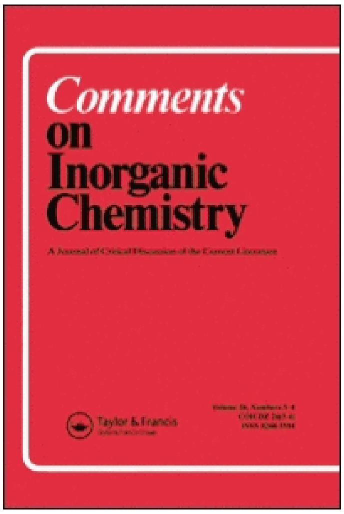

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HOW DO CORROLES STABILIZE HIGH VALENT METALS?

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HOW DO CORROLES STABILIZE HIGH VALENT METALS?

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Trianionic corroles are readily oxidized, yet they are able to stabilize metals in high oxidation states. In an attempt to solve this apparent puzzle, we have estimated both metal d and corrole π orbital energies by analysis of well established experimental data. Although the corrole π orbitals are at higher energies than those of closely related porphyrins, the d orbital energies are even higher, owing to greatly enhanced σ bonding dictated by the relatively rigid macrocyclic trianionic—ligand framework. Understanding the relative importance of corrole π and σ effects sheds new light on metallocorrole stability and reactivity that in turn will further advance this hot area of chemistry.

Keywords: porphyrins, corroles, chromium, manganese, iron

The rapidly increasing interest in the chemistry of metallocorroles has drawn attention to a puzzling fact:[1] although these trianionic ligands are readily oxidized, they stabilize high valent metal ions much more effectively than porphyrins or, for that matter, most other ligands.[2–5]

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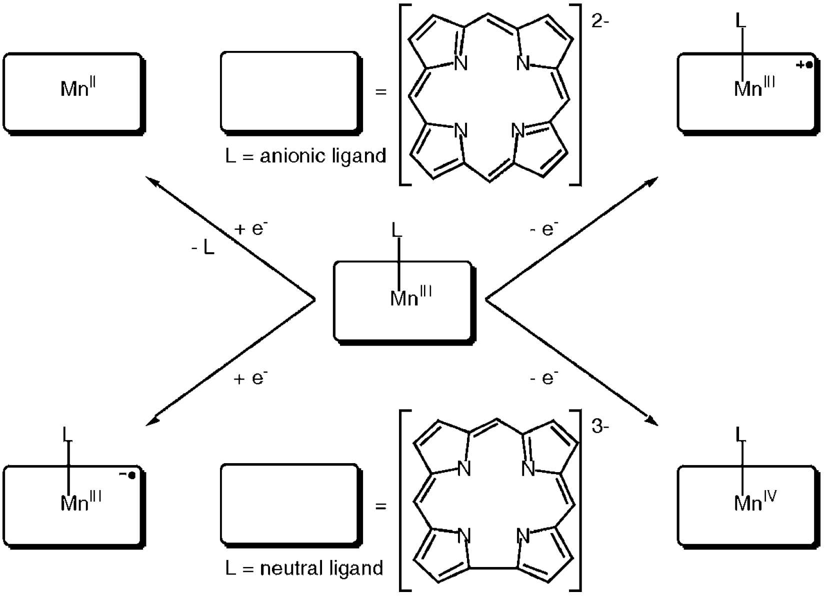


Scheme 1. Metal and ligand-centered redox reactions of manganese corroles and porphyrins.

We will put forward an electronic structural explanation for this stabilization after examining certain striking differences between the properties of manganese corroles and porphyrins (Scheme 1). Not only are multiple oxidation states of both macrocycles well characterized, they are encountered time and time again as participants in catalytic oxidations and other important chemical processes. Consider manganese(III): in this case both metallomacrocycles normally are air stable, 5-coordinate complexes; they display magnetic moments that are fully consistent with a high-spin d^4 metal ion, and they are labile with regard to coordination (exchange) of external ligands.[6] Importantly, they display similar electronic spectra due to the involvement of d electrons in π-π^* transitions. Despite these common features, there are very substantial differences in the redox properties of the manganese(III) complexes (Scheme 1); and differences in metallocorrole stabilities and reactivities are even more striking in other oxidation states.[7] To account for these differences, we will map the relative energies of frontier metal and macrocycle orbitals based on firmly established experimental results.

