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Electronic Structure of Gallium, Copper, and Nickel Complexes of Corrole. High-Valent Transition Metal Centers versus Noninnocent Ligands

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Received December 9, 1999. Revised Manuscript Received February 29, 2000

Abstract: Using regular nonlocal density functional theory (DFT) as well as combined DFT and configuration interaction calculations, we have carried out a first theoretical study of the electronic structure of metalcorroles. The valence orbital energy spectra and the calculated electronic absorption spectrum of (Cor)Ga (Cor³⁻ = corrolato), a prototype non-transition-metal corrole, are qualitatively similar to those of a metalloporphyrin such as zinc porphyrin. The “four-orbital model” holds well for corroles. The a₂ and b₁ HOMOs of (Cor)Ga are crude analogues of the well-known a_{1u} and a_{2u} porphyrin HOMOs, respectively. Thus, as in the case of porphyrins, there are two nearly equienergetic π -cation radical states for corroles. DFT also appears to provide a good description of the stabilization of high-valent transition-metal centers and of ligand noninnocence, two intertwined and central themes in metalcorrole chemistry. The calculated ground state of (Cor)Cu is a diamagnetic d⁸ Cu(III) state, with Cu(II) π -cation radical states only slightly higher in energy, which faithfully mirrors the experimental scenario. In contrast, there are no known Cu(III) porphyrin complexes. For (Cor)Ni, low-spin Ni(II) π -cation radical states are significantly lower in energy than a Ni(III) state, again consistent with experiment, reflecting the favorable energetics of d⁸ square planar complexes. The various optimized geometries reveal significant, characteristic structural changes accompanying the formation of A₂- and B₁-type corrole π -cation radicals. We predict that the resonance Raman spectra of metalcorroles should reflect these structural features and, thereby, assist in the assignment of valence tautomeric states of transition-metal corrole complexes.

I. Introduction

The chemistry of porphyrins and related macrocycles appears to be a never-ending wellspring of interesting problems, of both fundamental and applied nature, for researchers across the entire spectrum of the chemical sciences.¹ After 50 years of theoretical study,² quantum chemists wonder at the Shakespearean variety of the electronic structures of these molecules that seemingly “age cannot wither nor custom stale”.³ At present, the chemistry of corroles provides a good example of the vibrancy of porphyrin-related research.^{4,5} First synthesized by A. W. Johnson⁶ in the 1960s, corroles are attracting renewed interest as a result of a number of recent developments. As trianionic ligands, corroles have been found to stabilize high-valent states of a

variety of transition metals including Cr, Mn, Fe, Co, and Cu.^{4,5} Second, corroles are now readily available as a result of one-pot syntheses.^{7,8} Third, early results indicate that transition-metal corroles should be excellent catalysts, in terms of stability and efficiency, for a variety of synthetic reactions.⁹ As a result of these developments, the chemistry of corroles is experiencing rapid, even explosive, growth.^{4,5}

Theoretical chemists have a major role to play in the current development of corrole chemistry. The high-valent nature of many transition-metal corrole complexes raises the prospect of multiple valence-tautomeric states.¹⁰ In other words, what are the energetics of metal- versus ligand-centered oxidation? How do these states differ in terms of electron distribution? Before addressing these issues involving transition metals, however, we need to take a step back and characterize some basic aspects of the electronic structure of non-transition-metal derivatives of corrole. To our knowledge, there are no major first-principles theoretical studies of the electronic structure of corroles.¹¹ A recent local density functional theoretical study focused on the

