

## Cooperative bimetallic oxidative addition reactions\*

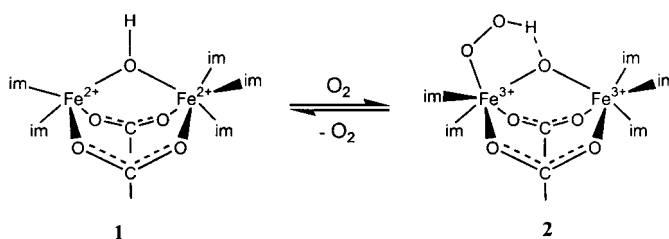
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**Abstract:** The factors that control the oxidation of metals in bimetallic complexes are investigated in relation to the possibility of developing one-site addition two-metal oxidation reactions such as those that occur in the respiratory protein, hemerythrin. It is shown that the behavior of bimetallic complexes is not represented by the sum of the analogous monometallic parts because of metal and ligand interactions.

### INTRODUCTION

The active site of the respiratory protein, hemerythrin, consists of two iron atoms bridged by acetate and hydroxide ligands, and the other coordination positions are occupied by imidazole(im) ligands, **1** [1]. Dioxygen adds to the 5-coordinate  $\text{Fe}^{2+}$  site to form the hydroperoxide di- $\text{Fe}^{3+}$  complex, **2**, [2]. This process can be referred to as a one-site addition two-metal oxidation reaction. The mechanism by which this reaction occurs is subtle because the reduction of the  $\text{O}_2$  substrate presumably occurs by successive proton-coupled electron transfer steps from the two  $\text{Fe}^{2+}$  atoms to form the product, **2**. Conceptually, this process is an intriguing phenomenon that does not appear to have been reproduced in a synthetic system. This review puts the issue in a wider context and seeks to elicit the factors that control one-site addition multimetal oxidation reactions. Such an understanding would provide a basis for the multi-electron reduction of substrates bound to a single metal. Especially important is the 4-electron reduction of  $\text{O}_2$  to produce catalytically active oxo species. Figure 1 outlines a number of one-site addition two-metal oxidation reactions which bimetallic complexes may undergo.



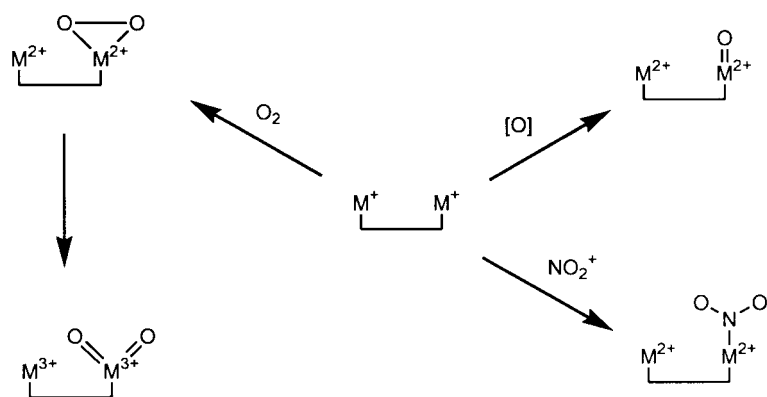
There are, of course, numerous other possibilities for this process which could provide distinct reactivity patterns, hitherto not observed.

### BIMETALLIC COMPLEX DESIGN

The first generation of binucleating ligands was based on two premises. First, the ligand should have a 6-coordinate and 4-coordinate site so that the substrate is directed to the coordinatively unsaturated

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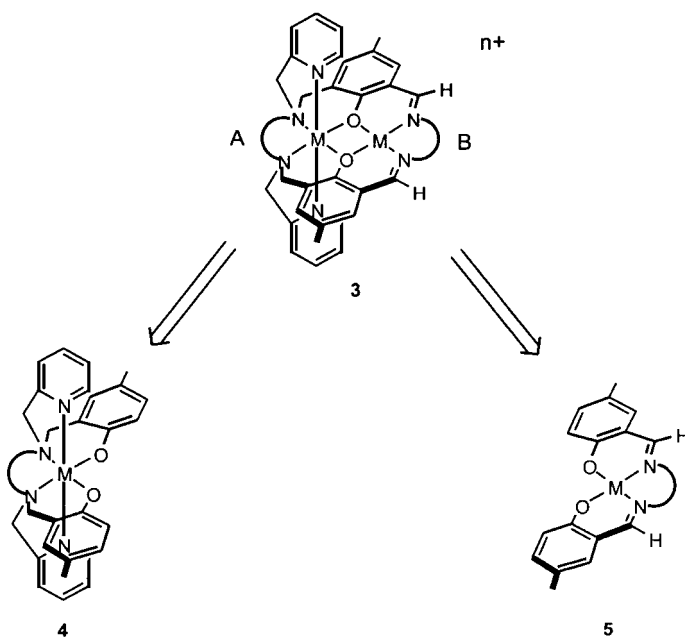
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**Fig. 1** Some possible one-site addition two-metal oxidation reactions.

