

# Heterobimetallic Mn/Co hybrid complexes composed of proximate organometallic and classical coordination sites

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## Abstract

A series of highly unsymmetric heterobinuclear Mn/Co complexes is reported, in which an organometallic CpMn(CO)<sub>2</sub> fragment and a classical Werner-type cobalt(II) subunit are arranged in close proximity by means of a bridging pyrazolate. Two ligand scaffolds are employed that differ by the chelate size of the tripodal tetradentate {N<sub>4</sub>} binding site for cobalt. Molecular structures of three complexes with either nitrate or acetate coligands have been characterized by X-ray crystallography. IR and UV–Vis-spectroelectrochemistry reveals that oxidation of the heterobimetallic systems is highly localized at the organometallic manganese site, while electrochemical reduction occurs at cobalt. Structural and spectroscopic features as well as trends for the redox potentials of the Mn<sup>I</sup>/Mn<sup>II</sup> couple suggest that changes at the cobalt(II) Werner-type subunit have only minor effects on the properties of the organometallic site.

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## 1. Introduction

The search for well-defined heterobimetallic complexes in recent years has been largely stimulated by the discovery of binuclear active sites in various metalloproteins. These metallobiosites are often highly unsymmetric. The metal centers reside in chemically different environments [1], have different accessibilities and assume quite distinct roles in the overall catalytic process. A prominent case is the respiratory protein hemerythrin that contains in its active site both a five-coordinate iron where the O<sub>2</sub> substrate binds and an adjacent six-coordinate iron providing the second electron for dioxygen to hydroperoxide reduction [2]. Such intriguing metal ion cooperativity (sometimes referred to as one-site addition two-metal oxidation) has triggered the search for suitably designed

unsymmetrical bimetallic complexes that could lead to similar reactivity patterns in a synthetic system [3]. Asymmetry in bridged binuclear metalloenzymes has provided lessons for the synthetic chemist also in a much broader sense, and a variety of unsymmetric compartmental ligand scaffolds have been designed in order to study the mutual effects of the two metals [1,4]. One strategy to achieve coordination site distinction is the attachment of two different chelating side arms to an endogenous bridging moiety such as phenolate [4,5], pyrazolate [6] or oxadiazole [7]. Few known systems, however, approach an extreme situation where both an organometallic and a Werner-type fragment with the same metal ion are preorganized in close proximity [8,9].

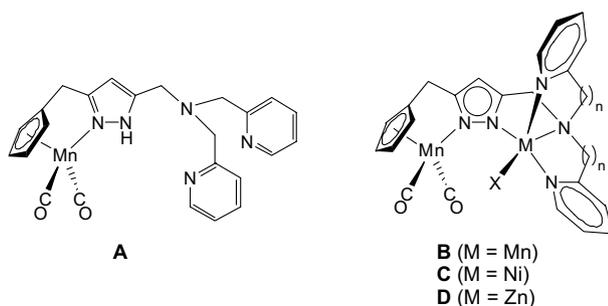
In the case of pyrazolate-based homobimetallic complexes, the two metal ions spanned by the heterocycle are commonly in the same oxidation state [10,11]. It should be noted though that the pyrazolate bridge provides significant electronic coupling, and mutual metal oxidative deac-

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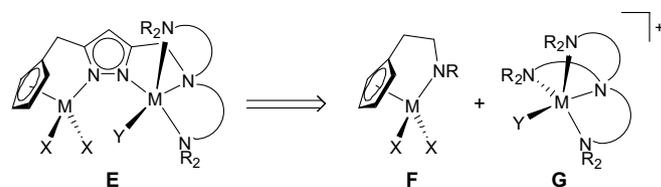
tivation upon oxidative addition to one of the two metals as well as fast electron transfer in mixed-valent species have been reported [12,13]. We have studied in detail a pyrazolate-bridged bimetallic system with two CpMn(CO)<sub>2</sub> moieties appended to the 3- and 5-positions of the heterocycle. This dimanganese complex was shown to undergo two sequential one-electron metal-centered oxidations with fast intramolecular thermal electron transfer ( $k_{ET} \approx 2.6 \times 10^{10} \text{ s}^{-1}$  at 298 K) in the mixed-valent Mn<sup>I</sup>Mn<sup>II</sup> state having a formal low-spin d<sup>5</sup>d<sup>6</sup> electronic configuration [13]. In a further elaboration, the multifunctional type **A** system with both a CpMn(CO)<sub>2</sub> subunit and a {N<sub>4</sub>} ligand compartment tethered to the central pyrazole has been developed (Scheme 1). The {N<sub>4</sub>} compartment is reminiscent of conventional mononucleating ligands of the tripodal tetradentate tris(pyridylalkyl)amine type. Manganese(II), nickel(II) or zinc(II) ions with different coligands X can be accommodated in the Werner-type compartment to give highly unsymmetric homo- or heterobimetallic systems **B–D** [8,9,14], where variations in the Werner-type site were shown to induce only subtle changes of the redox properties of the organometallic site.

