Electronic Structure of Transition Metal−Isocorrole Complexes: A First Quantum Chemical Study

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DFT calculations indicate that the broad electronic-structural features of metalloisocorroles are rather similar to those of analogous metallocorroles. Thus, like their corrole analogues, many metalloisocorroles feature substantially non-innocent ligands. Another key point is that both corroles and isocorroles can exhibit at least two kinds of radical character, a_2 and b_1. However, corrole and isocorrole derivatives also differ significantly in a few ways: for example, the $S = 1/2$ CoPh complexes of corrole and isocorrole exhibit ground states of different symmetries ($^2A''$ and $^2A'$, respectively, in C_s notation), reflecting different interplays of metal(d_π)–ligand(p_π) interactions in corrole versus isocorrole derivatives. The ligand non-innocence phenomena encountered in this study are broadly reminiscent of similar phenomena in peroxidase compound I intermediates and their synthetic models. It seems reasonable, therefore, to adopt the view that this study, along with related studies on corrole derivatives, provides a broader chemical context for appreciating the electronic structures of high-valent heme protein intermediates.

Compared with the current explosion of research on corrole derivatives,[1] the chemistry of isocorrole derivatives has remained essentially unexplored since their initial synthesis and characterization by Vogel and co-workers in 1997.[2] In this context, we chose to map out the broad electronic-structural features of prototype isocorrole first-row transition-metal complexes, using density functional theory (PW91/TZP) calculations as the key tool.[3−7] While chiefly of interest to porphyrin chemists, we were gratified to find that the results impinge on a range of issues of broader interest. For example, we believe that the findings deepen our understanding of the electron distributions of high-valent transition-metal complexes and of the phenomenon of ligand non-innocence. Indirectly, the results also help place the electronic structures of high-valent heme protein intermediates in a broader chemical context.[8−12]

Our results on Sc(IsoC), Ga(IsoC), Ni(IsoC), and Cu(IsoC) (IsoC = isocorrolato) as well as analogous results on the corresponding corrole[13] complexes provide a good starting point for our discussion. Table 1 presents selected adiabatic[14] ionization potentials and excitation energies for these complexes. The results show that the two lowest ionized states of Sc(IsoC) and Ga(IsoC) are almost degenerate, as they are for the analogous corrole derivatives,[13] which is clearly reminiscent of the behavior of porphyrin A_{1u} and A_{2u} radicals.[15] Figure 1 depicts the open-shell orbitals of the $^2A_2$ and $^2B_1$ π-cation radical states of $[Ga(IsoC)]^+$ and of $[Ga(Cor)]^+$ and it is worth noting that the a_2 and b_1 orbitals crudely resemble the porphyrin a_{1u} and a_{2u} HOMOs in shape, respectively.[13] Another point worth noting is that the corrole and isocorrole ionization potentials (*IP*s) are significantly lower than those of analogous metalloporphyrins, that is, metallocorroles and metalloisocorroles are significantly easier to oxidize than the analogous metalloporphyrins.[13]

As in the case of Ni(Cor),[13] two Ni^{II} π-cation radical states compete as ground states for Ni(IsoC), the high-valent Ni^{III} state being more than 1 eV higher in energy. In contrast, high-valent Cu^{III} ground states are predicted for Cu(IsoC), with low-lying Cu^{II} π-cation radical states, which again parallels the situation with Cu−corroles.[13] However, a careful examination of Table 1 reveals an interesting twist in the Cu−isocorrole case. In the case of Cu−corroles, temperature-dependent NMR spectroscopy strongly suggests the presence of thermally accessible paramagnetic excited states, consistent with the DFT results.[16−18] In contrast, for Cu(IsoC), the Cu^{II} π-cation radical states are not as low in energy, relative to the ground state, as they are for Cu(Cor), suggesting that, unlike Cu−corroles, Cu−isocorroles may not exhibit significantly temperature-dependent NMR spectra.

Table 2 presents some key structural parameters of the optimized geometries of the molecules studied in this work. All the isocorrole derivatives exhibit slightly but consistently shorter metal−nitrogen distances than the corresponding corrole derivatives. In particular, the

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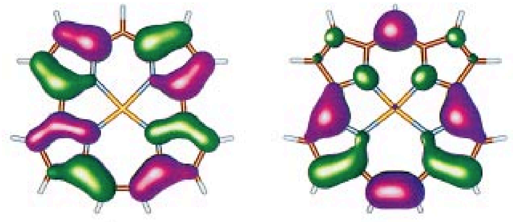
Table 1. Relative energies [eV] of different electronic states of metalloisocorroles and metallocorroles

