH}_2)]^+$  the conformational puckering of the phenolic groups leads to a twisted disposition of the four oxygen atoms such that normal bond lengths are not achieved when a second metal is introduced. Given the structure of the  $[\text{Co}(\text{tnacH}_2)]^+$  complex and the instability of the bimetallic complexes of  $[\text{Co}(\text{enacH}_2)]^+$ , it would appear that the most secure way of obtaining stable bimetallic species is by the use of macrocyclic binucleating ligands.

### 3. Macrocyclic Complexes

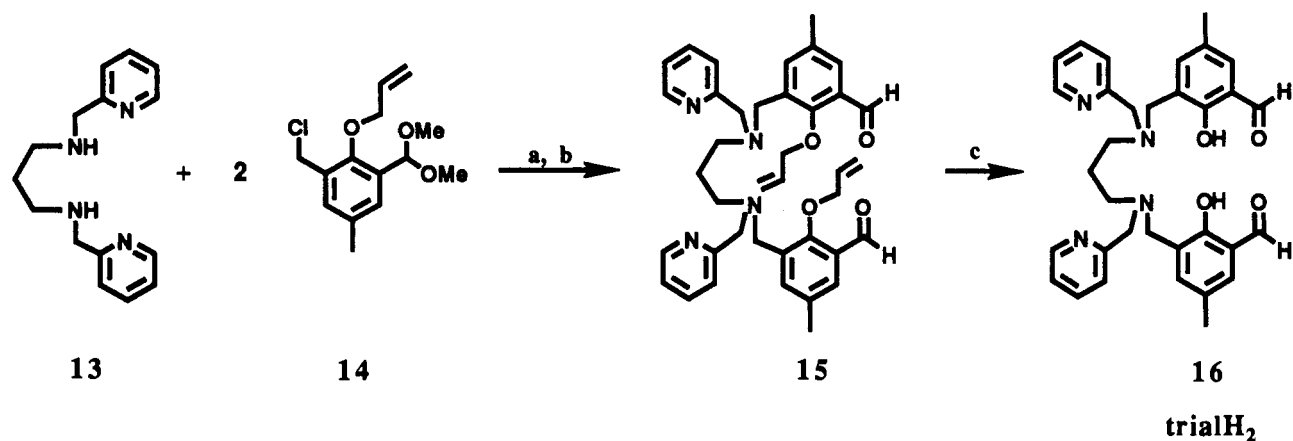
Precursors to the ligand cytim, 4, were prepared by published procedures.<sup>1a</sup> The compound 13<sup>10</sup> was condensed with 14<sup>1a</sup> in 1,4-dioxane in the presence of  $\text{Na}_2\text{CO}_3$  to give, after deprotection of the acetals, the phenol protected compound 15 (Scheme 2). Deprotection of the allylated phenols was achieved by reaction with sodium dimethylmalonate in the presence of the catalyst,  $[\text{Pd}(\text{PPh}_3)_4]$ .<sup>1a</sup> Compound 16 is an oil which was purified by isolation of its insoluble neutral monozinc complex,  $[\text{Zn}(\text{trial})]$ . This yellow zinc compound was found to be too insoluble to measure its  $^1\text{H}$  NMR spectrum.

Reaction of the dialdehyde ligand 16 with cobaltous acetate gave the neutral insoluble  $\text{Co}(\text{II})$  complex  $[\text{Co}(\text{trial})]$ , which could be oxidized to the soluble  $\text{Co}(\text{III})$  monocationic complex  $[\text{Co}$

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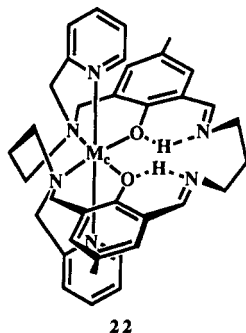
Scheme 2



a.  $\text{Na}_2\text{CO}_3$ , 1,4-dioxane,  $100^\circ\text{C}$ , ~100% b. aq HCl ~100% c.  $[(\text{PPh}_3)_4\text{Pd}(0)]$ ,  $\text{NaCH}(\text{CO}_2\text{CH}_3)_2$ , THF, ~100%

(trial)]<sup>+</sup> with ferrocenium hexafluorophosphate in acetonitrile solutions. The <sup>1</sup>H NMR spectrum of the diamagnetic Co(III) complex indicated that three topological isomers were present, two of which were  $C_2$  symmetrical and one unsymmetrical, in the ratio  $C_2:C_2:C_1 = 7:3:1$ . The isomer in lowest proportion is the unsymmetrical  $C_1$  isomer with cis pyridines and cis phenolates. The  $C_2$  symmetrical isomers correspond to the one with trans pyridines and the one with trans phenolates, although it was not possible to determine which was predominant. Although these isomers were not separated this observation suggests that the insoluble Zn(II) complex derived from **16** is likely to consist of a mixture of topological isomers. If this is so then the result contrasts with the complex **2** which gave a single  $C_2$  symmetric isomer.<sup>1a</sup> This difference in behavior can be ascribed to the greater flexibility provided by the trimethylenediamine ring compared to the ethylenediamine link. Moreover, formation of the macrocycle **4** in high yield by a Schiff base template condensation process similar to **2** → **3** requires that topological rearrangement occur. This is illustrated in Scheme 3. Molecular models indicate that cyclization is unlikely to occur with **17** but can occur with **18** and **19** as illustrated. In addition, the cyclized product **20** is likely to be less stable than **21** and could convert to **21**.

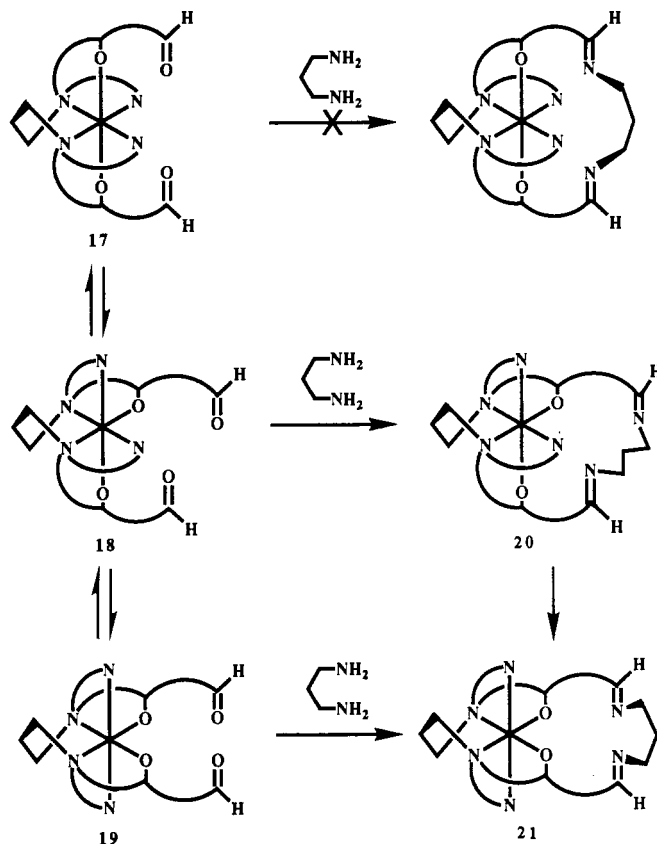
When either of the Zn(II) or Co(II) dialdehyde complexes of type **17**–**19** are suspended in ethanol and 1 equiv of trimethylenediamine and 2 equiv of acetic acid in ethanol are slowly added at  $25^\circ\text{C}$ , clear yellow solutions are obtained slowly. Addition of  $\text{PF}_6^-$  ions leads to the precipitation of the products of the formula  $[\text{M}(\text{cytim})(\text{H}^+)_2](\text{PF}_6)_2$ . As we show later these monometallic complexes have the structure **22**. The <sup>1</sup>H NMR spectrum of the



22

diamagnetic Zn(II) complex confirms the existence of a single isomer with a  $C_2$  symmetric structure and reveals the protons in the open-site cavity as a broad singlet at 12.43 ppm. The azomethine protons are coupled to these cavity protons and occur as a doublet at 8.14 ppm,  $J = 12.1$  Hz. Upon the addition of  $\text{D}_2\text{O}$ , rapid proton exchange occurs and the cavity proton signals

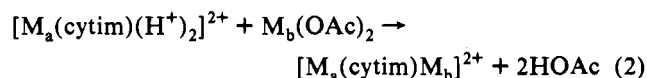
Scheme 3



disappear as does any observable coupling to the azomethine resonances. The high yield of the cyclization suggests extensive isomer rearrangement occurs (Scheme 3) during the reaction.

#### 4. Bimetallic Complexes

The ready isolation of complexes of the type **22**,  $[\text{M}(\text{cytim})(\text{H}^+)_2]^{2+}$  provides ideal precursors for the mild synthesis of heterobimetallic complexes (eq 2). The reaction depicted in eq



**2** can be driven to the right by added base and is exceptionally mild since the incorporation of the second metal depends on the fast removal of the cavity protons. Under such circumstances we

would expect that the complexation of the second metal would be much faster than site scrambling of the metals.