Our starting point is the molecular orbital energy level scheme for manganese(III) porphyrins that was published by Boucher over 35 years ago with the goal of interpreting their very rich electronic spectra (d-type hyper).[8] Quite impressively, and somewhat unexpectedly, a virtually identical orbital energy level ordering has been obtained in recent years from much more sophisticated theoretical work.[9] There is thus general agreement that the four singly occupied d orbitals are located between the HOMO and LUMO of the porphyrin, a placement that is consistent with strong mixing of metal d-d with porphyrin-based HOMO-LUMO electronic transitions. According to this picture, both reductions and oxidations of manganese(III) porphyrins should be metal-centered. But metal-centered oxidation does not occur; except in the case of strongly π-donating ligands (RO^-, O^{2-}), this reaction clearly is a porphyrin-centered process (Scheme 1, top).[10] A plausible explanation is that the increased charge on the metal pulls the d orbitals below the porphyrin HOMO to which they are quite close in energy even in the trivalent state. An important point to be taken up later is that the energetic difference between the two possible oxidation products, manganese(III) porphyrin radical and manganese(IV), is estimated to be only 0.86 eV.[11] We can thus safely adopt the originally proposed energy levels in manganese(III) porphyrins as a guide for construction of an energy diagram that also includes manganese(III) corroles. The former is drawn on the right side of Figure 1 together with the 2.2 eV energy difference between the porphyrin HOMO and LUMO established many years ago by Kadish.[12] We could add at this stage that very similar HOMO-LUMO gaps have been determined for corroles as well.[13]

Redox differences between manganese complexes of corroles and porphyrins as well as the stability/reactivity properties of the various oxidation states were used for construction of the energy diagram on the left side of Figure 1. Specifically, we note that electrochemical reduction of manganese(III) porphyrins produces manganese(II), whereas oxidation yields porphyrin-radical(cation) manganese(III) complexes (Scheme 1, top). In striking contrast, corrole-radical(anion) manganese(III) and manganese(IV) complexes are the products of reduction and oxidation, respectively, of manganese(III) corroles (Scheme 1, bottom). This intriguing difference may be appreciated further by considering limiting values for the Mn^{III}/Mn^{II} and Mn^{III}/Mn^{IV} redox couples (vs. SCE) in the two systems. Whereas reduction to manganese(II) occurs at about -0.2 V in tetraarylporphyrin complexes,[10] the metal is not affected down to a potential where the corrole is reduced (–1.9 V for [(oec)Mn]).[7j] On the other hand, oxidation to manganese(IV) takes place between 0.3 and