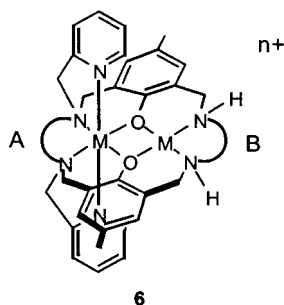
metal. Second, it was assumed that the reactivities of the metals in the two sites would be similar to those observed in analogous monometallic complexes, that is, the reactivity would represent the sum of the parts. These ideas are represented in Fig. 2.

The monometallic complex, **4**, is expected to be readily oxidized when  $M = \text{Fe}^{2+}$  or  $\text{Co}^{2+}$ , for example. The other complex, **5**, is known to absorb O<sub>2</sub>, when  $M = \text{Co}^{2+}$ , to give a superoxide  $-\text{Co}^{3+}$  species [3]. Similarly, when  $M = \text{Cr}^{3+}$  the complex, **5**, is oxidized to the Cr<sup>5+</sup> oxo complex with oxo transfer reagents [4]. Given these observations, one might be tempted to conclude that the di-Co<sup>2+</sup> complex of, **3**, might absorb O<sub>2</sub> to form a di-Co<sup>3+</sup> complex with a peroxide ligand coordinated to the 4-coordinate site. Similarly, **3** bearing Co<sup>2+</sup> or Fe<sup>2+</sup> in the 6-coordinate site and Cr<sup>3+</sup> in the other site might be expected to form a Cr<sup>4+</sup>-oxo complex with 1-electron oxidation of the other metal (Co<sup>3+</sup> or Fe<sup>3+</sup>). Other combinations can be envisioned.



**Fig. 2** The proposed bimetallic complex, **3**, which may be considered to be the conglomeration of the monometallic parts, **4** and **5**.

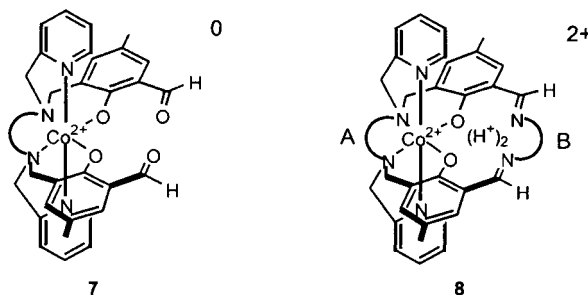
Using standard organic procedures, the ligand represented in **3** was prepared as well as the analog where the two imines were reduced to amines, **6**. The chelate links were, among others, combinations consisting of two or three methylene groups. A variety of homo- and site-specific heterobimetallic complexes of the first transition series were prepared and characterized [5]. In addition, a number of monometallic complexes containing the metal in the 6-coordinate site and having two hydrogen bonded protons in the 4-coordinate site were isolated.



## REACTIVITY

After having prepared the bimetallic complexes, the first surprise was to find that the di-Co<sup>2+</sup> complex of the system, **3**, was completely inert to O<sub>2</sub>. The same holds for the di-Fe<sup>2+</sup> analog. Consequently, the di-Co<sup>2+</sup> system was investigated in terms of its monometallic constituent parts. Oxidation by the ferrocenium ion (fc<sup>+</sup>) was used as a reference for oxidative susceptibility. Addition of fc<sup>+</sup> to the di-Co<sup>2+</sup> system, **3**, with any of the four combinations of dimethylene or trimethylene links (A or B) did not lead to oxidation of the Co<sup>2+</sup> ions.

Addition of fc<sup>+</sup> to acetonitrile solutions of the Co<sup>2+</sup> monometallic complexes of the complexes, **7**, lead to clean oxidation to the Co<sup>3+</sup> complex, confirming the earlier assumption that the sexadentate ligand of **7** would allow for ready oxidation of its Co<sup>2+</sup> complex. The analogous macrocyclic monometallic imine complex, **8**, behaves somewhat differently. The oxidant, fc<sup>+</sup>, produces the Co<sup>3+</sup> complex when link A is dimethylene but fc<sup>+</sup> does not oxidize the Co<sup>2+</sup> complex when a trimethylene A-link is present. The size of the B link does not affect either of these results. Since oxidation of the Co<sup>2+</sup> to Co<sup>3+</sup> involves bond-length contraction, it was supposed that the rigidity of the macrocyclic framework of **8**, as opposed to the acyclic system **7**, would play a role in preventing bond-length contraction in the case of the larger trimethylene A-ring. If this is so, then the reduced, more flexible, monometallic amine complex, **9**, might be expected to allow for metal oxidation for all of the present ring sizes as was observed for the nonmacrocyclic system, **7**. This was found to be the case. These results were the first indication that conformational effects may play a role in controlling the redox potentials in bimetallic complexes, a supposition confirmed by the redox behavior of bimetallic complexes.



