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Invited Contribution from Recipient of ACS Award in Inorganic Chemistry

Cooperative Bimetallic Redox Reactivity†

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Binucleating ligands possessing contiguous 6-coordinate and 4-coordinate sites are described, and the redox properties of their bimetallic complexes have been investigated. The design of the two parts of these ligands is based on the redox and reactivity patterns of the corresponding monometallic complexes. If the two sites were to behave as they do in the corresponding monometallic complexes, these bimetallic complexes would be expected to bind a substrate, such as dioxygen, and to reduce it by two electrons, one from each metal, as occurs in the respiratory protein, hemerythrin. This was found not to be the case. In these bimetallic complexes, oxidation of one metal leads to the deactivation of the other metal to oxidation. The origins of this mutual deactivation appear to be connected with ligand reorganization, through-bond electronic coupling, and electrostatic interactions between neighboring metals. It is suggested that, in the systems described, ligand reorganization is the dominant deactivating effect. It is shown that, in a bimetallic system where these deactivating effects are minimized, substrates can be added to the 4-coordinate metal and cause oxidation of both metals. The development of these types of systems could lead to new oxidative addition reactions and to the evolution of new catalysts.

Introduction

It has long been anticipated that suitably designed multimetallic complexes could provide distinct reactivity patterns different from those shown by analogous monometallic systems. In particular, the reducing power of multimetallic systems is expected to be greater simply because each of the metals could contribute to the reduction process within their normally accessible oxidation states. The classical bimetallic dioxygen complexes of cobalt(III) are examples where each of the starting cobalt(II) ions contributes one electron to O_2 to form peroxide bridging complexes.[1] There are numerous dimeric complexes of this kind with various metals, and this behavior has been exploited in ingenious ways especially with face-to-face iron porphyrin complexes.[2] In all of these cases, the dioxygen ligand is bound to both of the metals as is the case in the respiratory protein, hemocyanin.[3] What has not been reproduced in a synthetic bimetallic system is the circumstance where dioxygen is bound to one of the metals but is reduced by two electrons, one electron from each of the metals, to form a peroxide ligand bound to one metal. As will be discussed presently, such one-site addition two-metal reductions could provide important new reactivity patterns.

Brice Bosnich, a native of Australia, obtained his undergraduate degree at the University of Sydney and his Ph.D. at the Australian National University. He has held posts at University College, London, and at the University of Toronto and is now at the University of Chicago. His work has spanned both coordination and organometallic chemistry; a common theme of his endeavors is an interest in inorganic stereochemistry. This has led him to develop relationships between circular dichroism and absolute configurations and to conduct studies in diastereoselective complexation and in molecular mechanics of organometallic complexes. His work on asymmetric catalysis was a continuation of this theme and led to the development of new catalysts, which displayed high selectivity based on an understanding of the mechanisms of catalysis. His current interests are in cooperative bimetallic reactivity and in supramolecular recognition.

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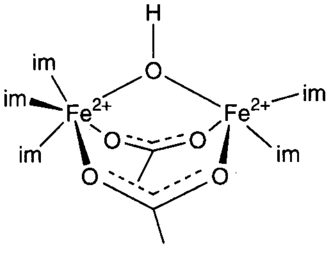
A known example of the above reactivity is found in the respiratory protein, hemerythrin.[4] The active site of this protein consists of a dimeric iron complex, where the two iron atoms are bridged by two acetate ligands and one hydroxide ligand, one iron has, additionally, three imidazole ligands, and the other has two imidazole ligands, **1**. Thus, one iron atom is 6-coordinate and the other is 5-coordinate. In the process of dioxygen uptake, the initial Fe(II)−Fe(II) complex is transformed to an Fe(III)−Fe(III)−hydroperoxide species.[5] These simple observations belie the potential complexity of the process. Since the two electrons will be transferred to the dioxygen molecule sequentially, there must exist a superoxide intermediate bound to an Fe(III) iron of a mixed-valence complex. Presumably this superoxide intermediate interacts with the proton of the hydroxide bridge. Such hydrogen bonding may be crucial in inducing the second electron transfer step from the (6-coordinate) Fe(II) to the superoxide ligand. The rate of electron transfer depends on the reorganizational energy, the driving force, and the coupling between the two centers.[6] The coupling need only be a few wavenumbers, but the reorganizational energy can be large and, to some extent, is offset by the driving force. It could be argued that transferring the proton from the hydroxyl bridge to the dioxygen ligand to give an oxo bridge will increase the driving force for electron transfer. If this is so, the second electron transfer event could be triggered by the proton transfer. An outline of the presumed process is illustrated in eq 1. It is not clear, however, whether the proton transfer is crucial for the second electron transfer or whether the proton transfer serves to stabilize the end-on peroxide ligand. One is inclined to suppose that both are important in the dioxygen uptake in hemerythrin.



im is imidazole

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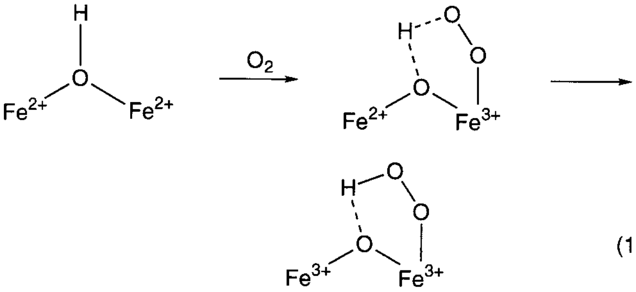
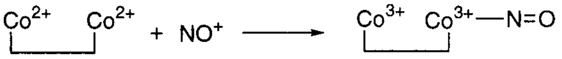


(1)

The ability of hemerythrin to act as a one-site addition two-electron reductant has led us to inquire whether such behavior could be reproduced as a general phenomenon with suitably designed bimetallic complexes. Such systems need not include the structural elements found in hemerythrin, nor do they require the same ligands or metals to be incorporated, and the substrates need not be restricted to dioxygen. Three examples of these possibilities, among many, are illustrated in eqs 2, 3, and 4.