Starting from the monometallic complexes, [Zn(cytim)Zn(OAc)]PF<sub>6</sub>, [Zn(cytim)ZnCl]PF<sub>6</sub>, [Zn(cytim)Cu](PF<sub>6</sub>)<sub>2</sub>, [Zn(cytim)CoCl]PF<sub>6</sub>, [Co(cytim)ZnCl]PF<sub>6</sub>, [Co(cytim)Cu](PF<sub>6</sub>)<sub>2</sub>, and [Co(cytim)CoCl]PF<sub>6</sub>, were prepared by the method illustrated in eq 2. Apart from the copper containing complexes, the others required a chloride or acetate ligand in order to obtain pure crystalline compounds. In some cases triethylamine was added in order to complete the reaction.

In CD<sub>3</sub>CN solution the complex [Zn(cytim)Zn(OAc)]PF<sub>6</sub> shows a <sup>1</sup>H NMR spectrum at 25 °C which indicates a C<sub>2</sub> symmetric structure, but the signals are broad. When this is cooled to -45 °C, the signals sharpen and the spectrum indicates that the C<sub>2</sub> axis of the complex is lost. These results suggest that at 25 °C the acetate ligand is rapidly exchanging between the two axial sites of the open-site Zn(II) giving a time-averaged C<sub>2</sub> structure.<sup>11</sup> Cooling slows the exchanging, which results in the appearance of a spectrum consistent with an unsymmetrical structure. In CD<sub>2</sub>Cl<sub>2</sub> the <sup>1</sup>H NMR spectrum of this complex indicates an unsymmetrical structure. The [Zn(cytim)ZnCl]PF<sub>6</sub> complex in either CD<sub>3</sub>CN or CD<sub>2</sub>Cl<sub>2</sub> solutions gives <sup>1</sup>H NMR spectra consistent with an unsymmetrical structure at 25 °C, but upon the addition of AgPF<sub>6</sub> to remove the coordinated chloride the <sup>1</sup>H NMR spectrum becomes consistent with a C<sub>2</sub> symmetric molecule. These results indicate that the structure of the dizinc complexes in solution contain trans-disposed pyridine ligands which lie above and below the mean macrocyclic plane (see 22). This conclusion is confirmed by the crystal structure of [Zn(cytim)Zn(OAc)]PF<sub>6</sub>·MeOH which we discuss presently.

Very little dissociation of the fifth ligand coordinated to the open-site metal appears to occur in acetonitrile solutions because all of the [M<sub>a</sub>(cytim)M<sub>b</sub>L]PF<sub>6</sub> complexes are 1:1 electrolytes,<sup>12</sup> (see Experimental Section). The copper-containing complexes are 2:1 electrolytes. Thus the symmetrical broad <sup>1</sup>H NMR signals observed for [Zn(cytim)Zn(OAc)]PF<sub>6</sub> in CD<sub>3</sub>CN at 25 °C cannot be interpreted in terms of extensive acetate dissociation. When 10% D<sub>2</sub>O is added to the CD<sub>3</sub>CN solutions of [Zn(cytim)Zn(OAc)]<sup>+</sup> and [Zn(cytim)ZnCl]<sup>+</sup>, C<sub>2</sub> symmetric <sup>1</sup>H NMR spectra are observed, consistent with the dissociation of the acetate and chloride ligands, respectively.

We have noted previously that the Co(II) complexes [Co(trial)] and [Co(tnacH<sub>2</sub>)] were oxidized by the ferrocenium ion. It was therefore surprising to us that neither the [Co(cytim)-(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> nor the [Co(cytim)ZnCl]<sup>+</sup> complex could be oxidized by ferrocenium ions. As we will show presently, the redox potentials are consistent with these observations.

## 5. Physical Properties

The room temperature magnetic moments were measured on powdered solid samples and are collected in Table 1 together with the expected spin-only values  $\mu_{so}$  for the total interacting spin-free system. For complexes containing a single paramagnetic ion the  $\mu_{eff}$  values are higher than the  $\mu_{so}$  numbers presumably because of temperature independent paramagnetism and, additionally, orbital contributions in the case of the Co(II) complexes. After these effects are taken into account the  $\mu_{eff}$  values for the [Co(cytim)CoCl]<sup>+</sup> and [Co(cytim)Cu]<sup>2+</sup> complexes are similar to the predicted  $\mu_{so}$  values, suggesting that there is only weak spin-coupling between the electrons on the two metals. Similar results were observed with bimetallic complexes of the analogous cyclim ligand in which the trimethylene link of the closed-site was replaced by an ethylenediamine link.<sup>1a</sup>

The electronic absorption spectra of the cytim complexes were measured in acetonitrile solutions over the range 300–2000 nm. The absorption peaks and their corresponding extinction coef-

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

complex	$\mu_{eff}$ , <sup>c</sup> $\mu_B$	$\mu_{so}$ , <sup>d</sup> $\mu_B$
[Co(cytim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	4.64	3.87
[Co(cytim)ZnCl]PF <sub>6</sub>	4.77	3.87
[Co(cytim)Cu](PF <sub>6</sub> ) <sub>2</sub>	4.98	4.90
[Co(cytim)CoCl]PF <sub>6</sub>	6.41	6.93
[Zn(cytim)Cu](PF <sub>6</sub> ) <sub>2</sub>	1.97	1.73
[Zn(cytim)CoCl]PF <sub>6</sub>	4.29	3.87

<sup>a</sup> Magnetic susceptibilities were determined at 25 °C on powdered samples. <sup>b</sup> The magnetic moments are reported per binuclear complex. <sup>c</sup> Approximate error =  $\pm 0.05 \mu_B$ . <sup>d</sup> Spin only values are determined for the bimetallic ensemble (where  $\mu_{so} = [n(n+2)]^{1/2}$  and  $n$  = total number of unpaired spins; e.g. for the Co(II)–Co(II) complex,  $n = 6$ ).

ficients are given in Table 2. The absorption spectra of the [Co(enacH<sub>2</sub>)]<sup>+</sup> and [Co(tnacH<sub>2</sub>)]<sup>+</sup> ions are included. All of the cytim complexes show an intense absorption band between about 350 and 400 nm which we ascribe to the  $\pi \rightarrow \pi^*$  transitions of the azomethine chromophores.<sup>13</sup> Below and contiguous with these occur the d–d bands associated with Co(II) and Cu(II) in the various complexes. The [Zn(cytim)Cu]<sup>2+</sup> complex displays three bands to lower energies of the azomethine absorption, one at 432 nm and two others at 581 and 731 nm. The 432-nm absorption is probably a charge transfer band associated with the Cu(II) ion and the coordinated phenolates.<sup>14</sup> The two bands to lower energies are d–d absorptions. The fact that the d-electron manifold is split, with one component occurring at low energy (731 nm), suggests that the Cu(II) ion is in a distorted 4-coordinate environment.<sup>15a</sup> The d–d absorptions of [Co(cytim)ZnCl]<sup>+</sup> and of [Zn(cytim)CoCl]<sup>+</sup> are shown in Figure 1. Three bands are resolved at 499, 542 and 1001 nm for the [Co(cytim)ZnCl]<sup>+</sup> complex consistent with a spin-free octahedral Co(II) complex.<sup>15b</sup> The [Zn(cytim)CoCl]<sup>+</sup> shows six resolved d–d transitions ranging from 487 to 1622 nm (Table 2; Figure 1), consistent with spectra observed for 5-coordinate spin-free Co(II) complexes.<sup>15c</sup> Assuming that no significant structural changes occur and no intermetal transitions are present, then we might expect that the normalized sum of the spectra of the [Co(cytim)ZnCl]<sup>+</sup> and [Zn(cytim)CoCl]<sup>+</sup> complexes should equal the observed spectrum of [Co(cytim)CoCl]<sup>+</sup>. As shown in Figure 2, the calculated (summed) and observed spectra are in excellent agreement.

The redox potentials of the cobalt and copper containing complexes were determined by cyclic voltammetry in acetonitrile solutions using tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte and a Ag/AgNO<sub>3</sub> electrode. The redox couples are quoted versus the ferrocene/ferrocenium couple,<sup>16</sup> used as an internal standard where possible. The ligand-based couples were observed to more negative values than 1.7 V. These waves are generally irreversible and their position depends on the nature of the metal or metals present in the complex. The metal redox couples are given in Table 3 and are classified according to the site occupancy of the metal. All of the waves were found to be quasi-reversible and the wave separations are given.

Perhaps the most significant observation that is apparent from the data in Table 3 is the variation of the closed-site Co(III)/Co(II) potentials. The noncyclic complexes, [Co(enacH<sub>2</sub>)]<sup>+</sup> and [Co(tnacH<sub>2</sub>)]<sup>+</sup>, have redox couples that are significantly more negative than the ferrocene/ferrocenium couple and are consistent with ready oxidation of the Co(II) analogues with the ferrocenium ion. In macrocyclic cytim complexes, however, the closed-site Co(III)/Co(II) couples occur at much more positive potentials.