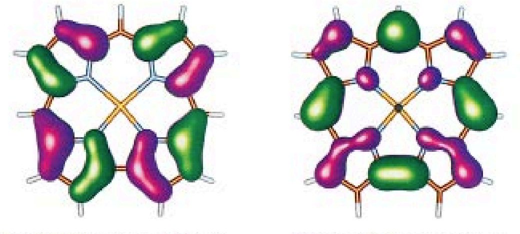
Species studied[a][b]	State	E [eV] Isocorrole	Corrole
$\mathrm{Sc^{III}(L)}$	$^1\mathrm{A}_1$	0.0000	0.0000
$[\mathrm{Sc^{III}(L)}]^+$	$^2\mathrm{B}_1$	6.5730	6.3644
$[\mathrm{Sc^{III}(L)}]^+$	$^2\mathrm{A}_2$	6.6641	6.7080
$[\mathrm{Sc^{III}(L)}]^-$	$^2\mathrm{B}_1$	−1.5260	−1.1558
$\mathrm{Ni^{III}(L)}$	$^2\mathrm{A}_1$	1.3075	1.2705
$\mathrm{Ni^{II}(L^{\cdot})}$	$^2\mathrm{B}_1$	0.0000	0.0174
$\mathrm{Ni^{II}(L^{\cdot})}$	$^2\mathrm{A}_2$	0.1373	0.0000
$\mathrm{Cu^{III}(L)}$	$^1\mathrm{A}_1$	0.0000	0.0000
$\mathrm{Cu^{II}(L^{\cdot})}$	$(x^2{-}y^2)^1\mathrm{a}_2{}^1\ (^3\mathrm{B}_1)$	0.4084	0.3551
$\mathrm{Cu^{II}(L^{\cdot})}$	$(x^2{-}y^2)^1\mathrm{b}_1{}^1\ (^3\mathrm{A}_2)$	0.3033	0.1618
$\mathrm{Ga^{III}(L)}$	$^1\mathrm{A}_1$	0.0000	0.0000
$[\mathrm{Ga^{III}(L)}]^+$	$^2\mathrm{B}_1$	6.6658	6.6270
$[\mathrm{Ga^{III}(L)}]^+$	$^2\mathrm{A}_2$	6.7152	6.7007
$[\mathrm{Ga^{III}(L)}]^-$	$^2\mathrm{B}_1$	−1.5522	−0.8830

[a] L = corrolato or isocorrolato. [b] Note that although the electron affinities of Sc(L) and Ga(L) have been computed, they are not explicitly commented upon in this paper.



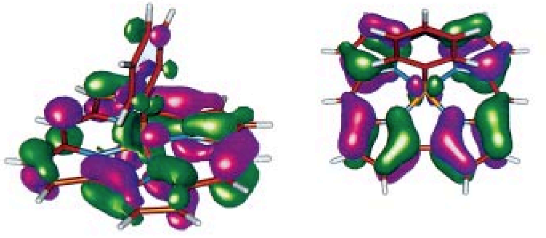
$[\mathrm{Ga(IsoC)}]^+$, $^2\mathrm{A}_2$: a_2 HOMO

$[\mathrm{Ga(IsoC)}]^+$, $^2\mathrm{B}_1$: b_1 HOMO



$[\mathrm{Ga(Cor)}]^+$, $^2\mathrm{A}_2$: a_2 HOMO

$[\mathrm{Ga(Cor)}]^+$, $^2\mathrm{B}_1$: b_1 HOMO



Co(IsoC)Ph, $^2\mathrm{A}'$: a′ HOMO

Co(Cor)Ph, $^2\mathrm{A}''$: a″ HOMO

Figure 1. Majority-spin HOMOs of $[\mathrm{Ga(IsoC)}]^+$ and $[\mathrm{Ga(Cor)}]^+$, Co(IsoC)Ph and Co(Cor)Ph

metal−nitrogen distances in Cu(IsoC) are 0.02−0.03 Å shorter than those in Cu(Cor). This may well explain the greater stability of the d^8 $\mathrm{Cu^{III}}$ state, relative to $\mathrm{Cu^{II}}$ π-cation radical states, in the isocorrole case than in the corrole case.[13]