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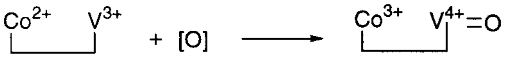

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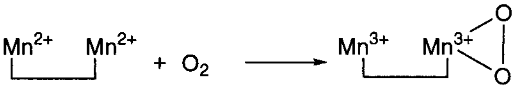
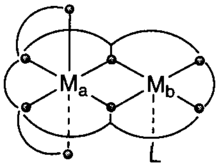


(4)

In each of these examples, the substrate is a two-electron oxidant which is reduced by both of the metals although the substrate resides on only one metal. This behavior, were it achieved, would represent a new form of oxidative addition. Whereas classical oxidative addition involves two-electron oxidation of a single metal, the systems in question involve one-electron oxidation of each of the two metals. It is clear that, with the appropriate multimetallic system, more than two electrons could be used to reduce the substrate. For example, appropriate metal combinations could be used for four-electron reductions of dioxygen to give dioxo complexes. Such systems have clear implications for catalytic oxidation using molecular oxygen. A further advantage of the oxidative addition reactions of the types illustrated in eqs 2−4 is that the metals can be chosen for particular tasks. Thus, in the case of eq 3, the vanadium serves the dual purpose of providing a stable oxo complex and of providing an electron. Were the site occupancies reversed, no stable oxo complex would form even if two-electron oxidation of the metals were to occur. It is not difficult to imagine other designed systems which could serve in a similar manner for other substrates and metals.

Strategy

In order to investigate the possibilities of one-site addition two-metal oxidations we constructed a set of binucleating ligands where each of the sites was known to undergo the required reactions in analogous monometallic complexes. In order to ensure that the substrate was directed to the required site, the binucleating ligand had a 6-coordinate site and a contiguous 4-coordinate site, **2**. A binucleating macrocyclic system was employed in order to provide stability for the chosen structure, although this was not a crucial feature of the design. Thus a bimetallic system, **2**, with an axial ligand, L, would be expected to bind the substrate via metal M_b, which could be oxidized, but the substrate could be further reduced by metal M_a, in the 6-coordinate site. Once the architecture of the ligand was determined, the question as to the types of donor ligands necessary to perform the required tasks with a metal set had to be determined. These decisions represented a tradeoff between what is possible and what can easily be made in reasonable quantities. It was decided to incorporate salen type coordinating



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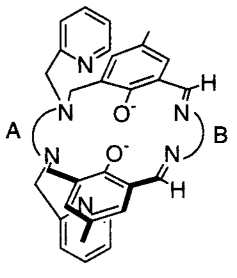
ligands in the 4-coordinate site because metal complexes of this kind are known to form dioxygen[7] and oxo[8] complexes and because the phenolic group could be used to bridge the two metals.[7] Further, the imines of the salen part of the ligand could be reduced to amines and thus would readily provide a new set of ligands. The remaining issue related to the nature of the 6-coordinate donor set. This decision was largely guided by synthetic imperatives. The two types of binucleating ligands that were prepared are shown, **3** and **4**.



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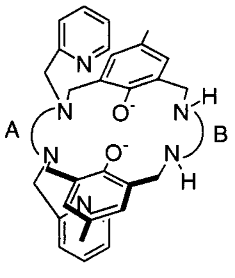

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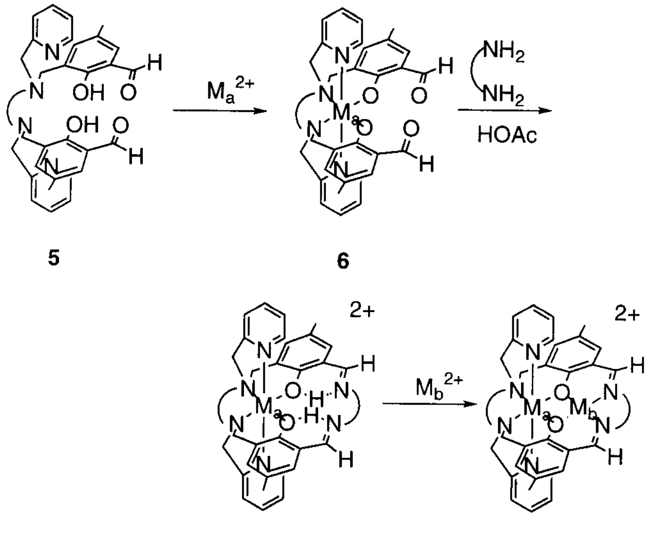
The chelate links A and B can contain two (en) or three (tn) saturated carbon atoms. The nomenclature adopted for these complexes is as follows: the metal in the 6-coordinate site is written first, followed by the binucleating ligand, followed by the metal in the 4-coordinate site, followed by unidentate ligands bound to this latter metal. The ligands are designated as follows: the 6-coordinate link, A, is written first, followed by the B-link, followed by im if imines are present, **3**, or am if amines are incorporated, **4**. Thus, a heterobimetallic complex would be written [Co(entnim)NiCl]$^+$, for example, indicating that Co^{2+} is in the 6-coordinate site, the ligand has a dimethylene A-link and a trimethylene B-link, and imines are present.

Were the redox properties of bimetallic complexes of ligands of the type, **3**, to display properties similar to those of the monometallic analogues, we would expect that the 6-coordinate site would support, among others, the following oxidation states: Fe(II)/Fe(III), Mn(II)/Mn(III), and Co(II)/Co(III). With appropriate metals, the 4-coordinate site is expected to form stable dioxygen, nitrosyl, and oxo ligands in analogy to monometallic complexes of this ligand system. One might therefore be tempted to conclude that a complex of the type [Fe^{2+}(**3**)V^{3+}Cl$_2$]$^+$ would react with an oxo transfer reagent such as iodosobenzene to give [Fe^{3+}(**3**)V^{4+}O]$^{2+}$.

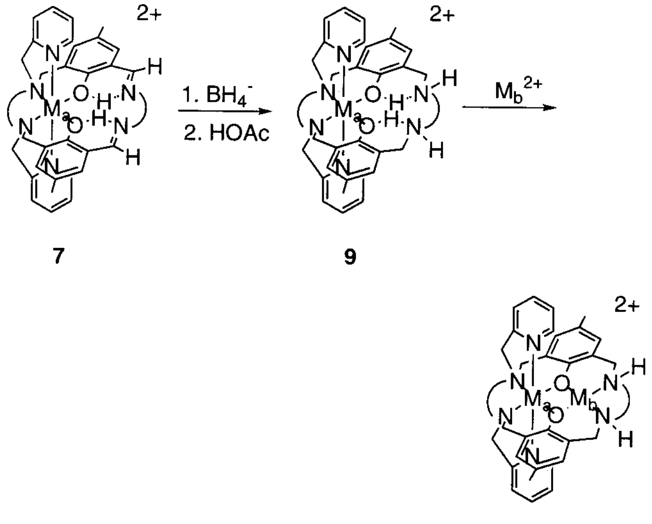
Synthesis

The synthesis of the binucleating ligands, **3** and **4**, begins with the dialdehydes, **5**, which are prepared by standard organic procedures.[10−16] Addition of a divalent metal acetate of the first transition series to **5** gives the insoluble neutral complexes **6**.