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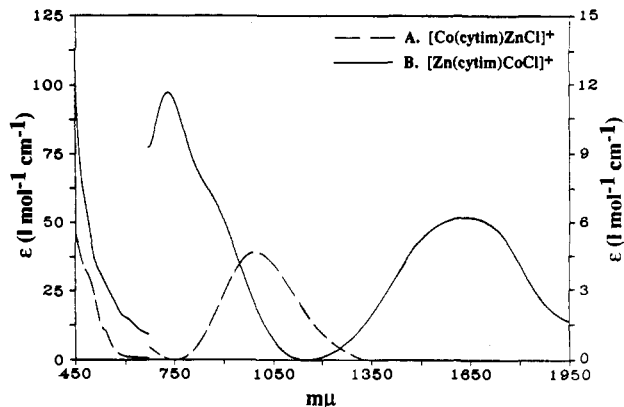
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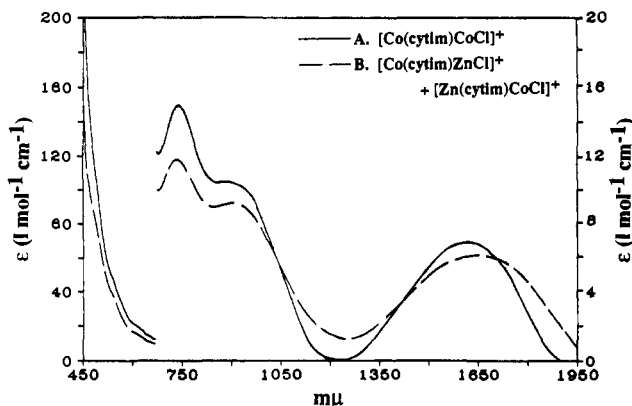
**Table 2.** Electronic Absorption Maxima and Intensities of the Charge Transfer and d-d Transitions for Cytim Complexes<sup>a</sup>

complex	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup> )						
[Zn(cytim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	396 (10700)						
[Co(cytim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	402 (10900)					1000 (6)	
[Zn(cytim)Zn(OAc)]PF <sub>6</sub>	348 (10400)						
[Zn(cytim)ZnCl]PF <sub>6</sub>	348 (10900)						
[Zn(cytim)Cu](PF <sub>6</sub> ) <sub>2</sub>	352 (7960)	432 (599)	581 (71)		731 (33)		
[Zn(cytim)CoCl]PF <sub>6</sub>	346 (9650)	487 (52)	544 (32)	616 (17)	732 (14)	906 (7)	1622 (7)
[Co(cytim)ZnCl]PF <sub>6</sub>	354 (9760)	499 (28)	542 (10)			1001 (5)	
[Co(cytim)Cu](PF <sub>6</sub> ) <sub>2</sub>	355 (9790)	425 (814)	549 (110)	616 (78)	741 (34)	979 (5)	
[Co(cytim)CoCl]PF <sub>6</sub>	347 (8180)	494 (103)	543 (50)	624 (20)	730 (15)	904 (11)	1616 (6)
[Co(enacH <sub>2</sub> )]PF <sub>6</sub>	312 (11600)	325 (9700)	392 (2190)	531 (720)			
[Co(tnacH <sub>2</sub> )]PF <sub>6</sub>	302 (10400)	369 (3770)	421 (4920)	650 (980)			

<sup>a</sup> All spectra were run in CH<sub>3</sub>CN.



**Figure 1.** Electronic absorption spectra of [Co(cytim)ZnCl]<sup>+</sup> and [Zn(cytim)CoCl]<sup>+</sup> complexes in acetonitrile solutions.



**Figure 2.** Electronic absorption spectrum of [Co(cytim)CoCl]<sup>+</sup> and composite spectrum of [Co(cytim)ZnCl]<sup>+</sup> and [Zn(cytim)CoCl]<sup>+</sup>.

It is therefore not surprising that we were unable to oxidize [Co(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> with the ferrocenium ion. This should also apply for oxidation of [Co(cytim)Cu](PF<sub>6</sub>)<sub>2</sub>. Thermodynamically, both [Co(cytim)ZnCl]PF<sub>6</sub> and [Co(cytim)CoCl]PF<sub>6</sub> should be oxidized by the ferrocenium ion but attempts at oxidizing the former failed. Presumably the more negative Co(III)/Co(II) potentials observed for [Co(cytim)ZnCl]<sup>+</sup> and [Co(cytim)CoCl]<sup>+</sup> compared to [Co(cytim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> and [Co(cytim)Cu]<sup>2+</sup> are related, at least partly, to the overall charges of the complexes. Unlike the closed-site Co(III)/Co(II) couples, the open-site Co(II)/Co(I)<sup>17</sup> and Cu(II)/Cu(I) couples are essentially insensitive to the metal occupying the closed-site. The somewhat more positive potentials of the open-site Cu(II)/Cu(I) couples compared

**Table 3.** Redox Potentials and Peak Separations for Mono- and Bimetallic Complexes of Cytim, enacH<sub>2</sub>, and tnacH<sub>2</sub><sup>a,b</sup>

complex	$E_f$ , V ( $E_{\text{pa}} - E_{\text{pc}}$ , V)	
	closed-site Co(III/II) couple	open-site M(II/I) couple
[Co(cytim)(H <sup>+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	0.04 (0.160)	
[Co(cytim)ZnCl]PF <sub>6</sub>	-0.11 (0.069)	
[Zn(cytim)CoCl]PF <sub>6</sub>		-1.70 (0.138)
[Co(cytim)CoCl]PF <sub>6</sub>	-0.04 (0.091)	-1.68 (0.102)
[Zn(cytim)Cu](PF <sub>6</sub> ) <sub>2</sub>		-0.98 (0.069)
[Co(cytim)Cu](PF <sub>6</sub> ) <sub>2</sub>	0.09 (0.104)	-0.94 (0.064)
[Co(enacH <sub>2</sub> )]PF <sub>6</sub>	-0.27 (0.141)	
[Co(tnacH <sub>2</sub> )]PF <sub>6</sub>	-0.19 (0.115)	

<sup>a</sup> 5 × 10<sup>-4</sup> M sample, 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>3</sub>CN. Solutions were deaerated with Ar for 10 min prior to each run. <sup>b</sup> Reduction potentials are reported relative to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple, assigned a value of 0.00 V. The Fc<sup>+</sup>/Fc couple is +0.15 V vs Ag/AgNO<sub>3</sub>.

to analogous complexes<sup>18,19</sup> are consistent with the electronic spectra which indicate a nonplanar coordination site.

The variation of the closed-site Co(III)/Co(II) couples appears to depend on structure, the neighboring open-site metal, and possibly the charge of the complex. The structural effect is exemplified by the relative ease of oxidation by ferrocenium of the [Co(cytim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> and [Co(cyclim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> complexes. Ferrocenium ion readily oxidizes the latter to the stable [Co(cyclim)(H<sup>+</sup>)<sub>2</sub>]<sup>3+</sup> complex<sup>20</sup> whereas, as we have noted, the former is not oxidized under the same conditions. The [Co(cyclim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> gives a highly irreversible wave and we are unable to report a reliable Co(III)/Co(II) couple but the ferrocenium oxidation clearly indicates a potential more negative than that for [Co(cytim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>. We ascribe this difference to an inability of the cytim structure to adjust to the shorter bond lengths of Co(III) complexes over the corresponding Co(II) complexes.<sup>21,22</sup> In cyclim complexes the ethylenediamine chelate accommodates the Co(III) ion better than the larger bite angle of the trimethylenediamine chelate in cytim. This is supported by the Co(III)/Co(II) couples observed for the [Co(enacH<sub>2</sub>)]<sup>+</sup> and [Co(tnacH<sub>2</sub>)]<sup>+</sup> complexes (Table 3).

The variation in the closed-site Co(III)/Co(II) couples of the [Co(cytim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>, [Co(cytim)Cu]<sup>2+</sup>, [Co(cytim)ZnCl]<sup>+</sup>, and [Co(cytim)CoCl]<sup>+</sup> could arise from three factors: the overall charge, electronic interactions between metals, and structural variations. For the first two dipositively charged complexes there is a small difference in the Co(III)/Co(II) couples, and this could be ascribed to structural variations. On the other hand the two

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**Table 4.** Crystal Data for [Zn(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (I) and [Zn(cytim)Zn(OAc)]PF<sub>6</sub>·MeOH (II)

	C <sub>36</sub> H <sub>42</sub> N <sub>6</sub> O <sub>2</sub> · P <sub>2</sub> F <sub>12</sub> Zn (I)	C <sub>38</sub> H <sub>43</sub> N <sub>6</sub> O <sub>4</sub> PF <sub>6</sub> Zn <sub>2</sub> · CH <sub>3</sub> OH (II)
fw	946.1	955.5
cryst system	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>Ia</i>
<i>a</i> , Å	8.701(3)	16.075(2)
<i>b</i> , Å	11.380(4)	15.714(2)
<i>c</i> , Å	21.481(8)	17.497(2)
$\alpha$ , deg	78.27(3)	
$\beta$ , deg	79.74(3)	106.02(1)
$\gamma$ , deg	79.39(3)	
<i>V</i> , Å <sup>3</sup>	2025.1(12)	4248.3(10)
<i>Z</i>	2	4
<i>D</i> (calc), g cm <sup>-3</sup>	1.552	1.494
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	7.82	12.43
temp, K	295	295
wavelength, Å	0.710 73	0.710 73
<i>R</i> ( <i>F</i> ), %	6.61	7.36
<i>R</i> <sub>w</sub> ( <i>F</i> ), %	7.91	7.82

<sup>a</sup>  $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ . <sup>b</sup>  $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$ ;  $w^{-1} = \sigma^2 F_o + g F_o^2$ .