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relative energetics of different tetrapyrrolic corrole isomers, both in their free-base forms and as a function of different sizes of complexed non-transition-metal ions.¹² Some basic unanswered questions are as follows. Does Gouterman's four-orbital model¹³ apply to corrole? What are some of the lowest ionization potentials (IPs) and the electron affinity (EA) of a prototype metallocorrole? Are the two HOMOs of corroles near-degenerate and is there the possibility of two different types of metallocorrole cation radicals, analogues of the well-known A_{1u} - and A_{2u} -type metalloporphyrin radicals?¹⁴ What are the unpaired spin density profiles of corrole π -cation radicals? Here we have investigated these questions using nonlocal density functional theory. Having laid the necessary groundwork, we have also studied the twin issues of stabilization of high-valent transition-metal centers versus ligand noninnocence, increasingly central aspects of the chemistry of metallocorroles. In particular, we describe the relative energetics, spin density profiles, and key structural features of metal(III) versus metal(II) corrole radical states for Cu and Ni corrole complexes. Overall, these early theoretical results should serve as a springboard for future theoretical studies of many important issues such as the electronic effects of peripheral substitution and other structural perturbations, the diverse electronic structures of middle-transition-metal (Mn, Fe, Co) corroles, and excited states and electronic spectra.^{4,5}

II. Methods

For the majority of the calculations, we have used nonlocal density functional theory (NLDFT), the PW91 exchange correlation functional, triple- ζ Slater-type basis sets, a spin-unrestricted formalism, a fine mesh for numerical integrations, and full geometry optimizations under C_{2v} symmetry constraints, as implemented in the program system ADF.¹⁵ For (Cor)Ga (Cor³⁻ = corrolato), vertical IPs and the vertical EA were calculated as energy differences between the un-ionized state and ionized states of different electron occupancies, the geometry being that optimized for the un-ionized state. Using the Gaussian98 program,¹⁶ we have also carried out a single-point RHF/6-311G(d,p) calculation on the NLDFT optimized geometry of (Cor)Ga.

The singlet excited states of (Cor)Ga were studied with the DFT/SCI method described by Grimme.¹⁷ The method is based on the single-excitation configuration interaction (SCI) approach with the CI Hamiltonian matrix elements modified and corrected empirically.

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Table 1. Frontier Orbital Energies (eV) of (Cor)Ga from RHF/6-311G(d,p) and PW91/TZP Calculations

MO	RHF/6-311G(d,p)	PW91/TZP
HOMO-6	-10.231 (a_2)	-6.681 (b_1)
HOMO-5	-10.134 (a_2)	-6.668 (b_2)
HOMO-4	-9.802 (b_1)	-6.225 (a_2)
HOMO-3	-9.359 (b_1)	-6.172 (b_1)
HOMO-2	-9.055 (a_2)	-5.919 (a_2)
HOMO-1	-6.534 (b_1)	-4.824 (a_2)
HOMO	-6.146 (a_2)	-4.723 (b_1)
LUMO	0.533 (a_2)	-2.793 (a_2)
LUMO+1	1.478 (b_1)	-2.439 (b_1)
LUMO+2	2.541 (b_1)	-1.196 (b_1)
LUMO+3	3.645 (a_1)	-0.401 (a_1)
LUMO+4	3.908 (b_2)	-0.362 (b_1)

Molecular orbital eigenvalues are taken from NLDFT calculations for the construction of the CI Hamiltonian matrix. These calculations have been performed with the TURBOMOLE^{18,19} suite of programs, the B3LYP exchange-correlation functional, and valence double- ζ Gaussian basis sets with d-polarization functions for carbon and nitrogen (C, N: [3s2p1d]; H: [2s]) (VDZP).²⁰ All single excitations from the occupied valence MOs to the virtual space were included in the DFT/SCI calculations.

Throughout, the C_{2v} symmetry labels refer to the metallocorrole molecule being in the yz plane with the z axis as the molecular 2-fold axis. With respect to the molecular plane, the a_1 and b_2 orbitals are σ and the a_2 and b_1 orbitals are π .

III. Results and Discussion

(A) Ga(III) Corrole and Its Ionized and Excited States.