Unlike the diimine analogs, **3**, the di-Co<sup>2+</sup> complexes of the reduced ligand, **6**, were found to be susceptible to oxidation, but in an interesting way. Thus irrespective of the A or B link size, addition of one equivalent of fc<sup>+</sup> to the di-Co<sup>2+</sup> complexes, **6**, lead to the immediate formation of the mixed valence, Co<sup>3+</sup> - Co<sup>2+</sup>, complex, where the Co<sup>3+</sup> is in the 6-coordinate site. Addition of a second equivalent of fc<sup>+</sup> to these mixed valence complexes did not lead to oxidation of the remaining Co<sup>2+</sup> ion in the 4-coordinate site even when exogenous ligands were present. When the di-Co<sup>2+</sup> complexes of **6** are exposed to O<sub>2</sub>, immediate reaction occurred and, although the dioxygen complexes were not isolated, various work-ups led to the unambiguous finding that the products were mixed valence complexes but, now, the Co<sup>3+</sup> ion resided in the 4-coordinate site (with two exogenous ligands). When fc<sup>+</sup> is added to these new mixed valence complexes, no oxidation of the Co<sup>2+</sup> ion in the 6-coordinate site occurs. Although it was found that the mixed valence complex bearing the Co<sup>3+</sup> ion in the 6-coordinate site is thermodynamically the more stable, it is clear that both sites can support the Co<sup>3+</sup> state. It thus appears that when one metal site is oxidized the other is deactivated to metal oxidation. A further experiment illustrates this mutual deactivation.

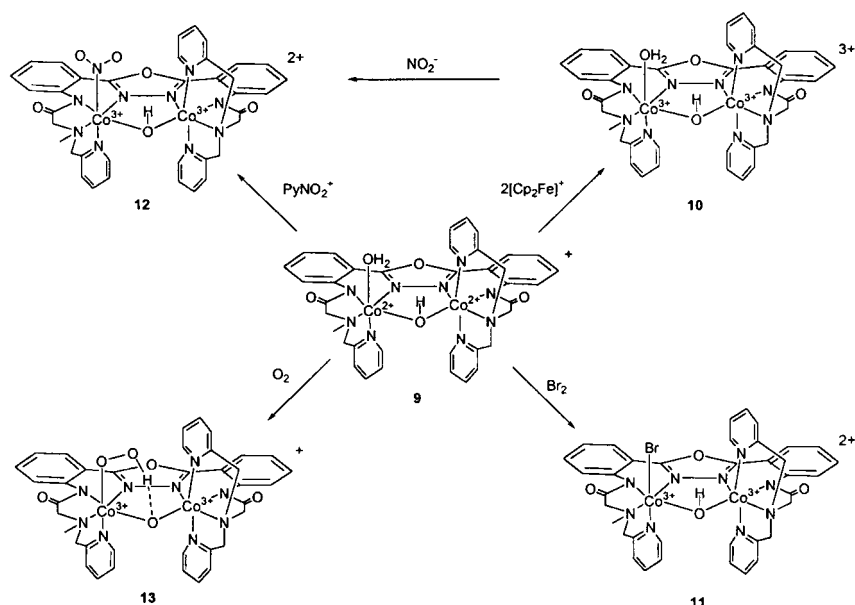
A diimine complex bearing Fe<sup>2+</sup> in the 6-coordinate site and V<sup>3+</sup>Cl<sub>2</sub> in the 4-coordinate site was oxidized with iodosobenzene, an oxo transfer reagent. It was found that monometallic Fe<sup>2+</sup> complex, **8**, is very readily oxidized to the Fe<sup>3+</sup> state. Further, it was expected that oxo transfer to the Fe<sup>3+</sup> V<sup>3+</sup>Cl<sub>2</sub> complex would lead to an oxidatively unstable V<sup>5+</sup>=O intermediate which would provide a strong driving force for electron transfer from the Fe<sup>2+</sup> to form the thermodynamically stable vanadyl (V<sup>4+</sup>=O) group. In the event, the Fe<sup>2+</sup> V<sup>4+</sup>=O complex was formed, not the expected Fe<sup>3+</sup> V<sup>4+</sup>=O complex. The redox potential for the monometallic Fe<sup>2+</sup> complex, **8**, differs from the Fe<sup>2+</sup>/Fe<sup>3+</sup> potential of the Fe<sup>2+</sup> V<sup>4+</sup>=O complex by about 18 kcal mole<sup>-1</sup>. The latter being more difficult to oxidize, a fact that illustrates an enormous mutual deactivation phenomenon.