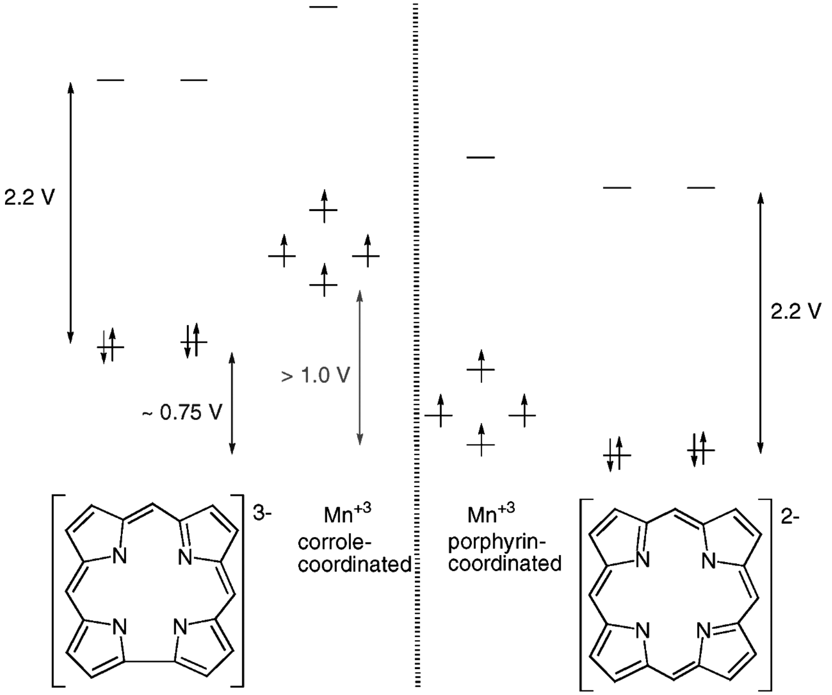


Figure 1. Semiquantitative energy level diagram for manganese(III) ligated by dianionic porphyrin (right) and trianionic corrole (left).

0.7 V for octaalkyl- and tris-C_6F_5-substituted corroles,[7j,7b] but tetraphenylporphyrin oxidation at 1.2 V is more favorable than any Mn^{III}/Mn^{IV} redox process.[10] Another striking example is the comparison between (nitrido)manganese(V) corroles and porphyrins. A Mn^{V}/Mn^{VI} redox process with an $E_{1/2}$ value of 0.59 V takes place in the corrole case (with *meso*-C_6F_5 substituents),[7k] whereas there is no evidence for any change in the oxidation state of the metal up to an applied potential of 1.52 V for a porphyrin with *meso*-*p*-toluyl substituents.[14]

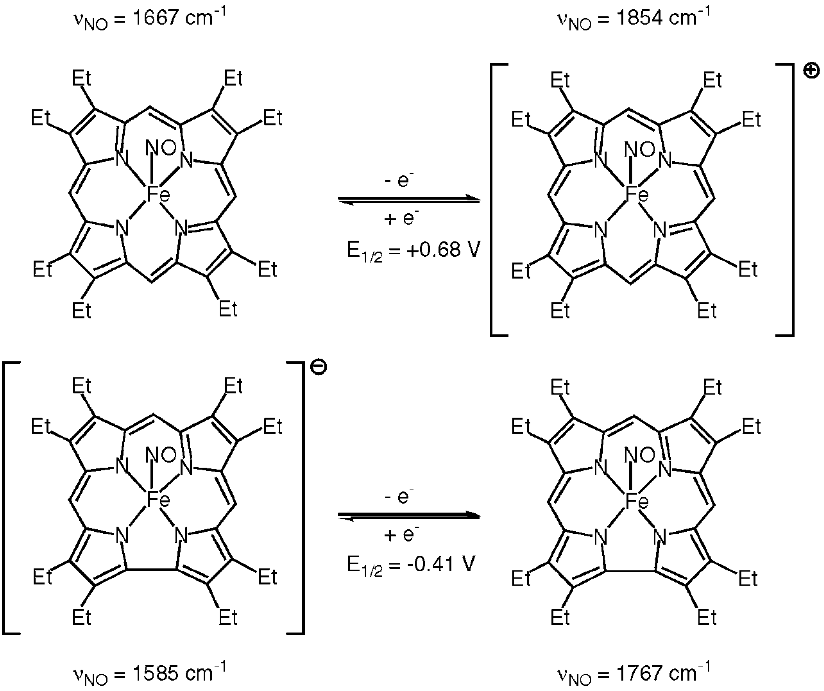
Differences in corroles and porphyrins also are reflected in their chemistry, i.e., the relative stabilities and reactivities of various oxidation states. While manganese(II) corroles are not accessible, spontaneous and/or light induced reactions leading to reduction of manganese(III) porphyrins are quite common.[15] On the other hand, manganese(III) corroles can be converted to very stable manganese(IV) derivatives by utilization of mild oxidants[7] (note that even aerobic oxidation of Mn(III) was recently documented).[7j] Preparation of manganese(IV) porphyrins, however, requires strong oxidants; these species are stable only when bound to π-donor oxygen ligands.[16] A particularly impressive example comes from reactivity studies of (oxo)manganese(V) corroles and porphyrins: the rate constants for the reaction of cyclooctene with structurally similar (oxo)manganese(V) corroles and porphyrins were found to differ by 5 orders of magnitude, with the latter the more reactive species.[7g] Also very telling is an investigation that revealed that the manganese(VI) oxidation state is accessible, even with a corrole that is substituted by 3 C_6F_5 groups and 8 bromine atoms (there are no Mn(VI) porphyrins).[7k] Importantly, the conclusions about manganese oxidation states for both corroles and porphyrins are widely accepted, as they rely on findings from many complementary physical and chemical methods.