**Table 5.** Selected Bond Distances and Angles for [Zn(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (I)

Bond Distances (Å)			
Zn–O(1)	2.086(6)	Zn–N(3)	2.188(7)
Zn–O(2)	2.130(6)	Zn–N(4)	2.153(6)
Zn–N(1)	2.178(7)	O(1)–C(34)	1.325(12)
Zn–N(2)	2.183(7)	O(2)–C(17)	1.325(12)
Bond Angles (deg)			
O(1)–Zn–O(2)	85.7(2)	N(2)–Zn–N(3)	93.8(3)
O(1)–Zn–N(1)	91.7(3)	O(1)–Zn–N(4)	89.2(2)
O(2)–Zn–N(1)	85.3(2)	O(2)–Zn–N(4)	91.8(2)
O(1)–Zn–N(2)	169.4(2)	N(1)–Zn–N(4)	176.9(3)
O(2)–Zn–N(2)	91.1(3)	N(2)–Zn–N(4)	101.0(3)
N(1)–Zn–N(2)	78.0(3)	N(3)–Zn–N(4)	78.7(2)
O(1)–Zn–N(3)	91.0(3)	Zn–O(1)–C(34)	122.2(5)
O(2)–Zn–N(3)	170.0(2)	Zn–O(2)–C(17)	122.0(5)
N(1)–Zn–N(3)	104.2(3)		

unipositively charged complexes show a large difference in the Co(III)/Co(II) potentials. Since the variations in structure are likely to be small in going from [Co(cytim)ZnCl]<sup>+</sup> to [Co(cytim)CoCl]<sup>+</sup>, as suggested by the electronic spectra, we are disposed to ascribe the difference to electronic interactions between metals.

## 6. Crystal Structures

The single-crystal X-ray diffraction structures of [Zn(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> and of [Zn(cytim)Zn(OAc)]PF<sub>6</sub>·MeOH were determined. Crystallographic data are provided in Table 4 and selected bond lengths and angles are listed in Tables 5 and 6 for the two structures. Figure 3 illustrates two perspectives of the structure of the [Zn(cytim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> ion. The structure is essentially C<sub>2</sub> symmetric with trans-disposed pyridine ligands. The trimethylenediamine link of the closed-site has a skew conformation, the phenolic residues are in a highly twisted array, and the trimethylenediamine fragment is skewed and disposes the nitrogen atoms (N(5) and N(6)) above and below the mean macrocyclic plane. All bond lengths are unexceptional but certain metal donor atom angles bear comment. The N(2)–Zn–N(3) bond angle is 93.8° and the opposing angle O(1)–Zn–O(2) is

**Table 6.** Selected Bond Distances and Angles for [Zn(cytim)Zn(OAc)]PF<sub>6</sub>·MeOH (II)

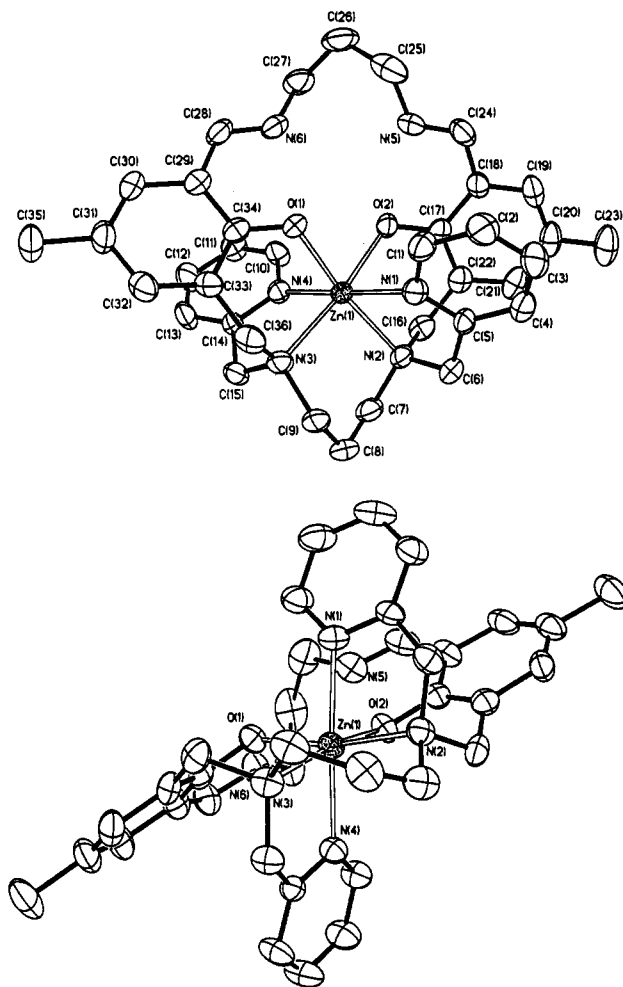
Bond Distances (Å)			
Zn(1)–O(1)	2.049(12)	Zn(2)–O(2)	2.106(14)
Zn(1)–O(2)	2.085(11)	Zn(2)–O(3)	1.978(15)
Zn(1)–N(1)	2.192(15)	Zn(2)–N(5)	2.121(17)
Zn(1)–N(2)	2.133(15)	Zn(2)–N(6)	2.066(14)
Zn(1)–N(3)	2.184(15)	O(1)–C(34)	1.334(20)
Zn(1)–N(4)	2.221(15)	O(2)–C(17)	1.302(22)
Zn(2)–O(1)	2.095(11)		
Bond Angles (deg)			
O(1)–Zn(1)–O(2)	80.6(5)	O(1)–Zn(2)–O(3)	96.4(5)
O(1)–Zn(1)–N(1)	92.2(5)	O(2)–Zn(2)–O(3)	108.5(6)
O(1)–Zn(1)–N(2)	97.0(5)	O(1)–Zn(2)–N(5)	162.6(7)
O(1)–Zn(1)–N(3)	167.8(5)	O(2)–Zn(2)–N(5)	85.3(6)
O(2)–Zn(1)–N(2)	93.6(5)	O(3)–Zn(2)–N(5)	96.0(6)
N(1)–Zn(1)–N(2)	77.7(6)	O(1)–Zn(2)–N(6)	90.1(5)
O(1)–Zn(1)–N(3)	93.3(5)	O(2)–Zn(2)–N(6)	129.0(6)
O(2)–Zn(1)–N(3)	167.1(5)	O(3)–Zn(2)–N(6)	122.3(7)
N(1)–Zn(1)–N(3)	94.6(5)	N(5)–Zn(2)–N(6)	93.6(6)
N(2)–Zn(1)–N(3)	94.4(5)	Zn(1)–O(1)–Zn(2)	100.0(5)
O(1)–Zn(1)–N(4)	89.4(5)	Zn(1)–O(1)–C(34)	129.0(11)
O(2)–Zn(1)–N(4)	90.7(5)	Zn(2)–O(1)–C(34)	128.8(10)
N(1)–Zn(1)–N(4)	172.3(5)	Zn(1)–O(2)–Zn(2)	98.5(5)
N(2)–Zn(1)–N(4)	101.5(6)	Zn(1)–O(2)–C(17)	127.6(11)
N(3)–Zn(1)–N(4)	77.8(6)	Zn(2)–O(2)–C(17)	126.8(12)
O(1)–Zn(2)–O(2)	79.1(5)		

85.7°. It is generally found that the latter angle in bimetallic complexes of this kind is about 70–80°. Consequently, were a second metal added to the open-site cavity of this complex very little change in the O(1)–Zn–O(2) angle would be required to accommodate the metal. Thus we would not expect any gross structural changes in the closed-site when bimetallic complexes are formed. The situation is quite different when the trimethylenediamine link is replaced by ethylenediamine to produce the cyclim ligand (see 3). The corresponding ethylenediamine N–M–N angle in bimetallic cyclim complexes is generally about 80°, and consequently the opposite O–M–O angle will of necessity expand over that observed for cytim complexes. Thus whereas monometallic cyclim complexes of the type<sup>20</sup> [M(cyclim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> form C<sub>2</sub> symmetric complexes, the bimetallic compounds form unsymmetrical structures with cis pyridines. These unsymmetrical structures are formed in part as a consequence of the contraction of the closed-site O–M–O angle which is found to be about 70–75° in [M(cyclim)ML]<sup>n+</sup> complexes.<sup>1a</sup>

The two protons which exist in the open-site cavity of [Zn(cytim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup> were not found in the diffraction analysis but it is probable that they exist as hydrogen-bonded entities spanning O(2)–N(5) and O(1)–N(6). The open-site cavity has the following dimensions: O(1)–N(6) = 2.6 Å, O(2)–N(5) = 2.6 Å, O(1)–N(5) = 3.6 Å, and O(2)–N(6) = 3.7 Å. Given that first row divalent transition metals generally have metal–ligand bond lengths on the order of 2 Å, the diagonal distances O(1)–N(5) and O(2)–N(6) are not long enough to accommodate a second metal in the twisted conformation observed in Figure 3. It is therefore expected that coordination of a second metal would require some conformational adjustment, depending on the precise coordination geometry.