We are now in a position to discuss some of the intricacies of the electron distributions of corrole and isocorrole middle transition metal derivatives.[19−24] Figure 2 depicts the Mulliken spin populations of different M(IsoC)X complexes (M = Mn, Fe; X = Cl, Ph), along with those of the $^2\mathrm{A}_2$ and $^2\mathrm{B}_1$ π-cation radical states of $[\mathrm{Ga(IsoC)}]^+$, for comparison. The notable point here is that the isocorrole macrocycle in the case of the M(IsoC)Cl (M = Mn, Fe) complexes carries significant minority spin-density distributed roughly in the form of the isocorrole b_1 HOMO. In other words, the electronic structures of these complexes may be viewed in terms of an $S = 2$ $\mathrm{Mn^{III}}$ or an $S = 3/2$ $\mathrm{Fe^{III}}$ center antiferromagnetically coupled to an isocorrole b_1 radical. In contrast, the isocorrole ligand in the case of M(IsoC)Ph (M = Mn, Fe) carries little spin-density and the metal center in these species is best viewed as "truly" high-valent, i.e. $\mathrm{Mn^{IV}}$ and $\mathrm{Fe^{IV}}$. These findings closely parallel similar findings on corrole−Mn and −Fe derivatives.[25]

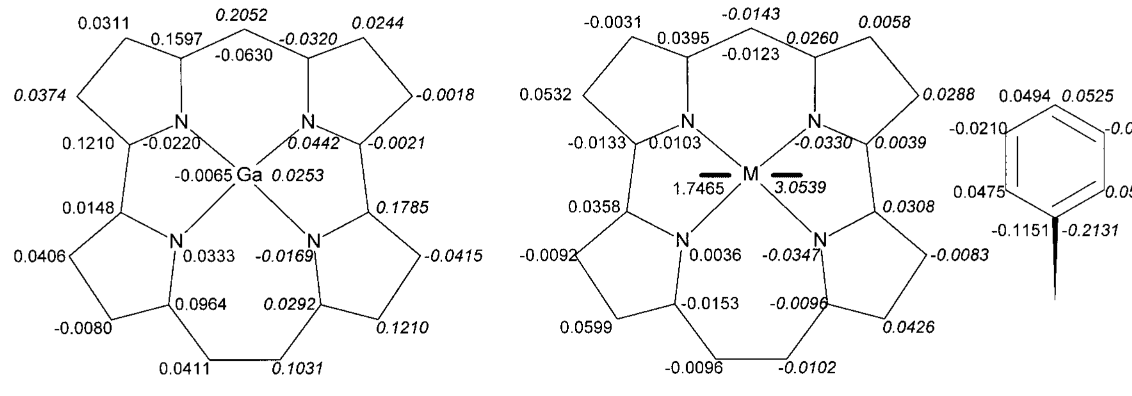
The electronic structures of Co(IsoC)Ph and Co(Cor)Ph appear to be of particular interest.[26,27] First, the electron spin-density profiles (Figure 2) are qualitatively different from those found in the Mn and Fe complexes. Thus, the corrole[27] or isocorrole ligand in the cobalt complexes carries large amounts of majority spin; indeed, the single unpaired electron spin appears to be roughly evenly distributed between the Co center and the macrocycle in these complexes as a result of a $\mathrm{Co(d_\pi)}$−macrocycle(π) orbital interaction. Figure 1 depicts the majority-spin HOMOs of Co(IsoC)Ph and Co(Cor)Ph. The shapes of these MOs resemble the spin-density profiles of the two compounds, which reveals an interesting point: while the corrole a_2 HOMO (a″ in C_s) is largely responsible for ligand radical character in Co(Cor)Ph, the isocorrole b_1 (a′ in C_s) HOMO plays that role in Co(IsoC)Ph.

Overall, the broad electronic-structural features of metalloisocorroles are rather similar to those of the analogous metallocorroles. Thus, like their corrole analogues, many metalloisocorroles feature substantially non-innocent ligands. Another significant point is that both corroles and isocorroles can exhibit at least two kinds of radical character: a_2 and b_1. Having emphasized the similarities, we need to note that corrole and isocorrole derivatives also differ significantly in a few ways. For example, as mentioned above, the $S = 1/2$ CoPh complexes of corrole and isocorrole exhibit ground states of different symmetries ($^2\mathrm{A}''$ and $^2\mathrm{A}'$, respectively, in C_s notation), reflecting different interplays of $\mathrm{metal(d_\pi)}$−$\mathrm{ligand(p_\pi)}$ interactions in corroles versus isocorrole derivatives. We believe that these results broaden our understanding of high-valent transition-metal complexes and of ligand non-innocence. The ligand non-innocence phenomena encountered in this study are broadly reminiscent of similar phenomena in peroxidase

Table 2. Comparison of selected optimized geometrical parameters [Å] of the Ga, Sc, Cu, Mn, Fe and Co complexes of isocorrole and corrole