The short summary above clearly demonstrates that corrole π electrons and metal d electrons in the manganese(III) complexes are energetically very well separated, with the former being much lower. We emphasize that this conclusion is absolutely dictated by experimental results that show that addition of an electron is to corrole π^* and that up to 3 electrons can be removed from the metal d orbitals. It follows that the occupied d orbitals must be placed at much higher energy than the corrole HOMO and actually quite close to the unoccupied π^*, in a semiquantitative energy level diagram relative to that of manganese(III) porphyrins (Figure 1, right part). The option of lowering the energy levels of the corrole can be rejected, as it would be in conflict with many results that leave no doubt that the corrole π orbitals are actually at much *higher* energies than those of porphyrins. We also know this to be the case from considerations of chemical reactivity: corroles undergo electrophilic substitution under much milder reaction conditions than porphyrins,[17] a manifestation of the high energy of the corrole π HOMO. Consider, for example, that manganese corroles can be brominated at all β-pyrrole carbon atoms even in the absence of a catalyst.[7b] On a more quantitative scale, it is well established that the reduction potentials of main group metal porphyrins and corroles with identical substituents (octaethylporphyrin and octaethylcorrole, for example) differ by about 0.75 V, with porphyrins easier to reduce and harder to oxidize.[13b–c,18]

Values of reduction potentials were used to complete Figure 1. First the corrole π orbitals were placed 0.75 V higher than those of porphyrin, thereby reflecting the different energies required for removing or adding electrons to these macrocycles. Then, the metal d orbitals of the corrole were shifted by about 1 V relative to those of a porphyrin for reasons discussed above: the singly occupied d orbitals of metallocorroles must be well above the corrole HOMO. The diagram emphasizes the following finding when comparing isoelectronic metal complexes of corroles and porphyrins. *Both the π and d orbitals are at much higher energies in metallocorroles, with the difference being larger for the d orbitals.* In other words, corroles reduce the oxidizing power of metal d orbitals bound to them so substantially that the otherwise facile oxidation of the electron-rich π system is disfavored. In fact, metal ions that are oxidizing in other environments (consider manganese(III), for example) become reducing agents when coordinated by corroles. The central question now becomes: what is responsible for the increase in metal d orbital energies?

We turn to our investigation of the very stable (oxo)chromium(V) corrole for an answer. Based on analysis of the X-ray structure and the d^1 EPR hyperfine coupling constants, corrole σ-donation was found to be a key factor in the overall stabilization of the Cr^V center.[2b] This point of view was later adopted by other workers as well, of which the most relevant for this commentary is that of Eikey et al. in their analysis of the stability of (arylamido)manganese(V) corroles.[7e] The large σ effect of the trianionic corroles on metal d orbitals relative to dianionic porphyrins is attributable in large measure to the required placement of three negative charges in a fairly rigid equatorial coordination plane that is optimized for only two such charges. According to simple LFT considerations, the energy of the $d_{x^2-y^2}$ orbital would be expected to be very high under such circumstances. That this is an extraordinarily large effect is reflected in the nonexistence of metallocorroles with singly or doubly occupied $d_{x^2-y^2}$ orbitals: indeed, there are no examples of high spin iron(III), high spin cobalt(III), or stable copper(II) corroles. Instead, the ground states of iron(III) corroles are either low or intermediate spin, all cobalt(III) complexes are low spin, and all isolated copper corroles contain copper(III).[5] Experimental evidence for the unusually high energy of the other σ-symmetry orbital, d_{z^2}, includes the well-established low affinity of axial ligands for iron(III) and cobalt(III) corroles and the dominance of 5-coordinate metallocorrole structures.[19,20] With the metal ion located well above the equatorial plane defined by the 4 N atoms (by 0.29 (Mn^{III}),[6b] 0.37 (Fe^{IV}),[3c] 0.43 (Mn^{IV}),[7b] 0.60 (Mn^V),[7c] and 0.73 (Mo^V) Å),[21] the d_{xz} and d_{yz} orbitals are also at high energy, as they acquire σ antibonding character. Another view, probably even easier to understand, is to consider what happens when an extra charge is added to a coordination compound without allowing for adjustment of metal-ligand bonds. A normal response in the comparison of manganese(III) complexes of dianionic porphyrin and trianionic corrole would be elongation of metal-ligand bonds. However, the even more contracted coordination core of a corrole relative to a porphyrin disfavors elongation. Consequently, all d orbitals are at much higher energy in the corrole complex.