5 **6** **7** **8**

When the A-link is en, the structure of **6** is as shown, where the pyridine ligands are trans disposed. But when tn is present, all three geometric isomers of **6** exist in solution as determined by the ^{1}H NMR spectrum of the Zn(II) complex. Reaction of the complexes **6** with diamines in the presence of acetic acid leads to the high-yield (>80% isolated yield) formation of the macrocyclic complexes **7**. The compounds **7** all have the structure shown, where the pyridine ligands are trans disposed, the metal is in the 6-coordinate site, and the 4-coordinate site contains two protons. They were isolated as their PF$_6^-$ salts, as were all of the complexes of the present series. Isolation of the complexes **7** provides materials suitable for mild incorporation of the second metal, **7** → **8**. If due care is taken, site-specific hetereobimetallic complexes can be prepared with little or no site scrambling. Reduction of the diimine complexes, **7**, is readily achieved in high yield by BH$_4^-$ ions probably because the imine groups are activated to reaction by protonation. No reduction of the metal in the 6-coordinate site is observed, and the products are the diprotonated complexes, **9**.



7 **9** **10**

As before, complexes **9** allow for the mild incorporation of the second metal, **9** → **10**. By these methods, we have been able to prepare and isolate complexes with all of the permutations of the en and tn links A and B (**3** and **4**). Thus, the synthetic routes appear to be flexible and general.

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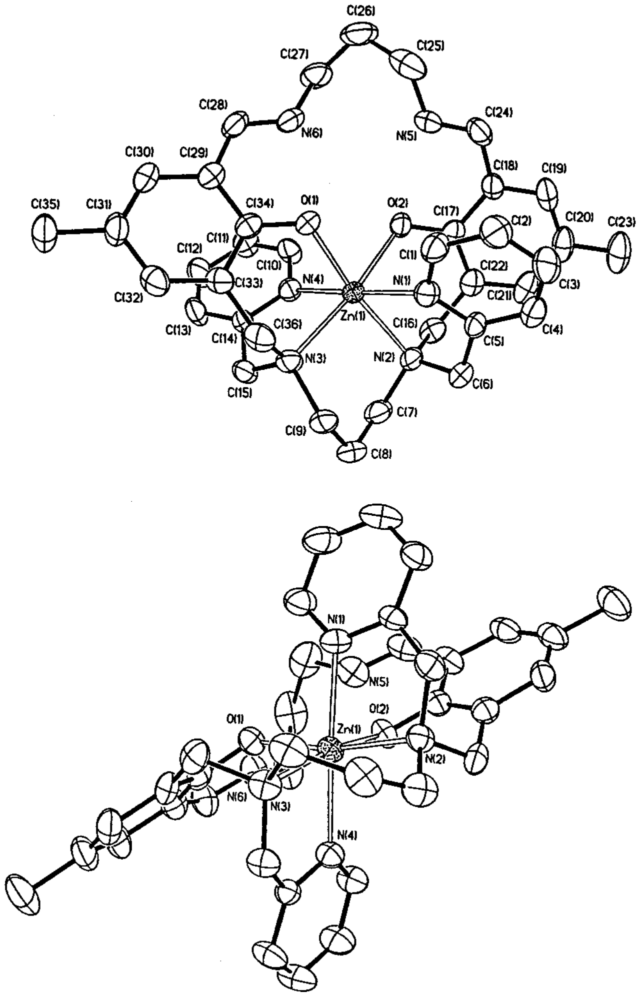


Figure 1. Two perspectives of the structure of the [Zn(tntnim)(H$^+$)$_2$]$^{3+}$ ion. The hydrogen atoms are not shown for clarity. Reproduced with permission from ref 13. Copyright 1994 American Chemical Society.

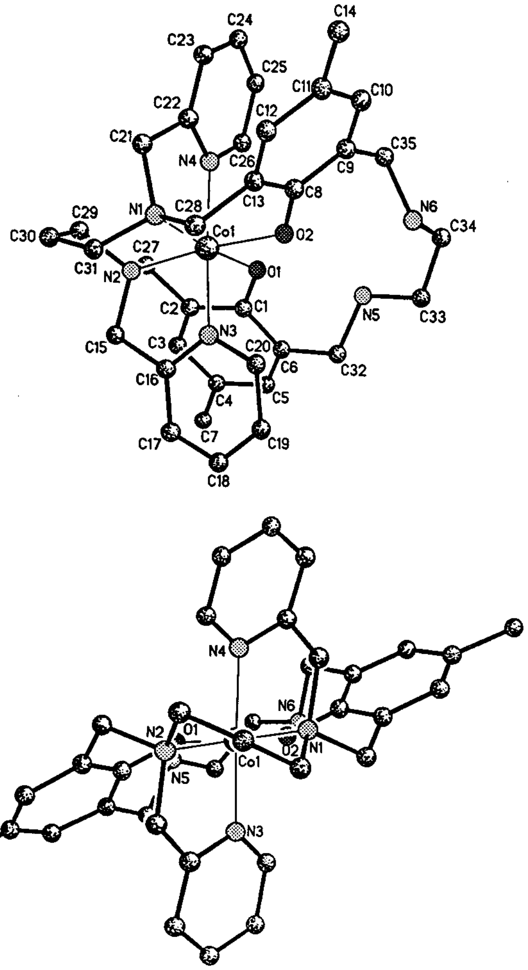


Figure 2. Two perspectives of the structure of the [Co(tnenam)(H$^+$)$_2$]$^{3+}$ ion. The hydrogen atoms are not shown for clarity. Reproduced with permission from ref 15. Copyright 1996 American Chemical Society.

Structures

The structural characteristics of these complexes serve more than to confirm that the correct molecules have indeed been prepared. Certain structural features are crucial for an understanding of their reactivity patterns. Figure 1 shows the structure of [Zn(tntnim)(H$^+$)$_2$] $^{2+}$ in two perspectives. The cavity bearing the two protons, which were not crystallographically determined, is clearly evident with the four donor atoms, two oxygen and two nitrogen atoms, positioned in a twisted square plane. The two pyridine ligands are disposed trans lying above and below the mean macrocyclic plane. The two phenolic groups are highly twisted, leading to the positioning of the two imine nitrogen atoms above and below the mean macrocyclic plane. A similar structure obtains for the complex [Co(tnenam)(H$^+$)$_2$]$^{3+}$, but in this case the oxygen and nitrogen atoms of the cavity are roughly in a square plane, which is a consequence of the reduction of the imine bonds (Figure 2). This reduction allows for greater flexibility of the system.