## ORIGINS OF BIMETALLIC DEACTIVATION

Three possible sources for the mutual metal oxidation deactivation can be envisioned. First, through-space electrostatic interactions between positively charged metals are expected to be greater when both metals are oxidized than in the half or fully reduced contiguous metals. Second, through-bond covalent interactions via the bridging atoms could lead to oxidative deactivation by the oxidized metal drawing electron density away from its neighbor. Finally, oxidation of one metal can lead to ligand conformational changes which could hinder the oxidation of the neighboring metal. This effect, which can be called mechanical coupling, is expected to be particularly pronounced in macrocyclic systems such as those discussed here. Of these three effects, it is probable that the electrostatic and covalent interaction will not be decisive since they are present in hemerythrin. It seems likely that mechanical coupling is the dominant source of oxidative deactivation in the systems so far discussed. If this is the case, it may be possible to obtain one-site addition two-metal oxidations in bimetallic systems where mechanical coupling is minimized.

## ONE-SITE ADDITIONS TWO-METAL OXIDATIONS

After exploring a variety of binucleating ligands, it was found that the binucleating ligand shown in **9**, gave some of the desired results when Co<sup>2+</sup> and an OH<sup>-</sup> bridge were incorporated, **9**. Without dwelling on the design of this ligand, it will be noted that oxidation of one metal is unlikely to cause appreciable mechanical coupling between the two metal centers because the rigid oxadiazole bridge will tend to conformationally insulate one site from the other. Some of the results obtained with the di-Co<sup>2+</sup> complex are shown in Fig. 3. Addition of two equivalents of fc<sup>+</sup> gives the di-Co<sup>3+</sup> complex, **10**, which reacts with NO<sub>2</sub><sup>-</sup> ions to give the di-Co<sup>3+</sup> nitro complex, **12**. This same nitro complex is obtained in quantitative yield by addition of one equivalent of pyridine NO<sub>2</sub><sup>+</sup> BF<sub>4</sub><sup>-</sup> (pyNO<sub>2</sub><sup>+</sup> BF<sub>4</sub><sup>-</sup>) to the di-Co<sup>2+</sup> complex,



**Fig. 3** Examples of one-site addition two-metal oxidation reaction to the complex **9**.

**9.** Addition of  $\text{Br}_2$  to **9** gave the di- $\text{Co}^{3+}$  bromo complex, **11**. Complex, **9**, reacts with  $\text{O}_2$  to give a di- $\text{Co}^{3+}$  hydroperoxide complex, **13**. Although the mechanisms by which these one-site addition two-metal oxidations occur are yet to be determined, it is clear that the system, **9**, provides no thermodynamic impediments to the reaction. Unlike the macrocyclic systems discussed earlier, the ligand, **9**, does not appear to provide strong mechanical coupling between the two sites because the rigid oxadiazole bridge and the hydroxo bridge appear to localize the conformational consequences of bond-length change largely to the individual metal sites.

The mechanisms by which these one-site addition two-metal oxidation reactions occur present some intriguing questions. Oxidation of **9** by  $\text{fc}^+$  is a step-wise process where one equivalent of  $\text{fc}^+$  leads to the mixed valence,  $\text{Co}^{3+}\text{Co}^{2+}$ , complex, the  $\text{Co}^{3+}$  appears to be in the 6-coordinate site. It could be argued that the reactions of  $\text{pyNO}_2^+$  to give **12** and of  $\text{Br}_2$  to give **11** occur by a step-wise path where  $\text{pyNO}_2^+$  or  $\text{Br}_2$  first oxidize the  $\text{Co}^{2+}$  in the 6-coordinate site to give  $\text{NO}_2$  and  $\text{Br}$ , respectively. The  $\text{NO}_2$  and  $\text{Br}$  radicals then add to the  $\text{Co}^{2+}$  in the 5-coordinate site to give the respective products. The alternative mechanism would involve the addition of  $\text{NO}_2^+$  or  $\text{Br}^+$  to the  $\text{Co}^{2+}$  in the 5-coordinate site, with the release of pyridine or  $\text{Br}^-$ , respectively, followed by sequential electron transfer from the two  $\text{Co}^{2+}$  ions. A number of experiments were performed in order to distinguish these two mechanisms, but no unambiguous conclusion could be drawn. As yet, we have not isolated the dioxygen adduct in a pure state. Whatever the precise mechanisms, however, it is gratifying to report that one-site additions two-metal oxidation reactions have been observed for the first time in a synthetic system.

## ACKNOWLEDGMENTS

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