Figure 4 illustrates two perspectives of the structure of [Zn(cytim)Zn(OAc)]PF<sub>6</sub>·MeOH. We note that the C<sub>2</sub> symmetrical structure of the closed-site is retained and the general twisted ligand structure resembles that observed in the monometallic complex, [Zn(cytim)(H<sup>+</sup>)<sub>2</sub>]<sup>2+</sup>. The bond lengths and most of the bond angles are not at variance with expectations. We note that the N(2)–Zn(1)–N(3) angle is larger (94.4°) and the opposing angle O(1)–Zn(1)–O(2) is smaller (80.6°) compared to the monometallic analogue. These modest angle changes are apparently accommodated by ligand conformational adjustments without requiring the gross structural changes that are observed for the cyclim bimetallic complexes. As a consequence of the highly twisted structure of the open-site in the monometallic

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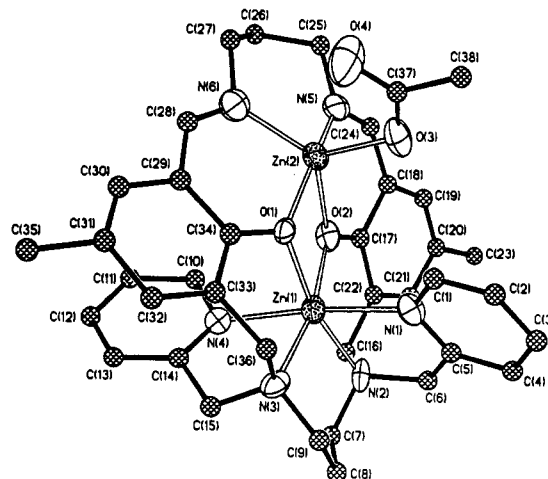


**Figure 3.** Two views of the molecular structure of  $[\text{Zn}(\text{cytim})(\text{H}^+)_2](\text{PF}_6)_2$  (I) drawn with 35% probability ellipsoids. The hydrogen atoms have been deleted for clarity.

complex, the open-site zinc ion ( $\text{Zn}(2)$ ) is in a distorted trigonal bipyramidal environment where  $\text{N}(5)$  and  $\text{O}(1)$  represent the axial bonds. It will be recalled that the electronic spectra of bimetallic complexes bearing  $\text{Cu}(\text{II})$  and  $\text{Co}(\text{II})$  in the open-site indicated that these metals were in distorted coordination environments. The crystal structure of  $[\text{Zn}(\text{cytim})\text{Zn}(\text{OAc})]\text{PF}_6\cdot\text{MeOH}$  gives credence to this conclusion.

## 7. Conclusions

From the point of view of employing these types of complexes for oxidative addition in the way described at the beginning of this paper, these redox variations are significant. The oxidizability of the closed-site metal not only depends on the nature of the ligands but also depends on the subtle structural variations, on the neighboring metal, and, as expected, on the overall charge. It is disconcerting to find that although the cytim ligand has solved the stereochemical problem of obtaining symmetrical complexes, the solution was obtained at the cost of an unfavorable redox couple for the closed-site cobalt. As expected, the  $[\text{Co}(\text{cytim})\text{CoCl}]^+$  complex is inert to oxygen. One possible method of making the closed-site  $\text{Co}(\text{III})$  state accessible is to reduce the two diimine linkages of the cytim ligand to amines. Such a ligand, cytam, is expected to be more flexible and therefore more able to adjust to the bond length changes accompanying the  $\text{Co}(\text{II}) \rightarrow \text{Co}(\text{III})$  transformation. We have recently prepared cytam and find the  $[\text{Co}(\text{cytam})\text{Co}]^{2+}$  complex to be very sensitive to  $\text{O}_2$ , but as yet, we have been unable to characterize the products. This oxygen sensitivity illustrates the subtle factors governing the oxidizability of metals in these types of complexes. If one were to persevere with complexes of the cytim ligand, cooperative



**Figure 4.** Two views of the molecular structure of  $[\text{Zn}(\text{cytim})\text{Zn}(\text{OAc})]\text{PF}_6\cdot\text{MeOH}$  (II) drawn with 35% probability ellipsoids. Hydrogen atoms and the solvent molecule have been deleted for clarity.

oxidative addition might be achieved by placing intrinsically more oxidizable metals in the closed-site such as  $\text{Cr}(\text{II})$  for  $\text{Fe}(\text{II})$  and by using the kinetically inert metals  $\text{Cr}(\text{III})$  or  $\text{Co}(\text{III})$  in the open-site in order to obtain stable dioxygen complexes. We are currently investigating these possibilities and the chemistry of the cytam ligand.

## Experimental Section

Conductance measurements were made at  $25^\circ\text{C}$  with a YSI Model 35 conductance meter on  $0.001\text{ M}$   $\text{CH}_3\text{CN}$  solutions of the complexes. Magnetic susceptibilities of powdered samples were measured using a Johnson Matthey magnetic susceptibility balance. UV/vis spectra were obtained on a Varian (Cary) 2400 spectrophotometer using spectral grade  $\text{CH}_3\text{CN}$ . Cyclic voltammograms were recorded using a Bioanalytical Systems BAS 100 electrochemical analyzer on deaerated  $\text{CH}_3\text{CN}$  solutions which were  $0.1\text{ M}$  in  $n\text{-Bu}_4\text{NBF}_4$  supporting electrolyte and  $5 \times 10^{-4}\text{ M}$  in sample. Redox potentials were measured using a Pt-button working electrode, a  $\text{Ag}/\text{AgNO}_3$  reference electrode, and a Pt-wire auxiliary electrode and are tabulated versus a ferrocene internal standard.<sup>15</sup> All samples were dried to constant weight under high vacuum ( $0.25\text{ mm}$ ) for at least 5 h prior to characterization. Solvents used in the preparative reactions were dried over  $\text{K}$  (THF) or  $\text{LiAlH}_4$  (1,4-dioxane). Ethanol refers to absolute ethanol. Preparations of cobalt complexes were conducted under argon with deaerated solvents. All dry complexes are air stable.

**Ligand Preparation (trialH<sub>2</sub>).** 1,7-Bis(2-pyridyl)-2,6-bis(2-(allyloxy)-3-formyl-5-methylbenzyl)-2,6-diazaheptane (**15**). 2-Allyloxy-3-(chloromethyl)-5-methylbenzaldehyde dimethyl acetal,<sup>1a</sup> **14** (9.02 g, 35.1 mmol), and 1,7-bis(2-pyridyl)-2,6-diazaheptane, **13**<sup>9</sup> (3.92 g, 15.3 mmol), were coupled by the published method.<sup>1a</sup> The bis(allyloxy) dialdehyde, **15**, was obtained as a viscous brown oil: 9.64 g ( $\sim 100\%$ ). <sup>1</sup>H NMR



(500 MHz, CDCl<sub>3</sub>):  $\delta$  1.80 (m, 2H), 2.27 (s, 6H), 2.49 (t,  $J = 7.2$  Hz, 4H), 3.61 (s, 4H), 4.36 (d,  $J = 5.8$  Hz, 4H), 5.23 (d,  $J = 10.1$  Hz, 2H), 5.33 (d,  $J = 18.3$  Hz, 2H), 5.98 (m, 2H), 7.06 (m, 2H), 7.29 (d,  $J = 7.8$  Hz, 2H), 7.45 (m, 4H), 7.52 (m, 2H), 8.43 (d,  $J = 4.4$  Hz, 2H), 10.21 (s, 2H).

**1,7-Bis(2-pyridyl)-2,6-bis(2-hydroxy-3-formyl-5-methylbenzyl)-2,6-diazahepptane (trialH<sub>2</sub>) (16).** The bis(allyloxy) dialdehyde, **15** (9.64 g, 15.9 mmol) was deprotected according to the published method. The trialH<sub>2</sub> ligand, **16**, was obtained as a viscous brown oil: 8.86 g (~100%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.80 (m, 2H), 2.22 (s, 6H), 2.52 (t,  $J = 7.2$  Hz, 4H), 3.66 (s, 4H), 3.73 (m, 4H), 7.08 (s, 2H), 7.12 (t,  $J = 6.1$  Hz, 2H), 7.21 (m, 2H), 7.31 (s, 2H), 7.58 (t,  $J = 7.5$  Hz, 2H), 8.46 (d,  $J = 4.3$  Hz, 2H), 10.18 (s, 2H).