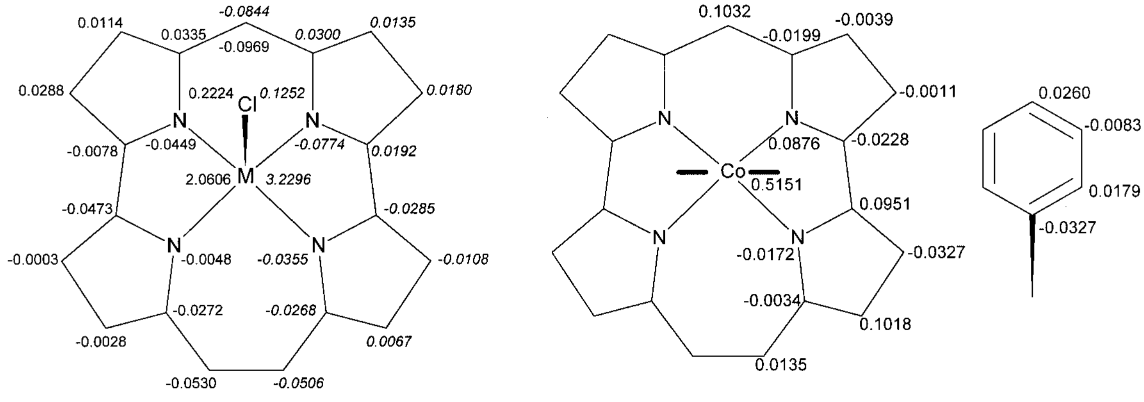
Central atom[a]	$d(M-N_1)$[b]		$d(M-N_2)$[b]		Mean $d(M-N)$[c]		$d(M-N_4)$[c]	
	(IsoC)	(Cor)	(IsoC)	(Cor)	(IsoC)	(Cor)	(IsoC)	(Cor)
Ga	1.906	1.911	1.905	1.924	1.906	1.918	0.000	0.000
Sc	1.823	1.943	1.873	2.049	1.848	2.016	0.000	0.000
Cu (Cu^{III})	1.839	1.887	1.874	1.864	1.857	1.876	0.000	0.000
Cu (Cu^{II} a_2 radical)	1.896	1.926	1.916	1.923	1.906	1.925	0.000	0.000
Cu (Cu^{II} b_1 radical)	1.900	1.915	1.909	1.913	1.905	1.914	0.000	0.000
MnPh (I)	1.894	1.918	1.917	1.922	1.901	1.920	0.353	0.344
MnPh (II)	1.893	1.916	1.913	1.925	1.903	1.921	0.329	0.347
FePh (I)	1.853	1.879	1.892	1.903	1.873	1.891	0.303	0.316
FePh (II)	1.851	1.882	1.893	1.930	1.872	1.906	0.282	0.340
CoPh (I)	1.832	1.858	1.884	1.888	1.858	1.873	0.194	0.211
CoPh (II)	1.830	1.860	1.883	1.890	1.857	1.875	0.165	0.224
MnCl	1.903	1.926	1.937	1.939	1.920	1.933	0.461	0.431
FeCl	1.837	1.893	1.920	1.926	1.894	1.910	0.426	0.407

[a] For the C_s metal-phenyl complexes, the axial phenyl group is perpendicular to the molecular symmetry plane for conformation I and lies in the molecular symmetry plane in conformation II. [b] The nitrogens referred to as N_1 belong to the pyrrole rings that are directly linked to the *meso*-carbon lying on a molecular symmetry plane, the other set of nitrogens being referred to as N_2. [c] "Mean $d(M-N)$" refers to the mean metal-nitrogen distance, while $d(M-N_4)$ refers to the out-of-plane displacement of the metal relative to the N_4 plane.



$[Ga(IsoC)]^+$ (C_{2v}) $^2A_2$ (normal) and $^2B_1$ (*italics*)

Fe(IsoC)Ph (normal) and Mn(IsoC)Ph (*italics*)



Fe(IsoC)Cl (normal) and Mn(IsoC)Cl (*italics*)

Co(IsoC)Ph

Figure 2. Gross atomic spin populations for selected molecules; note that certain atoms carry a significant minority spin population

compound I intermediates and their synthetic models. It seems reasonable to adopt the view, therefore, that this study, along with related studies on corrole derivatives, provides a broader chemical context for appreciating the electronic structures of high-valent heme protein intermediates.[28,29]

Supporting Information: Optimized Cartesian coordinates of the compounds studied. PW91/TZP atomic spin populations for relevant metallocorroles (see also footnote on the first page of this article).

Acknowledgments

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