Different structures are observed in bimetallic complexes depending on whether the 6-coordinate link (A) is en or tn. It appears that bimetallic complexes containing an en A-link are highly strained when the pyridine ligands are trans disposed, and the systems relieve this strain by forming complexes containing cis pyridine ligands. An example of such a structure, the complex [Co(entnim)CoCl]$^+$, is shown in Figure 3. In this structure the two cis pyridine ligands are on the opposite side of the mean macrocyclic plane to the chloro ligand. Systems with an en A-link can be forced to adopt a trans pyridine arrangement by incorporating a stereochemically stable metal such as cobalt(III) in the 6-coordinate site followed by incorporation of the second metal. As noted earlier, all of the monometallic macrocyclic complexes have a trans pyridine geometry irrespective of either link span. Thus oxidation of a cobalt(II) monometallic complex to its cobalt(III) analogue leads to a complex with trans-disposed pyridines which remain in this geometry after the second metal is inserted even if the cavity size is inadequate for accommodating the second metal. An

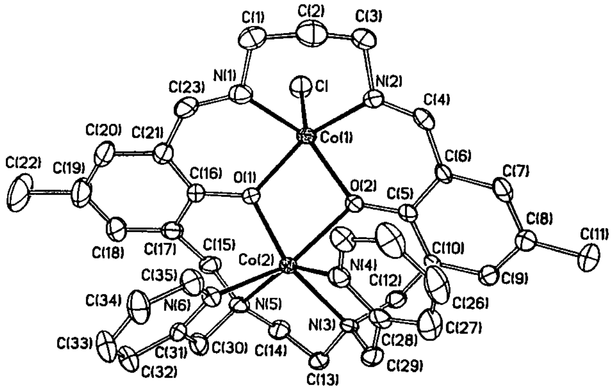


Figure 3. Structure of the [Co(entnam)CoCl]$^+$ ion. The hydrogen atoms are not shown for clarity. Reproduced with permission from ref 10. Copyright 1992 American Chemical Society.

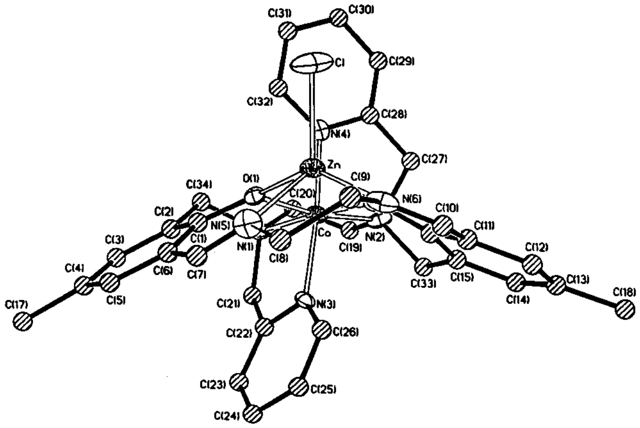


Figure 4. Structure of the [Co(enenim)ZnCl]$^{2+}$ ion. The hydrogen atoms are not shown for clarity. Reproduced with permission from ref 14. Copyright 1994 American Chemical Society.

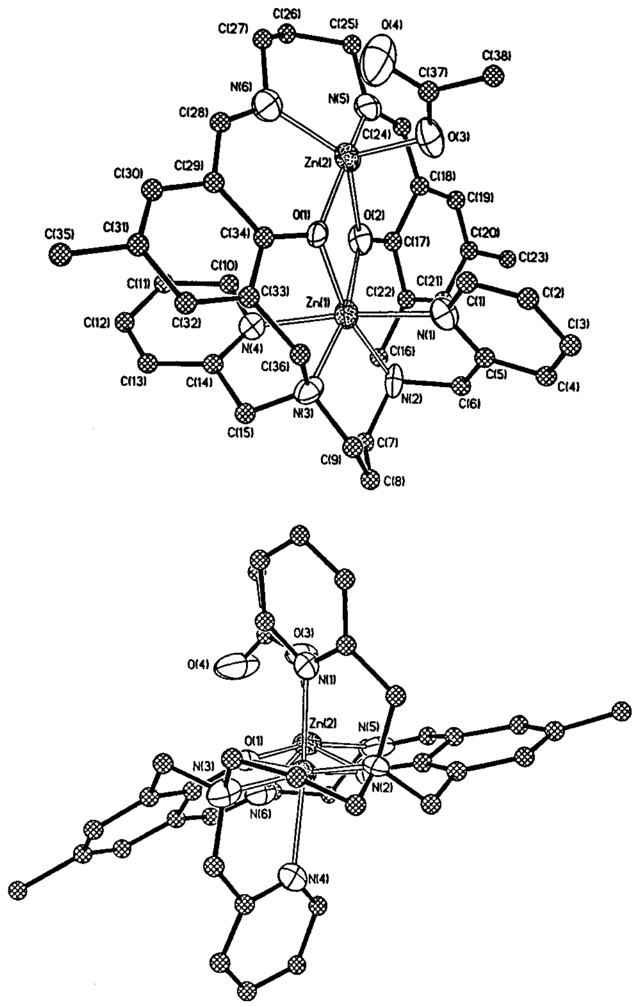


Figure 5. Two perspectives of the structure of the [Zn(tntnim)ZnOAc]$^{+}$ ion. The hydrogen atoms are omitted for clarity. Reproduced with permission from ref 13. Copyright 1994 American Chemical Society.

example of such a strained complex, [Co(enenim)ZnCl]$^{2+}$, is shown in Figure 4. It will be noted that although the pyridine ligands are trans disposed, the phenolic groups are splayed to one side of the macrocyclic plane. This is presumably a consequence of the inability of the zinc ion to fit into the 4-coordinate cavity, leading to the "popped-out" coordination seen in the structure. The out-of-plane zinc ion is on the opposite side of the macrocyle to the splayed disposition of the phenolic groups.

Table 1. Redox Potentials for Co(III)/Co(II) Couples of the [Co(encyim)MX]$^{n+}$ Complexes versus the Ferrocenium/Ferrocene Couple in Acetonitrile Solutions

complex	E_f (V)[a]
[Co(encyim)Zn]$^{3+}$	−0.44
[Co(encyim)Cu]$^{3+}$	−0.27
[Co(encyim)Ni]$^{3+}$	−0.38
[Co(encyim)Co]$^{3+}$	−0.33
[Co(encyim)Mn]$^{3+}$	−0.36
[Co(encyim)ZnCl]$^{2+}$	−0.43
[Co(encyim)NiCl]$^{2+}$	−0.37
[Co(encyim)CoCl]$^{2+}$	−0.38 (−1.82)[b]
[Co(encyim)MnCl]$^{2+}$	−0.32

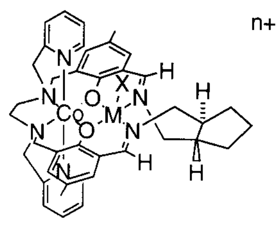
[a] Potentials refer to the cobalt in the 6-coordinate site. [b] Potential refers to the cobalt in the 4-coordinate site.