A key motivation for studying a non-transition-metal complex of corrole has been to determine whether the electronic structure conforms to a porphyrin-type four-orbital model. On the basis of the qualitative similarity of the electronic absorption spectra of porphyrins and corroles, experimentalists have conjectured that the four-orbital model should hold for corroles.^{3,4} Using simple π -electron CI calculations,^{11b} Hush and co-workers confirmed this expectation many years ago. The present calculations on (Cor)Ga simply give a more quantitative picture of the ionization and excitation energies of the corrole macrocycle. More importantly, they prepare the stage for calculations of more challenging aspects of corrole chemistry, viz. the question of metal- versus ligand-centered oxidation. Table 1 presents the RHF/6-311G(d,p)/PW91/TZP and PW91/TZP MO energies of (Cor)Ga. The two HOMOs, a_2 and b_1 , are near-degenerate, as are the two LUMOs, also a_2 and b_1 , and these four frontier orbitals are well-separated energetically from the rest of the orbital energy spectrum.

Table 2 shows the results of the DFT/SCI calculations on the excited states of (Cor)Ga, which are qualitatively very similar to those for a simple metalloporphyrin such as zinc porphyrin.^{21,22} The near-degenerate S_1 and S_2 states with energies around 2.33 eV and oscillator strengths around 0.025 correspond to the Q-bands whereas the S_3 and S_4 states with energies around 3.7 eV and much higher oscillator strengths around 1.25 correspond to the B or Soret bands. The four lowest excited states of (Cor)Ga share with the porphyrins a pronounced two-

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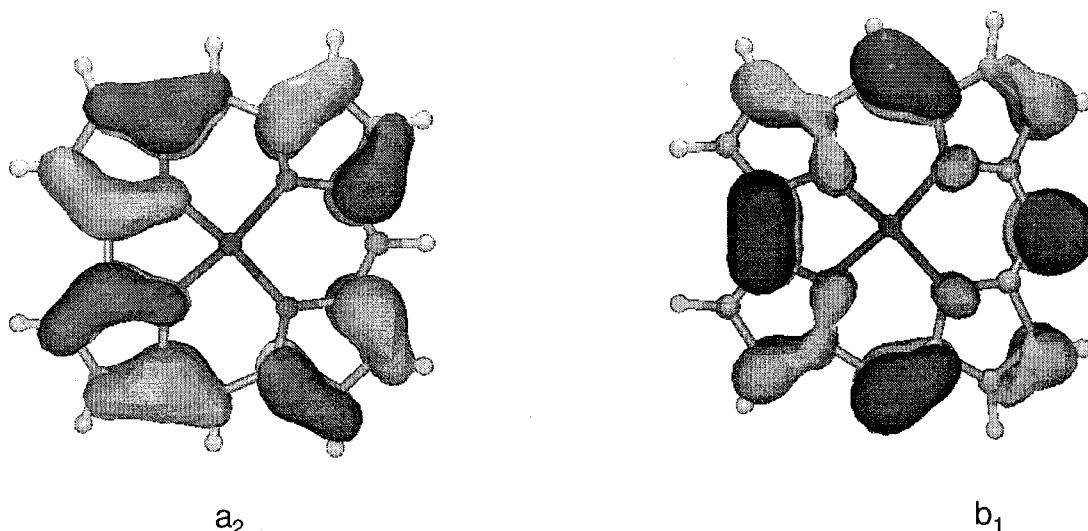
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Table 2. B3LYP/SCI Results on the Singlet Excited States of (Cor)Ga

state	energy (eV)	oscillator strength	composition
S ₁	2.32	0.0233	55% HOMO-LUMO, 42% HOMO-1 – LUMO+1
S ₂	2.34	0.0273	57% HOMO-1 – LUMO, 41% HOMO – LUMO+1
S ₃	3.66	1.1590	48% HOMO-1 – LUMO+1, 35% HOMO – LUMO
S ₄	3.80	1.3710	49% HOMO – LUMO+1, 33% HOMO-1 – LUMO
S ₅	4.24	0.0752	92% HOMO-2 – LUMO
S ₆	4.38	0.0131	89% HOMO – LUMO+2
S ₇	4.49	0.0058	80% HOMO-3 – LUMO, 13% HOMO-4 – LUMO+1
S ₈	4.57	0.0045	89% HOMO-1 – LUMO+2