Several interesting predictions can be made by examination of the energy level diagrams (Figure 1) for manganese corroles and porphyrins. Some already have been mentioned (the existence of copper(III) corroles, for example), but a brief discussion of iron corroles is instructive. Iron corrole nitrosyls were chosen for this purpose (Scheme 2) because they display clear-cut properties. [Although NO is a noninnocent ligand, relationships among NO stretching frequencies, M–N–O bond angles, para- vs. diamagnetism, and formal oxidation states often are helpful.[22]] The stable corrole and porphyrin complexes



Scheme 2. Metal-centered redox reactions of (nitrosyl)iron corroles and porphyrins.

(oec)Fe(NO) and (oep)Fe(NO) contain $[Fe(NO)]^{3+}$ and $[Fe(NO)]^{2+}$ units, respectively. There is no doubt that this distinction is real, as the complexes meet the criteria expected of $\{FeNO\}^{[6]}$ and $\{FeNO\}^{[7]}$ species. The NO stretching frequency of (oec)Fe(NO) is 1767 cm^{-1}, the Fe−N−O bond is linear (176.9°), and the compound is diamagnetic.[23] On the other hand, the NO stretching frequency of (oep)Fe(NO) is 1667 cm^{-1}, the Fe−N−O bond is bent (142.7°), and the isolated material is paramagnetic. The relevance of these two compounds in the current context is that a rare (possibly only) comparison of a metal-centered redox process can be made for a corrole and porphyrin that have almost identical structures. The difference in half-wave reduction potentials ($[Fe(NO)]^{3+}/[Fe(NO)]^{2+}$) is more than a volt, −0.41 for (oec)Fe(NO) and +0.65–0.71 V [range from work in different laboratories] for (oep)-Fe(NO) (Scheme 2)[24]. This comparison of the same metal-based process for virtually identical complexes reveals that the corrole d level is about 1.1 eV higher than that of porphyrin, an analysis that is entirely consistent with Figure 1, which shows that the effect of a corrole relative to a porphyrin is an increase in energy of about 0.75 eV in the π orbitals and >1 eV in the d orbitals.* Accordingly, it should not be surprising that there are many more examples of metal-based oxidation processes for iron corroles than for iron porphyrins.[3]

In summary, we have constructed semiquantitative diagrams that allow for meaningful comparisons of isoelectronic metallocorroles and metalloporphyrins. Based on firm experimental evidence, we show that strong σ-donation that in turn greatly increases the energies of metal d orbitals is a more dominant effect than the high energy of the corrole π system. The outcome is as follows: When only the π system is redox active, such as in d^{10} complexes, metallocorroles are much more prone to oxidation than metalloporphyrins. In open d-shell metallocorroles, however, oxidation of the metal will occur before that of the π system much more frequently than in metalloporphyrins.

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*A similar conclusion may be drawn by comparing (oxo)chromium complexes of a porphyrin with 4 *meso*-$C_6H_3F_2$ and a corrole with 3 C_6F_5 substituents. The difference in the Cr^{V}/Cr^{IV} redox potential is 0.92 V (0.98 vs. 0.07 V vs. SCE, respectively), while the difference for macrocycle-centered oxidation of the corresponding Zn and Ga complexes is only 0.13 V (0.87 vs. 0.75 V, respectively). Even after accounting for a shift of up to 0.35 V for Ga^{III} vs. Zn^{II}, it is apparent that the effect of the corrole on the d orbital energy is much larger than on the π-system.

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