**Monometallic Complexes.** [Co(trial)]PF<sub>6</sub>. To the crude trialH<sub>2</sub>, **16**, (8.50 g, 15.4 mmol) in ethanol (30 mL), was added Et<sub>3</sub>N (4.29 mL, 30.8 mmol) and Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (3.91 g, 15.4 mmol) in ethanol (30 mL). An orange solid rapidly precipitated. The mixture was stirred for 1 h. The solid was then collected and was washed with ethanol (3 × 10 mL), Et<sub>2</sub>O (2 × 10 mL), and pentane (2 × 10 mL) and was dried under a stream of nitrogen. The crude [Co(trial)] was obtained as an air-stable orange solid (3.09 g). To a stirred suspension of the [Co(trial)] (0.251 g, 0.411 mmol) in CH<sub>3</sub>CN (10 mL) was added [Cp<sub>2</sub>Fe]PF<sub>6</sub> (0.152 g, 0.458 mmol) in CH<sub>3</sub>CN (5 mL). The initial orange suspension turned dark green-brown immediately on addition of [Cp<sub>2</sub>Fe]PF<sub>6</sub>. The reaction mixture was stirred for 1 h and was filtered through Celite. The filtrate was concentrated to dryness. The product was triturated with Et<sub>2</sub>O (3 × 10 mL) in order to remove Cp<sub>2</sub>Fe. The residue was collected and was washed with ethanol (2 × 3 mL), Et<sub>2</sub>O (2 × 5 mL), and pentane (2 × 5 mL) and was dried under vacuum. The mixture of isomers of [Co(trial)]PF<sub>6</sub> was obtained as a dark brown solid (0.31 g, 100%). The <sup>1</sup>H NMR spectrum is discussed in the text.

[Co(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. To a stirred suspension of [Co(trial)] (0.56 g, 0.92 mmol) in ethanol (25 mL) was added dropwise over 1 h a solution of 1,3-diaminopropane (76.7  $\mu$ L, 0.92 mmol) and acetic acid (105  $\mu$ L, 1.84 mmol) in ethanol (17 mL). Thirty minutes after the addition was complete, all of the starting material had dissolved. The resulting dark red brown solution was stirred for 3.5 h. A filtered solution of NH<sub>4</sub>PF<sub>6</sub> (0.37 g, 2.30 mmol) in ethanol (8 mL) was added to the solution. An orange solid precipitated almost immediately. The solid was collected and was washed with ethanol (2 × 10 mL), Et<sub>2</sub>O (2 × 5 mL), and pentane (2 × 5 mL). It was dried under a stream of argon. The orange powder was recrystallized from CH<sub>3</sub>CN–ethanol. The [Co(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (0.57 g, 66%) was obtained as orange needles.  $\Delta_M = 283$  cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>. Anal. Calcd for C<sub>36</sub>H<sub>42</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Co: C, 46.01; H, 4.51; N, 8.95; Co, 6.27. Found: C, 45.99; H, 4.57; N, 8.92; Co, 5.97.

[Zn(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. The [Zn(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was prepared by the same method used for [Co(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, except an additional 2 equiv of acetic acid was added to the ethanolic suspension of [Zn(trial)] in the cyclization. The [Zn(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (0.71 g, 66%) was obtained as yellow plates from CH<sub>3</sub>CN–ethanol. Crystals suitable for X-ray crystal structure determination were grown by vapor diffusion of Et<sub>2</sub>O into a CH<sub>3</sub>CN solution of the complex.  $\Delta_M = 291$  cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  2.16 (m, 2H), 2.21 (s, 6H), 2.27 (m, 2H), 2.91 (m, 2H), 2.99 (m, 2H), 3.32 (d,  $J = 12.3$  Hz, 2H), 3.66 (d,  $J = 17.2$  Hz, 2H), 3.85 (m, 4H), 4.26 (m, 4H), 6.86 (d,  $J = 7.8$  Hz, 2H), 6.92 (s, 2H), 7.20 (t,  $J = 6.2$  Hz, 2H), 7.33 (s, 2H), 7.60 (t,  $J = 7.8$  Hz, 2H), 8.14 (d,  $J = 12.1$  Hz, 2H), 8.68 (d,  $J = 4.4$  Hz, 2H), 12.43 (br s, 2H). Anal. Calcd for C<sub>36</sub>H<sub>42</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Zn: C, 45.70; H, 4.48; N, 8.88; Zn, 6.91. Found: C, 46.04; H, 4.40; N, 9.01; Zn, 6.90.

**Bimetallic Complexes.** The bimetallic complexes in this paper were synthesized by two general methods.

**Method 1.** To a solution of the appropriate monometallic cyclized complex, [M(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, (0.100 mmol) in CH<sub>3</sub>CN (2.5 mL) was added a solution of the metal acetate (0.100 mmol) in ethanol (5 mL). The mixture was stirred for 10 min. The solution was partially concentrated at room temperature to reduce the CH<sub>3</sub>CN content, and ethanol was added in portions (2 × 5 mL). The solid was collected and was washed with ethanol (2 × 5 mL), Et<sub>2</sub>O (2 × 3 mL), and pentane (2 × 3 mL) and was dried under a stream of nitrogen.

**Method 2.** To a solution of the appropriate monometallic cyclized complex, [M(cytim)(H<sup>+</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, (0.100 mmol) in CH<sub>3</sub>CN (2.5 mL) was added Et<sub>3</sub>N (0.200 mmol) followed by a solution of the metal chloride (0.100 mmol) in ethanol (5 mL). The mixture was stirred for 10 min, after which it was partially concentrated at room temperature and was enriched in ethanol as in method 1. The solid was collected and was washed with ethanol (2 × 5 mL), Et<sub>2</sub>O (2 × 3 mL), and pentane (2 × 3 mL) and was dried under a stream of nitrogen.

**Purification.** All bimetallic complexes were purified by recrystallization from CH<sub>3</sub>CN–ethanol. The crude salt was dissolved in a minimal volume of CH<sub>3</sub>CN (~2 mL for ~0.15 g of complex) at room temperature and the solution was filtered. To the CH<sub>3</sub>CN solution was added absolute ethanol (~5 mL). A steady stream of nitrogen was passed over the solution in order to reduce the CH<sub>3</sub>CN content, and additional aliquots of ethanol (~3 × 3 mL) were added over time. The solution was typically allowed to stand overnight. The crystalline complex was then collected and washed with ethanol (3 × 3 mL), Et<sub>2</sub>O (2 × 3 mL), and pentane (2 × 3 mL) and was dried under high vacuum for 5–6 h. Reported yields are after recrystallization.

[Zn(cytim)Zn(OAc)]PF<sub>6</sub>. The complex was prepared by method 2, except Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O was used instead of ZnCl<sub>2</sub>. Recrystallization typically took several days yielding pale yellow crystals. Yield: 36%.  $\Delta_M = 116$  cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.65 (s, 3H), 1.92 (m, 6H), 2.17 (s, 3H), 2.24 (s, 3H), 2.80 (m, 2H), 3.06 (m, 2H), 3.54 (m, 4H), 4.23 (m, 6H), 6.76 (m, 2H), 7.07 (m, 4H), 7.34 (m, 2H), 7.53 (m, 1H), 7.88 (m, 2H), 8.08 (s, 1H), 8.53 (d,  $J = 3.9$  Hz, 1H), 9.09 (d,  $J = 2.0$  Hz, 1H). Anal. Calcd for C<sub>38</sub>H<sub>43</sub>N<sub>6</sub>O<sub>4</sub>PF<sub>6</sub>Zn<sub>2</sub>: C, 49.41; H, 4.70; N, 9.10; Zn, 14.16. Found: C, 49.62; H, 4.98; N, 9.32; Zn, 14.18. Crystals suitable for X-ray crystal structure determination were obtained by crystallizing the product first from CH<sub>3</sub>CN–methanol followed by recrystallization by vapor diffusion of Et<sub>2</sub>O into a CH<sub>3</sub>CN solution of the complex. Anal. Calcd for C<sub>38</sub>H<sub>43</sub>N<sub>6</sub>O<sub>4</sub>PF<sub>6</sub>Zn<sub>2</sub>·MeOH: C, 49.01; H, 4.97; N, 8.80. Found: C, 49.00; H, 5.05; N, 9.09.

[Zn(cytim)ZnCl]PF<sub>6</sub>. The complex was prepared by method 2. Recrystallization typically took several days, yielding pale yellow crystals. Yield: 95%.  $\Delta_M = 123$  cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.40 (m, 1H), 2.13 (m, 5H), 2.17 (s, 3H), 2.23 (s, 3H), 2.83 (m, 2H), 3.10 (m, 2H), 3.59 (m, 4H), 4.18 (m, 6H), 6.72 (s, 1H), 6.79 (d,  $J = 7.8$  Hz, 1H), 7.07 (m, 4H), 7.31 (d,  $J = 7.8$  Hz, 1H), 7.40 (t,  $J = 6.1$  Hz, 1H), 7.53 (t,  $J = 7.4$  Hz, 1H), 7.87 (m, 2H), 8.08 (s, 1H), 8.49 (d,  $J = 4.7$  Hz, 1H), 9.35 (d,  $J = 4.6$  Hz, 1H). Anal. Calcd for C<sub>36</sub>H<sub>40</sub>N<sub>6</sub>O<sub>2</sub>PF<sub>6</sub>ClZn<sub>2</sub>· $\frac{1}{2}$ C<sub>2</sub>H<sub>6</sub>O (confirmed by <sup>1</sup>H NMR): C, 48.14; H, 4.71; N, 9.11; Cl, 3.84; Zn, 14.16. Found: C, 48.10; H, 4.80; N, 8.93; Cl, 3.98; Zn, 15.07.