**Figure 1.** The two HOMOs of (Cor)Ga.**Table 3.** Relative Energies (eV) of Different Electronic States of Metalloporroles

compd	state	rel energy
[(Cor)Ga ^{III}] ⁰	¹ A ₁	0.000
[(Cor•)Ga ^{III}] ⁺	² B ₁	6.745
[(Cor•)Ga ^{III}] ⁺	² A ₂	6.840
[(Cor)Ga ^{III}] ⁻	² A ₂	-1.110
[(Cor)Cu ^{III}] ⁰	¹ A ₁	0.000
[(Cor•)Cu ^{II}] ⁰	(x ² – y ²) ¹ b ₁ ¹ (³ A ₂)	0.161
[(Cor•)Cu ^{II}] ⁰	(x ² – y ²) ¹ a ₂ ¹ (³ B ₁)	0.354
[(Cor)Ni ^{III}] ⁰	² A ₁	1.271
[(Cor•)Ni ^{II}] ⁰	² B ₁	0.018
[(Cor•)Ni ^{II}] ⁰	² A ₂	0.000

configuration character, consistent with the four-orbital model. Higher excited states are close in energy to S₄ but have significantly smaller oscillator strengths than S₃ and S₄.

Table 3 presents the relative energies of different ionized and excited states of (Cor)Ga, (Cor)Cu, and (Cor)Ni, calculated using normal ground-state DFT methods. The two lowest IPs and the EA of (Cor)Ga are 6.745, 6.840, and 1.110 eV, which correspond to ²B₁, ²A₂, and ²A₂ ionized states, respectively. IPs calculated at this level of theory (PW91/TZP) are expected to be in near-quantitative agreement with experiment.^{23,24,25} Each of the two lowest IPs of (Cor)Ga are lower than the lowest calculated IP of zinc porphyrin (7.04 eV), consistent with electrochemical findings.²⁶ Thus, in dichloromethane, the first oxidation potentials of (OECor)Sn(C₆H₅), (OECor)SnCl, and (OEP)SnCl₂ (OECor = β-octaethylcorrole, OEP = β-octaeth-

Table 4. Gross Atomic Spin Populations of [(Cor•)Ga^{III}]⁺

spin population			spin population		
atom	² B ₁	² A ₂	atom	² B ₁	² A ₂
m ₁	0.2383	-0.0490	β ₁	0.0579	0.0166
m ₂	0.1829	-0.0191	β ₂	-0.0047	0.0444
α ₁	-0.0421	0.1381	β ₃	0.0851	0.0058
α ₂	0.0205	0.1036	β ₄	-0.0357	0.0494
α ₃	-0.0267	0.1479	ν ₁	0.0377	-0.0231
α ₄	0.0944	0.0711	ν ₂	0.0183	0.0033
			μ	0.0392	0.0005

ylporphyrin) are 0.47, 0.67, and 1.36 V versus the saturated calomel electrode, respectively. Our calculations and electrochemical measurements thus agree that a corrole derivative has a lower IP than a closely analogous porphyrin derivative.

The two lowest IPs of (Cor)Ga are extremely close to each other. Thus, the a_{1u}/a_{2u} dichotomy that dominates the chemistry of porphyrin cation radicals has an analogue in corrole chemistry as well. The open-shell orbitals of the ²B₁ and ²A₂ states of [(Cor)Ga]⁺ are shown in Figure 1. Table 4 shows the gross atomic spin populations for the ²B₁ and ²A₂ states of [(Cor)Ga]⁺. There are crude similarities between the a₂ and b₁ HOMOs