These highly unsymmetric binuclear compounds of generic type **E** can be formally described as a combination of each one type **F** and one type **G** subunit, i.e., as an assembly of both a Werner-type and an organometallic entity in a highly preorganized bimetallic array (Scheme 2). Two characteristics of type **E** complexes are noteworthy: firstly, the rigid chelate arrangement precludes dissociation of the organometallic fragment from the bridging pyrazolate, and secondly, the  $\pi$  plane of the heterocycle roughly coincides with the mirror plane of the Mn(CO)<sub>2</sub> moiety. The latter situation is most favorable for Mn-pyrazolate  $\pi$ -interactions and hence for electronic communication between the Mn site and the second metal ion [13,15,16].

In this work, we have now investigated a series of new heterobimetallic complexes similar to the type **B–D** systems, but with cobalt(II) in the classical (**G**-type) coordination site. With both metal ions being redox active (Mn<sup>I</sup>/Mn<sup>II</sup> and Co<sup>I</sup>/Co<sup>II</sup>/Co<sup>III</sup>), it appeared particularly interesting whether one-electron redox processes would be strictly confined to one site and whether any mutual influence of the adjacent metal ions might be discernible.



Scheme 1.



Scheme 2.

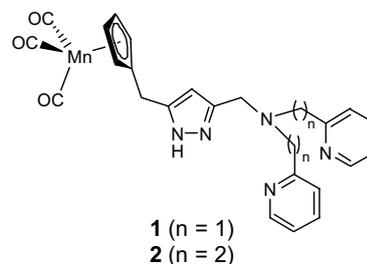
## 2. Results and discussion

### 2.1. Synthesis and structural characterization of complexes

Cymantren derivatives **1** and **2** (Scheme 3) can be prepared in several steps from simple pyrazole derivatives, as reported previously [8]. They differ in the length of the pyridylalkyl side arms appended to the pyrazole heterocycle, thus constituting Werner-type {N<sub>4</sub>} binding pockets with different chelate ring sizes. Photoinduced CO substitution leads to intramolecular coordination of the pyrazole-N to manganese, and a second metal ion may be accommodated in the {N<sub>4</sub>} donor compartment upon subsequent deprotonation.

Heterobimetallic complexes with cobalt ions are best prepared in a one-pot procedure. Solutions of **1** or **2** are first irradiated with a high pressure mercury lamp in a quartz tube at  $-40^\circ\text{C}$  and are then treated with one equivalent of KO<sup>t</sup>Bu and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, respectively. Single crystals of **3**·Et<sub>2</sub>O, **4**·0.5Et<sub>2</sub>O, and **5**·0.5Et<sub>2</sub>O could be obtained by slow diffusion of Et<sub>2</sub>O into DMF solutions of the products (Scheme 4). The ESI mass spectrum of **5** (CH<sub>2</sub>Cl<sub>2</sub> solution) shows dominant signals at  $m/z = 612$  for the anticipated ion and at  $m/z = 556$  for the complex devoid of two CO ligands. Details of the constitution of all three complexes have been elucidated by X-ray crystallography. Molecular structures are depicted in Figs. 1–3, together with selected atom distances and bond angles.

In all three complexes **3–5** the cobalt ion is nested in the classical {N<sub>4</sub>} coordination site and the pyrazolate spans the two metal ions. The coordination environment for cobalt is completed either by a nitrate (**3** and **4**) or by an acetate anion (**5**). In the case of **4** and **5** these coligands are bound in a symmetric bidentate fashion with almost identical Co1–O3 and Co1–O4 bond lengths to give a



Scheme 3.

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