[Zn(cytim)Zn](PF<sub>6</sub>)<sub>2</sub>. In an NMR tube, solid AgPF<sub>6</sub> (7.4 mg, 29  $\mu$ mol) was added to [Zn(cytim)ZnCl]PF<sub>6</sub> (21.8 mg, 24  $\mu$ mol) in CD<sub>2</sub>Cl<sub>2</sub> (0.6 mL), and the resultant mixture was shaken to precipitate AgCl. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.11 (m, 2H), 2.24 (s, 6H), 2.32 (m, 2H), 2.66 (m, 2H), 2.93 (m, 2H), 3.38 (d,  $J = 12.6$  Hz, 2H), 3.81 (m, 2H), 3.98 (m, 4H), 4.18 (d,  $J = 17.5$  Hz, 2H), 4.34 (d,  $J = 12.4$  Hz, 2H), 6.96 (s, 2H), 7.06 (d,  $J = 7.8$  Hz, 2H), 7.17 (d,  $J = 2.0$  Hz, 2H), 7.26 (t,  $J = 6.3$  Hz, 2H), 7.69 (t,  $J = 8.4$  Hz, 2H), 8.09 (s, 2H), 8.69 (d,  $J = 4.8$  Hz, 2H).

[Zn(cytim)Cu](PF<sub>6</sub>)<sub>2</sub>. The complex was prepared by method 1, except methanol was substituted for ethanol in the reaction. Recrystallization from CH<sub>3</sub>CN–ethanol produced fine brown needles. Yield: 74%.  $\Delta_M = 284$  cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>. Anal. Calcd for C<sub>36</sub>H<sub>40</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>ZnCu: C, 42.91; H, 4.01; N, 8.34; Zn, 6.49; Cu, 6.31. Found: C, 42.95; H, 4.02; N, 8.25; Zn, 6.50; Cu, 6.23.

[Zn(cytim)CoCl]PF<sub>6</sub>. The complex was prepared by method 2. Large brown needles were obtained after recrystallization. Yield: 52%.  $\Delta_M = 121$  cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>. Anal. Calcd for C<sub>36</sub>H<sub>40</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>ZnCo·C<sub>2</sub>H<sub>6</sub>O: C, 48.57; H, 4.81; N, 8.95; Cl, 3.77; Zn, 6.96; Co, 6.27. Found: C, 48.45; H, 4.92; N, 8.90; Cl, 3.60; Zn, 7.13; Co, 6.67.

[Co(cytim)ZnCl]PF<sub>6</sub>. The complex was prepared by method 2. Recrystallization typically took several days, yielding orange crystals. Yield: 29%.  $\Delta_M = 123$  cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>. Anal. Calcd for C<sub>36</sub>H<sub>40</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>CoZn· $\frac{1}{2}$ C<sub>2</sub>H<sub>6</sub>O: C, 48.48; H, 4.73; N, 9.17; Cl, 3.87; Co, 6.43; Zn, 7.13. Found: C, 48.60; H, 4.81; N, 9.50; Cl, 3.76; Co, 6.67; Zn, 7.56.

[Co(cytim)Cu](PF<sub>6</sub>)<sub>2</sub>. The complex was prepared by method 1. Fine brown needles were obtained after recrystallization. Yield: 69%.  $\Delta_M = 270$  cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>. Anal. Calcd for C<sub>36</sub>H<sub>40</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>CoCu: C, 43.18; H, 4.04; N, 8.40; Co, 5.88; Cu, 6.35. Found: C, 43.81; H, 4.24; N, 8.37; Co, 5.91; Cu, 6.44.

[Co(cytim)CoCl]PF<sub>6</sub>. The complex was prepared by method 2. Large red-brown needles were obtained after recrystallization. Yield: 66%.  $\Delta_M = 123$  cm<sup>2</sup>  $\Omega^{-1}$  mol<sup>-1</sup>. Anal. Calcd for C<sub>36</sub>H<sub>40</sub>N<sub>6</sub>O<sub>2</sub>PF<sub>6</sub>ClCo<sub>2</sub>·C<sub>2</sub>H<sub>6</sub>O: C, 48.90; H, 4.98; N, 9.01; Cl, 3.80; Co, 12.63. Found: C, 48.90; H, 5.03; N, 8.98; Cl, 3.44; Co, 13.26.

**Ligand Preparation (enacH<sub>4</sub> and tnacH<sub>4</sub>).** 2,2-Dimethyl-4-oxo-8-methylbenzo-1,3-dioxin (7). From the acid chloride, 6,<sup>5a</sup> the acetonide, 7, was synthesized by the method of Al-Rawi and Al-Shahiry.<sup>5b</sup>

**1,6-Bis(2-pyridyl)-2,5-bis(2-hydroxy-3-carboxybenzyl)-2,5-diazahexane (enacH<sub>4</sub>) (9a).** The acetonide, 7 (14.17 g, 73.7 mmol), *N*-bromo-

succinimide (13.20 g, 74.2 mmol), and azobis(isobutyronitrile) (0.60 g, 3.68 mmol) in  $\text{CCl}_4$  (200 mL) were refluxed for 5 h. The hot suspension was filtered and concentrated under reduced pressure to ~30 mL and was cooled at  $-25^\circ\text{C}$  for 24 h. The slurry was then filtered cold, and the white crystalline solid was washed with cold  $\text{CCl}_4$  ( $2 \times 5$  mL) and pentane ( $2 \times 5$  mL). The crude product was recrystallized from  $\text{CH}_2\text{Cl}_2$ -cyclohexane, yielding the bromide, **8** (9.19 g), as a white crystalline solid. A second crop was obtained from the filtrates and was similarly recrystallized (1.54 g). The total yield was 10.73 g (49%) [ $^1\text{H}$  NMR showed that 1.11 g of succinimide was present.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.79 (s, 6H), 4.48 (s, 2H), 7.10 (t,  $J = 7.7$  Hz, 1H), 7.60 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.94 (dd,  $J = 7.8, 1.7$  Hz, 1H)]. The mixture of succinimide and the bromide, **8** (9.62 g, 35.6 mmol), was reacted with 1,6-bis(2-pyridyl)-2,5-diazahexane<sup>24</sup> (4.31 g, 17.8 mmol) and anhydrous  $\text{Na}_2\text{CO}_3$  (19.17 g, 181.0 mmol) in dry THF (100 mL) under nitrogen. The stirred mixture was heated to reflux for 1 h and then stirred at room temperature for 24 h. The reaction mixture was filtered through Celite and was concentrated to a brown oil. The oil was dissolved in benzene- $\text{Et}_2\text{O}$  (135 mL-25 mL) and aqueous HCl (1 N, 112 mL) was added dropwise to the stirred solution at  $0^\circ\text{C}$ . The layers were then separated, and the aqueous phase was further extracted with benzene- $\text{Et}_2\text{O}$  ( $3 \times 70$  mL-15 mL). The aqueous layer was taken to pH ~7 with aqueous NaOH (1.00 N) and then to pH ~8 with solid  $\text{NaHCO}_3$ . It was then extracted with  $\text{CH}_2\text{Cl}_2$  ( $4 \times 100$  mL). The extracts were dried over  $\text{Na}_2\text{SO}_4$  and filtered and were concentrated under reduced pressure to give the crude coupled product as a viscous brown oil (11.39 g). The oil was purified on a short column (neutral alumina, activity I, 110 g,  $\text{CH}_2\text{Cl}_2$ ). Pure product was obtained by eluting with  $\text{CH}_2\text{Cl}_2$  as a yellow oil (9.50 g, 84%) [ $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.65 (s, 12H), 2.71 (s, 4H), 3.59 (s, 4H), 3.73 (s, 4H), 6.98 (t,  $J = 7.6$  Hz, 2H), 7.09 (t,  $J = 6.0$  Hz, 2H), 7.34 (d,  $J = 7.8$  Hz, 2H), 7.52 (t,  $J = 7.9$  Hz, 2H), 7.60 (d,  $J = 7.3$  Hz, 2H), 7.80 (d,  $J = 7.8$  Hz, 2H), 8.44 (d,  $J = 4.7$  Hz, 2H)]. To this product (9.50 g, 15.2 mmol) in methanol (45 mL) was added aqueous NaOH (1.00 N standardized, 130.00 mL, 130.0 mmol), generating a white gummy precipitate. The mixture was stirred at  $75^\circ\text{C}$  for 3 h. The resultant red-brown solution was cooled to  $0^\circ\text{C}$  and was exactly neutralized with aqueous HCl (2.01 N standardized, 64.71 mL, 130.0 mmol). The resultant pale yellow solution was concentrated to dryness under reduced pressure. The solid residue was dissolved in methanol (35 mL), and ethanol (45 mL) was added, precipitating NaCl. The slurry was kept at  $5^\circ\text{C}$  for 24 h, and then the solid NaCl (6.97 g, 119.0 mmol) was removed by filtration. The filtrate was concentrated under reduced pressure to a yellow foam, **9a** (7.48 g, 91%).  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ , DCl):  $\delta$  3.09 (s, 4H), 3.57 (s, 4H), 4.13 (s, 4H), 6.33 (t,  $J = 7.1$  Hz, 2H), 6.89 (d,  $J = 7.3$  Hz, 2H), 7.11 (d,  $J = 7.9$  Hz, 2H), 7.42 (t,  $J = 6.0$  Hz, 2H), 7.51 (d,  $J = 7.9$  Hz, 2H), 7.93 (t,  $J = 7.8$  Hz, 2H), 8.18 (d,  $J = 5.3$  Hz, 2H).