In all cases studied, bimetallic complexes containing a tn A-link produce complexes having trans-disposed pyridine ligands. An example of such a structure, the complex [Zn(tntnim)ZnOAc]$^{+}$, is shown in Figure 5. It will be noted that, even for this less metal confining ligand, the zinc ion in the 4-coordinate site is coordinated in a distorted trigonal bipyramidal geometry. Such structures are generally observed for 5-coordinate metals in this site when the pyridine ligands are in a trans geometry in the other site.

This brief survey of the structures illustrates that bimetallic complexes of the present ligands give distorted structures, and the degree of distortion is dependent on the size of the two chelate links, particularly the size of the A-link. Even with two tn links, distortions of the coordination structures are observed. The origins of the structural variations are undoubtedly complex and subtle, but the rigidity of the phenolic ligands plays a decisive role in causing the distortions. As will be noted for the limited number of structures presented here, the phenolic groups adopt a wide variety of conformations. It is reasonable to suppose that these variations reflect the differing conformational demands of the chelate links and the metals, which occupy the sites. Whereas the macrocyclic framework provides stability, it also restricts the number of conformations possible. It is evident from the foregoing discussion that the reactivities and redox chemistry of these bimetallic complexes are unlikely to be the sum of the properties of the two sites because the site structures are mutually dependent.

Physical Properties

Most of the physical properties of these complexes are unexceptional: the magnetic interactions between metals are those generally observed in bimetallic complexes, the d−d electronic spectra are those expected for the sites the metals occupy, and there are no intervalence transitions observed. The redox properties of the bimetallic complexes, however, are interesting and appear to correlate with the structural demands of the ligands and the metal. A number of redox potentials are listed in Table 1 for complexes of the type [Co(encyim)MX]$^{n+}$, which has the structure **11**. These complexes were prepared from



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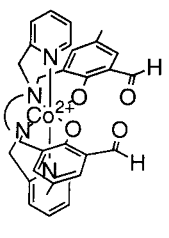
the cobalt(II) complex [Co(encyim)$(H^+)_2]^{2+}$, for which a single diastereomer exists because the chiral (1*S*, 2*S*)-*trans*-1,2-bis(aminomethyl)cyclopentane link (cy) induces a single chiral topology of the complex. Upon oxidation to the cobalt(III) complex, [Co(encyim)$(H^+)_2]^{3+}$, the trans pyridine ligand geometry is retained and a single diastereomer exists. The nonlabile cobalt(III) coordination geometry ensures that the geometry is retained when a second metal is introduced. Thus, all of the complexes in Table 1 have the structure **11**. Inspection of Table 1 indicates that the corresponding tripositively and dipositively charged complexes display similar redox potentials. Although variations are observed, they are not as large as those observed according to the metal occupancy of the 4-coordinate site. Thus the first three entries for the tripositively charged complexes show substantial redox potential variations which are different from the next two entries, the latter having similar values. There are a number of factors which could be advanced to rationalize these redox variations with occupancy of the 4-coordinate site, but we believe that the major factor is the stereochemical demands of the metal in this site. Crystal structures of these complexes clearly show that the four donor atoms of the 4-coordinate site are in a twisted array and that this distortion from the square planar arrangement is preserved by the stereochemically rigid Co(III) ion, whether protons or a metal is in this site. Whereas it is not possible to determine the expected magnitude of the energy associated with the distortions of the favored geometries of the metals in the 4-coordinate site, a number of observations can be made. Of the five metals, Zn(II), Cu(II), (high-spin) Ni(II), Co(II), and Mn(II), the energy of distorting Cu(II) from a square planar geometry is expected to be greatest. Consistently, the copper complex shows the greatest disparity in the Co(III)/Co(II) redox potential. Although neither the Zn(II) nor the (high-spin) Mn(II) ions are expected to impose strong stereochemical demands, the differences in redox potential may be associated with the difference in radii of the two metal ions. The larger Mn(II) ion will demand a large 4-coordinate cavity which, in turn, may affect the ability of the ligand to adjust to the stereochemical demands of the cobalt in the other site. It is not clear, however, why the Ni(II), Co(II), and Mn(II) complexes should have similar potentials based on these stereochemical arguments. Clearly additional factors such as electronic and charge interactions between the cobalt and the other metal play a role. Whatever the precise origins of the redox variations, it is obvious that the interaction occurs between the metals. These interactions are discussed more fully in the next section, where the redox chemistry of these types of complexes is described.

Redox Chemistry

It was asserted earlier that the 6-coordinate site will support the Co(III) state at least in monometallic complexes. This is the case because the monometallic Co(II) complexes of the type **12** are readily oxidized by ferrocenium ions to give stable Co(III) complexes. This is the case for both en and tn complexes.



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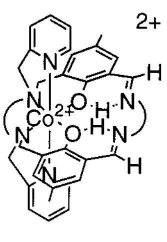

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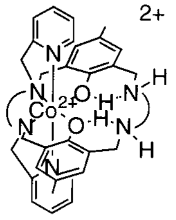
Table 2. Redox Potentials for the M(III)/M(II) Complexes of the Type [M(macrocyclic amine)$(H^+)_2]^{2+}$ and [M(macrocyclic imine)$(H^+)_2]^{2+}$

complex	E_f (V)[a]
[Mn(entnam)$(H^+)_2]^{2+}$	−0.08
[Mn(entnim)$(H^+)_2]^{2+}$	0.21
[Mn(tntnam)$(H^+)_2]^{2+}$	−0.01
[Mn(tntnim)$(H^+)_2]^{2+}$	0.40
[Fe(entnam)$(H^+)_2]^{2+}$	−0.51
[Fe(entnim)$(H^+)_2]^{2+}$	−0.15
[Fe(tntnam)$(H^+)_2]^{2+}$	−0.40
[Fe(tntnim)$(H^+)_2]^{2+}$	−0.01

On the other hand, monometallic complexes of the type **13** of the four ligands enenim, entnim, tnenim, and tntnim, behave in an unexpected way. The complexes with an en link at the 6-coordinate site, namely, those monometallic Co(II) complexes formed by the enenim and entnim ligands, form stable Co(III) complexes after ferrocenium ion oxidation, but those complexes bearing a tn 6-coordinate link, tnenim and tntnim, are not oxidized by ferrocenium ions. When the results of the oxidations of the non-macrocyclic ligands, **12**, are compared with the results of the macrocyclic ligands, **13**, it is clear that the presence of the macrocyclic imines is a controlling factor in this divergent behavior. Removal of the protons from the cavities of **13** does not alter the result, indicating that charge is not a controlling factor. Since in going from the Co(II) to the Co(III) state there is a contraction of the metal−ligand bond lengths and an octahedral geometry is firmly imposed, the ligand requires conformational adjustment to meet these demands. The 6-coordinate tn link will have a larger bite angle that the en link, and consequently the former is expected to experience greater conformational adjustments than the latter. The cyclic diimine link in these complexes, **13**, is expected to add rigidity and disallow a certain degree of flexibility to the systems compared with the non-macrocyclic sytems, **12**. Hence, in the cases of complexes where a tn is present in the 6-coordinate site, the ligand framework may not be able to adjust to the stereochemical demands of the Co(III) state as readily as when en is present in the 6-coordinate site. The size of the link, en, tn, or cy, in the 4-coordinate site has little influence on these results.