**1,7-Bis(2-pyridyl)-2,6-bis(2-hydroxy-3-carboxybenzyl)-2,6-diazahexane (tnacH<sub>4</sub>) (9b).** The diacid ligand tnacH<sub>4</sub> was synthesized by the same method as enacH<sub>4</sub> except 1,7-bis(2-pyridyl)-2,6-diazahexane was used in the coupling reaction. To the bis(acetonide) (1.95 g, 3.06 mmol) in methanol (20 mL) was added aqueous NaOH (1.00 N standardized, 27.00 mL, 27.0 mmol). The solution was cooled to  $0^\circ\text{C}$  and was exactly neutralized with aqueous HCl (2.04 N, 13.25 mL, 27.0 mmol). The resultant solution was concentrated to dryness under reduced pressure. Since the ligand was insoluble in common organic solvents, the solid residue was suspended in cold water (5 mL,  $5^\circ\text{C}$ ) and was sonicated to dissolve the NaCl. The remaining solid was washed with cold water ( $1 \times 3$  mL) and  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and was dried in a vacuum desiccator. The ligand **9b** was obtained as a white solid (42%).  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ , DCl):  $\delta$  2.77 (m, 2H), 3.68 (t,  $J = 7.7$  Hz, 4H), 4.68 (s, 4H), 5.06 (s, 4H), 6.99 (t,  $J = 7.8$  Hz, 2H), 7.65 (d,  $J = 7.3$  Hz, 2H), 7.82 (d,  $J = 7.9$  Hz, 2H), 8.11 (d,  $J = 6.9$  Hz, 2H), 8.31 (d,  $J = 8.0$  Hz, 2H), 8.63 (t,  $J = 8.0$  Hz, 2H), 8.85 (d,  $J = 5.8$  Hz, 2H).

**Monometallic Complexes.**  $[\text{Co}(\text{tnacH}_2)]\text{PF}_6$ . To a suspension of tnacH<sub>4</sub>, **9b** (0.50 g, 0.90 mmol), in DMSO (1.5 mL) was added a solution of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.22 g, 0.90 mmol) in DMSO (1.5 mL). The resulting mixture was heated at  $\sim 100^\circ\text{C}$  until the solid material had dissolved to give a brown solution. Upon cooling, a rust-colored solid precipitated.

Ethanol (20 mL) was added to the reaction mixture. The suspension was stirred for 30 min. The solid was collected and was washed with ethanol ( $3 \times 15$  mL),  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL), and pentane ( $2 \times 5$  mL) and then was dried under a stream of nitrogen. To a suspension of  $[\text{Co}(\text{tnacH}_2)]$  in  $\text{CH}_3\text{CN}$  (10 mL) was added  $[\text{Cp}_2\text{Fe}]\text{PF}_6$  (0.31 g, 0.93 mmol) in  $\text{CH}_3\text{CN}$  (5 mL). The solid material dissolved rapidly to produce a dark green solution. The solution was stirred for 30 min. It was filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was triturated with  $\text{Et}_2\text{O}$  ( $3 \times 5$  mL) to remove  $\text{Cp}_2\text{Fe}$ . The resultant solid was washed with ethanol ( $4 \times 10$  mL),  $\text{Et}_2\text{O}$  ( $3 \times 5$  mL), and pentane ( $2 \times 5$  mL) and was dried under vacuum. The green powder was recrystallized from  $\text{CH}_3\text{CN}$ -ethanol. The  $[\text{Co}(\text{tnacH}_2)]\text{PF}_6$  (0.34 g, 50%) was obtained as fine dark green needles.  $\Delta_M = 120 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  2.77 (m, 2H), 2.91 (m, 2H), 3.29 (d,  $J = 14.0$  Hz, 2H), 3.72 (m, 2H), 4.01 (d,  $J = 14.0$  Hz, 2H), 4.41 (d,  $J = 16.6$  Hz, 2H), 5.18 (d,  $J = 16.6$  Hz, 2H), 6.59 (t,  $J = 7.6$  Hz, 2H), 6.99 (d,  $J = 7.0$  Hz, 2H), 7.27 (t,  $J = 6.7$  Hz, 2H), 7.40 (dd,  $J = 7.9, 1.5$  Hz, 2H), 7.62 (d,  $J = 7.8$  Hz, 2H), 7.93 (dt,  $J = 7.7, 1.1$  Hz, 2H), 8.06 (d,  $J = 5.8$  Hz, 2H), 12.44 (s, 2H). Anal. Calcd for  $\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_6\text{PF}_6\text{Co}$ : C, 49.08; H, 3.99; N, 7.39; Co, 7.77. Found: C, 48.73; H, 4.18; N, 7.25; Co, 7.64.

$[\text{Co}(\text{enacH}_2)]\text{PF}_6$ . This complex was prepared by the same method used for  $[\text{Co}(\text{tnacH}_2)]\text{PF}_6$  except no heating was required to dissolve the ligand enacH<sub>4</sub> in DMSO. The  $[\text{Co}(\text{enacH}_2)]\text{PF}_6$  was obtained as fine maroon crystals after recrystallization from  $\text{CH}_3\text{CN}$ -ethanol (72%).  $\Delta_M = 125 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  3.39 (m, 4H), 3.63 (d, 15.1 Hz, 2H), 3.72 (d, 14.9 Hz, 2H), 4.52 (d, 19.0 Hz, 2H), 4.69 (d, 18.6 Hz, 2H), 6.83 (t,  $J = 7.6$  Hz, 2H), 7.27 (d,  $J = 7.4$  Hz, 2H), 7.39 (d,  $J = 7.8$  Hz, 2H), 7.52 (t,  $J = 6.7$  Hz, 2H), 7.83 (dd,  $J = 7.8, 1.8$  Hz, 2H), 7.99 (t,  $J = 7.7$  Hz, 2H), 8.48 (d,  $J = 5.9$  Hz, 2H), 13.89 (s, 2H). Anal. Calcd for  $\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_6\text{PF}_6\text{Co}$ : C, 48.39; H, 3.80; N, 7.53; Co, 7.92. Found: C, 48.96; H, 3.86; N, 7.34; Co, 7.20.

**X-ray Structure Determinations.** Both the yellow-green crystals of  $[\text{Zn}(\text{cytim})(\text{H}^+)_2](\text{PF}_6)_2$ , **I**, and the yellow crystals of  $[\text{Zn}(\text{cytim})\text{Zn}(\text{OAc})]\text{PF}_6 \cdot \text{MeOH}$ , **II**, were obtained by vapor diffusion of ether into acetonitrile solutions and were mounted on glass fibers with epoxy. Crystallographic data are collected in Table 1. The unit cell parameters were obtained from a least-squares fit of 24 reflections ( $18 \leq 2\theta < 23^\circ$ ) for both compounds. Photographic characterization revealed  $\bar{1}$  Laue symmetry for **I** and  $2/m$  Laue symmetry for **II**. The chemically sensible results of refinement established the space group as  $P\bar{1}$  for **I** and systematic absences in the diffraction data suggested either of the monoclinic space groups  $Cc$  or  $C2/c$  for **II**, but only the former is compatible with the chirality of the complex. To reduce the obtuse  $\beta$  angle in **II**, the cell was transformed to the space group  $Ia$ . Both crystals were well formed and  $\psi$  scans showed little variation in absorption; no absorption correction was applied for either crystal.

Both structures were solved by direct methods, which located the Zn atoms, and completed by difference Fourier synthesis. All non-hydrogen atoms in **I** were refined with anisotropic thermal parameters; in **II** the carbon atoms as well as the oxygen atom, O(50), in an assumed MeOH solvent molecule were refined isotropically due to the small number of observed reflections. The two-atom molecule in complex **II**, O(50) and C(50), was well separated from other atoms in the structure; high thermal parameters and bond lengths indicate that the solvent molecule is disordered. A Rogers test,  $\eta = 1.23(15)$ , indicated that the assigned absolute configuration of **II** is correct. The  $\text{PF}_6$  counterions in both structures were refined as fixed octahedra with common P-F bond distances which refined to 1.55 Å in **I** and 1.50 Å in **II**. In both structures, the hydrogen atoms were treated as idealized, updated isotropic contributions. Computations were made with the SHELXTL PLUS (4.27) program library (G. Sheldrick, Siemens, Madison, WI).

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**Supplementary Material Available:** Tables of detailed crystallographic data for **I** and **II**, including crystal and structure refinement data, atomic coordinates, bond lengths, bond angles, anisotropic displacements, and hydrogen atom parameters (23 pages). Ordering information is given on any current masthead page.