If these suppositions are correct, then it might be expected that if the imine groups were reduced to amines the resulting monometallic Co(II) complexes of all of the four ligands, **14**, would be oxidized to the Co(III) state. Consistently we find that all four monometallic Co(II) complexes, namely, those of enenam, entnam, tnenam, and tntnam, are oxidized by ferrocenium ions to form stable Co(III) complexes. This phenomenon, that oxidation occurs more readily with the amine ligands, is observed for metals other than cobalt even though the higher oxidation states of these metals are generally less stereochemically demanding. This is illustrated in Table 2 where the redox potentials are relative to the ferrocene/ferrocenium couple. The corresponding couples for the analogous cobalt complexes were irreversible.



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The differences in the redox potentials of the amine and imine complexes are large, 0.3−0.4 V, and presumably reflect the greater conformational flexibility of the amine ligands. Although the trivalent states of manganese and iron are less stereochemically demanding than that of cobalt, the conformational effect on the former two couples is pronounced.

The preceding discussion would suggest that Co(II) imine complexes of the type [Co(macrocyclic imine)CoCl]$^+$ may not display redox behavior that might be inferred from the characteristics of monometallic Co(II) complexes residing in the two bimetallic sites. This proved to be the case. For example, the complexes [Co(macrocyclic imine)CoCl]$^+$ were insensitive to dioxygen, and ferrocenium oxidation led to unidentified products despite the known reactivity of the two sites in monometallic complexes. The analogous amine complexes [Co(macrocyclic amine)CoCl]$^+$ (macrocyclic amine is tntnam or tnenam or entnam) did show interesting oxidation properties, however. When ferrocenium ions ([FeCp$_2$]$^+$) (1 equiv) are added to solutions of the dicobalt(II) complexes, the mixed-valence complexes shown in eq 5 are produced. Addition of a second equivalent of [FeCp$_2$]$^+$ to the mixed-valent product does not lead to the oxidation of the cobalt(II) ion in the 4-coordinate site. It was considered possible that NO$^+$ could act as a two-electron oxidant with these dicobalt(II) complexes to give the desired one-site addition two-metal oxidation products, [Co^{3+}(macrocyclic amine)Co^{3+}(NO)(Cl)]$^{2+}$. In the event, NO$^+$ acted as one-electron oxidant giving the same products as [FeCp$_2$]$^+$, namely, [Co^{3+}(macrocyclic amine)Co^{2+}Cl]$^{2+}$. Unlike the corresponding imine dicobalt(II) complexes, those of the amines are sensitive to dioxygen. Exposure to O$_2$ leads to formation of dark solutions, and whereas no dioxygen adducts were isolated, the other mixed-valence complexes of the type [Co^{2+}(macrocyclic amine)Co^{3+}(OAc)(CH$_3$CN)]$^{2+}$ were isolated. Addition of [FeCp$_2$]$^+$ to these mixed-valence complexes, where the Co(III) ion is in the 4-coordinate site, did not lead to oxidation of the Co(II) in the 6-coordinate site. Thus, we are faced with an unusual mutual deactivation phenomenon, namely, that although either site is capable of supporting the Co(III) state, the oxidation of the metal in one of the sites leads to deactivation of the metal in the other site. The two sites in the present complexes do not provide equal stabilities for the Co(III) state, however. When the mixed-valence complexes [Co^{2+}(macrocyclic amine)Co^{3+}(OAc)(CH$_3$CN)]$^{2+}$ are heated in water, electron transfer occurs and the mixed-valence complexes with the Co(III) ion in the 6-coordinate site are produced, indicating that this site provides a more stable environment for the Co(III) state.

$$[\mathrm{Co}^{2+}(\text{macrocyclic amine})\mathrm{Co}^{2+}\mathrm{Cl}]^+ \xrightarrow{[\mathrm{FeCp}_2]^+} [\mathrm{Co}^{3+}(\text{macrocyclic amine})\mathrm{Co}^{2+}\mathrm{Cl}]^{2+} \quad (5)$$

Given the inaccessibility of the dicobalt(III) state under mild conditions, we sought metal combinations where the higher oxidation states might be more readily obtained and where the product of addition would be stable. One such possibility was the product [Fe^{3+}(ligand)V^{4+}O]$^{3+}$, which could be derived from [Fe^{2+}(ligand)V^{3+}Cl$_2$]$^+$ after oxidation with an oxo transfer reagent. The VO^{2-} ion is a persistent and stable feature of V(IV) chemistry, and as can be seen in Table 2 the monometallic Fe(II) complexes are readily oxidized. Further, we anticipated that oxo transfer to V(III) would lead to initial oxidation to an unstable V^{5+}O entity, which would provide a strong driving force for intramolecular electron transfer from the Fe(II) to the V^{5+}O ion. We encountered difficulties in preparing the heterobimetallic complexes, Fe^{2+}−V^{3+}, for a number of these ligands, but we succeeded in obtaining pure crystals of [Fe(entnim)VCl$_2$]PF$_6$.[17] Figure 6 illustrates the structure of this complex ion, where it will be noted that the pyridine ligands are cis disposed, one of the chloro groups bridges the two metals, and one of the phenolic bridges is disconnected. Addition of iodosobenzene to [Fe^{2+}(entnim)ClVCl]$^+$ produces a green complex, [Fe^{2+}(entnim)V^{4+}O]$^+$, which also is formed slowly by dioxygen. The crystal structure of the complex ion of [Fe(entnim)VO]PF$_6$ is shown in Figure 7. In this structure the pyridine ligands are cis disposed and the metals are now bridged by both phenolic oxygen atoms. The mechanisms by which the vanadyl complex is formed are undoubtedly complex, but the resistance of the Fe(II) in the 6-coordinate site to oxidation is remarkable. Clearly the presence of vanadium in the 4-coordinate site deactivates the iron to oxidation. The redox potential for [Fe(entnim)(H$^+$)$_2$]$^{2+}$ (Table 2) is −0.15 V whereas its redox potential in [Fe(entnim)VO]$^{2+}$ is +0.69 V, a huge difference even after it is recognized that the monometallic complex [Fe(entnim)(H$^+$)$_2$]$^{2+}$ probably has trans-disposed pyridine ligands and the vanadyl complex has a cis pyridine ligand geometry. Whereas the present set of bimetallic complexes did not provide the desired reactivity patterns, they served to indicate the factors which lead to mutual metal deactivation in multimetallic complexes. We now discuss the probable origins of this mutual

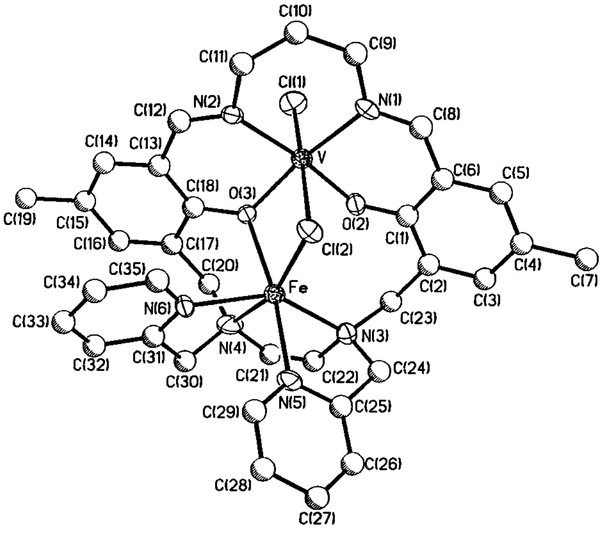

Figure 6. Structure of the [Fe(entnim)ClVCl]$^+$ ion. The hydrogen atoms are omitted for clarity. Reproduced with permission from ref 17. Copyright 1997 American Chemical Society.

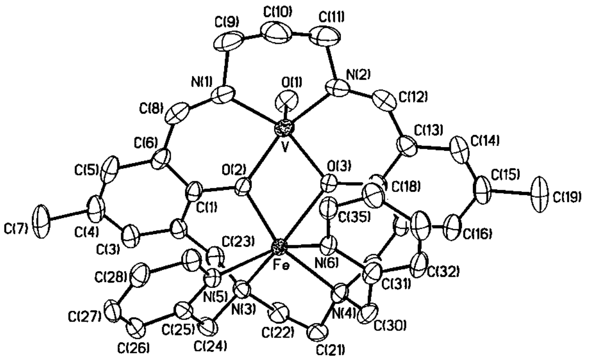

Figure 7. Structure of the [Fe(entnim)VO]$^{2+}$ ion. The hydrogen atoms are omitted for clarity. Reproduced with permission from ref 17. Copyright 1997 American Chemical Society.

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deactivation and thus how it might be avoided.

Origins of Mutual Deactivation

We consider three possible thermodynamic origins for metal oxidation deactivation. The first is the unfavorable through-space electrostatic interaction between the contiguous oxidized metals. Whereas this effect may be significant, it does not appear to be prohibitive because of the ready formation of dimeric peroxo complexes from the reaction of dioxygen with bimetallic complexes.[18] The second source of metal deactivation is through-bond coupling,[19] which refers to the electronic interaction of the metals via the bridging atom orbitals. Depending on the nature of the bridge, the geometry of the bridge, and the orbitals involved, this effect can be substantial.[20] Given the fact that peroxo complexs are formed from lower oxidation state bimetallic complexes with dioxygen with similar oxygen bridging groups,[18] through-bond coupling may not be a decisive impediment to two-metal oxidation in the present systems. Whereas these two effects may be significant in controlling metal oxidation deactivation in general, it is probable that the major factor in the present cases is mechanical coupling. Mechanical coupling refers to ligand reorganization that ensues during the oxidation of the metals. The energy of mechanical coupling consists of the sum of the terms associated with bond stretches, angle bends, torsional deformations, van der Waals interactions, and electrostatic interactions as defined by an appropriate molecular mechanics force field. Oxidation of a metal involves metal−ligand bond contraction and sometimes angle deformations. Consequently, in a multimetallic polynucleating ligand system, oxidation of one metal is not independent and it imposes conformational strain on the others. That is, they are mechanically coupled and the energy associated with oxidation contains terms associated with ligand reorganization.

Since the two-metal oxidations described here must involve sequential electron transfer, the stability and reactivity of the mixed-valence intermediate could provide a kinetic route to other unwanted reactions. For example, dioxygen reaction with the dicobalt(II) complexes is expected to proceed via the mixed-valence superoxide intermediate (eq 6). If intramolecular

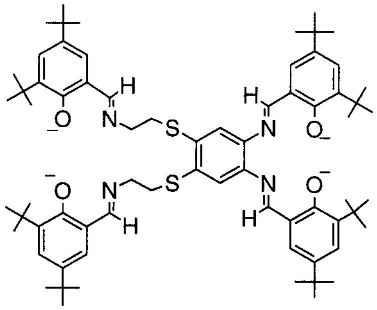
$$Co^{2+}{-}Co^{2+} \xrightarrow{O_2} Co^{2+}{-}Co^{3+}{-}O{-}O^{-} \rightarrow Co^{3+}{-}Co^{3+}{-}O^{-}{-}O^{-} \quad (6)$$

electron transfer in the intermediate were slow, the intermediate could undergo intermolecular reactions such as forming bridging peroxide complexes. Thus, even if the thermodynamics were favorable for two-metal oxidations, the kinetics may lead to unwanted reactions.

From the above discussion, it is clear that it is not possible to determine the reactivity of bimetallic, or more generally multimetallic complexes, from the reactivity patterns of the constituent sites as observed in monometallic complexes bearing these sites. Designing polynucleating ligands which form complexes which minimize these deactivating effects remains a major challenge.

A Weakly Coupled System

As discussed above, it follows that if suitable complexes were prepared of a binucleating ligand which provided minimal electrostatic, electronic, and mechanical coupling, two-metal oxidations of the present type should occur provided favorable kinetic factors obtain. For this purpose we have prepared the ligand **15**, in which the 6-coordinate and 4-coordinate sites are separated by a rigid benzene spacer.[21] Because of the rigid spacer we would expect little mechanical coupling and weak metal−metal electrostatic and electronic interactions. Ready electron transfer across the benzene spacer is expected to occur. Whereas the ligand **15** is somewhat of a contrivance in the sense that the two sites are essentially independent, it does provide a weakly coupled system. The heterobimetallic complex **16** was prepared and was reacted with iodoso-2,4,6-trimethylbenzene. The desired product, **17**, was obtained and characterized. This same product, **17**, is obtained by $[FeCp_2]^+$ oxidation of the $Co^{2+}{-}V{=}O$ complex, indicating that unlike the case of the [Fe(entnim)VO]$^{2+}$ complex, the metal in the 6-coordinate site (Co(II)) is not deactivated to oxidation. It should be noted that we have not established that **17** is formed by intramolecular electron transfer from the 6-coordinate Co(II) to the activated vanadium ion during or after the addition of the oxo ligand. We have, however, established that the desired product is thermodynami-



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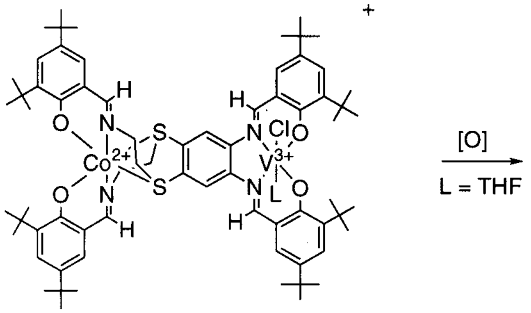

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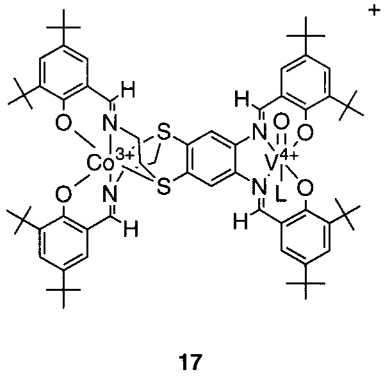

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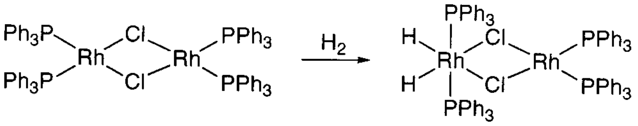
cally accessible by an oxo transfer reaction. This observation supports the hypothesis that when the various forms of coupling are minimized the bimetallic system can behave according to the reactivity of the expectations of the two sites.

Discussion

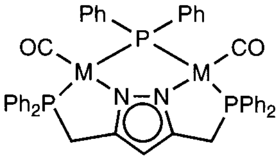
The studies reported here allow us to view the oxygen uptake of hemerythrin from a more detailed perspective, and in addition, the ligand design elements required to form complexes which may act as oxygenation catalysts using atmospheric dioxygen become clearer. The special elements incorporated in the dioxygen binding site of hemerythrin, aside from the protection provided by the protein, appear to involve two basic features. The ligands which coordinate to the iron atoms would seem to have considerable flexibility given that they emanate from the peptide side chains of a protein supramolecule. The two carboxylate bridging groups are not expected to impose strong steric constraints, and the imidazole ligands are likely to adjust readily to the oxidation changes in the metal. For dioxygen binding stability and possibly for the second electron transfer step from the 6-coordinate iron(II), the presence of the hydroxyl bridge may be crucial. Transfer of the hydroxyl proton to the dioxygen will engender stability to the hydroperoxide ligand, and as we noted earlier, the newly formed oxo bridge is likely to stabilize the iron(III) state and hence to provide a driving force for the second electron transfer. The presence of five imidazole ligands, three on one iron atom and two on the other, probably ensures that over-reduction of the dioxygen by four electrons is suppressed. The stability of the hydroperoxide ligand bound to a labile iron(III) atom is likely to be enhanced by the protection afforded by the protein. The release of neutral dioxygen from the diiron complex presumably follows the microscopic reverse of the binding process. Not surprisingly, perhaps, the dioxygen binding of hemerythrin represents a subtle orchestration of a number of structural and electronic elements, which are yet to be reproduced in a synthetic system.

Related, but not identical, issues are raised by a number of observations involving oxidative additions to bimetallic complexes where metal−metal bonds are not involved. Two examples involving mutual metal oxidative deactivations will be presented. The rhodium(I) dimer, **18**, derived from Wilkinson's catalyst, oxidatively adds dihydrogen to only one of the Rh atoms to give the mixed-valence complex **19**. The rate of dihydrogen addition to the first rhodium atom is almost identical to that observed for dihydrogen addition to the monomeric analogue, [Rh(PPh$_3$)$_3$Cl]. Dihydrogen was found not to add to the remaining Rh(I) atom of **19**, even under hydrogen pressure.[22] This somewhat curious observation that the first rhodium atom has a reactivity similar to that of the corresponding monomer but that the other rhodium atom becomes deactivated to oxidative addition is reminiscent of the results we have discussed here. It is not clear to us what the precise origins of this mutual deactivation are. It could be electronic in origin or steric in that the triphenylphosphine ligands could experience unfavorable interactions if the second dihydrogen were to add trans to the bridging chloro ligands.



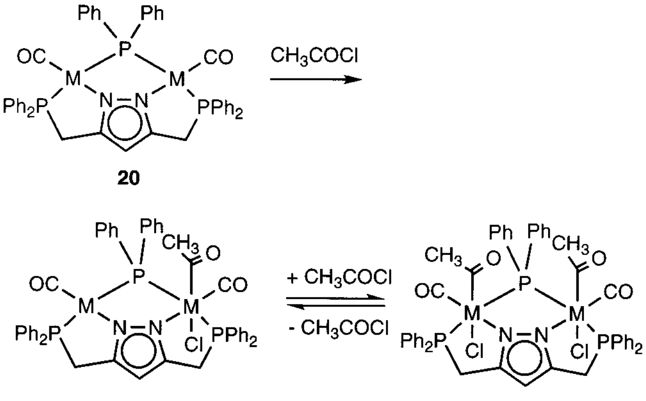
18 **19**

Similar metal deactivation is observed in the complexes[23] of the type **20**. Addition of 1 equiv of acetyl chloride to the dirhodium complex leads to irreversible addition to one rhodium atom giving a mixed-valence dimer, **21**. Addition of a second equivalent of acetyl chloride forms the diacetyl complex, **22**, reversibly ($K = 2.7$). As is commonly observed, the second rhodium atom is deactivated to oxidation after the first is oxidized. In the case of the analogous diiridium(I) complexes, two acetyl chloride electrophiles add irreversibly as might be expected.[24] Presumably in the case of the dirhodium complexes, the metal deactivation occurs by through-bond coupling via the bridges because mechanical coupling is unlikely to be a major component in these systems. Thus these bimetallic complexes may served to illustrate the effect of electronic and perhaps electrostatic coupling, which in these cases appears to be significant but not overwhelming.



M = Rh(I) or Ir(I)

20



21 **22**

The present work indicates that if mechanical coupling can be minimized in multimetallic complexes, oxidative additions of the kind considered here could occur. Consequently, it is possible to imagine developing systems which are capable of reducing substrates by as many electrons as is required. This occurs in many biological systems. The major restraint to this prospect is likely to be the difficulties associated with synthesis of appropriate ligands. Nonetheless, major advances in coordination chemistry are likely to occur with the design and synthesis of complex ligand systems.

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