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of (Cor)Ga and the a_{1u} and a_{2u} HOMOs of a typical metalloporphyrin, respectively. Indeed, after a hypothetical desymmetrization of a D_{4h} metalloporphyrin to a C_{2v} metallocorrole through extrusion of a meso methine unit, the a_{1u} and a_{2u} porphyrin HOMOs would transform as a_2 and b_1 in the corrole. Like the a_{1u} porphyrin HOMO, the a_2 corrole HOMO has zero or relatively small amplitudes at the “meso” positions. Like the a_{2u} porphyrin HOMO, the b_1 corrole HOMO has large amplitudes at the “meso” positions. However, this porphyrin–corrole analogy is limited and is intended mainly as a mnemonic for remembering the shapes of the corrole HOMOs. In this study, we have not considered the effects of peripheral substituents on the relative energies of 2B_1 and 2A_2 metallocorrole radicals. However, Figure 1, Table 4, and a large body of information on porphyrin cation radicals¹⁴ do permit some qualitative predictions. Thus, we expect that a metallocorrole with electron-donating meso substituents, such as a *meso*-triphenylcorrole derivative, should form 2B_1 cation radicals whereas a metallocorrole with electron-withdrawing meso substituents, such as a *meso*-tris(pentafluorophenyl)corrole derivative, should form 2A_2 cation radicals. Because the C_β spin populations are roughly comparable for the two lowest cationic states of [(Cor)Ga]⁺, the relative energetics of the 2B_1 and 2A_2 radicals of β -substituted metallocorroles is more delicately balanced and hence difficult to predict.

(b) Energetics of Cu(III) and Ni(III) Corrole and Their Valence Tautomers. Having established some of the fundamentals of corrole electronic structure, we can begin to explore the electronic structures of transition-metal corroles in all their rich variety. Here we illustrate the utility of NLDFT calculations for comparing the energetics of metal- versus ligand-centered oxidation in copper and nickel corroles. Table 3 presents the energies of the different electronic states studied.

The calculated ground state of (Cor)Cu is a Cu(III) state, with the two Cu(II) corrole radical states only slightly higher in energy. This result faithfully mirrors the experimental scenario.²⁷ Thus, the NMR spectra of a copper octaalkylcorrole exhibited strong temperature dependence; sharp signals were obtained at room temperature, whereas significant line-broadening occurred with increasing temperature. This temperature-dependent magnetic behavior was ascribed to an equilibrium between a diamagnetic d^8 Cu(III) corrole and a paramagnetic Cu(II) corrole π -cation radical of higher energy.

For (Cor)Ni, Ni(II) corrole radical states are much preferred over a Ni(III) state, again consistent with experiment. The UV–vis spectrum of a nickel β -octaalkylcorrole exhibits an unusually weak Soret absorption, suggesting a corrole radical. In addition, the EPR spectrum is unlike that of Ni(III) porphyrins.²⁷

The above results reflect the favorable energetics of metal d^8 configurations for square-planar complexes. However, the stabilization of Cu(III) appears to be unique to corroles and other ligands with high negative charge. Thus, to our knowledge, Cu(III) porphyrins are unknown. In this connection, it may be worth pointing out that Ag(III) is much more readily stabilized, and Ag(III) complexes are known for both dianionic porphyrin and trianionic inverted porphyrin ligands.^{28,29}

(c) Optimized Molecular Structures. Table 5 presents key structural parameters from the different PW91/TZP optimized

Table 5. Selected Optimized Distances (Å) and Angles (deg)

contract appreciably on the formation of B₁-type π -cation radicals. The bonds a₃, b₄, c₁, c₂, c₃, and c₄ (which include all C α –C β bonds) expand appreciably and the bonds a₂, a₄, b₁, b₃, d₁, and d₂ (which include all C β –C β bonds) contract appreciably on the formation A₂-type π -cation radicals. The metal–nitrogen bonds are shorter in A₂-type π -cation radicals than in B₁-type radicals consistent with the higher amplitudes of the b₁ MO on the corrole nitrogens relative to the a₂ MO and decreasing metal–nitrogen attraction with decreasing occupancy of the b₁ MO. Note also the short metal–nitrogen bond distances for Cu(III) corrole, compared to the Cu(II) corrole radical valence tautomers. Although these small geometrical differences between different valence tautomers may not be easily observable from crystallographic analyses, they clearly reflect significant differences in bond force constants between the different species, which should be discernible from resonance Raman studies of metallocorroles. As in the case of metalloporphyrins, we expect that a number of structure-sensitive vibrational marker bands³⁰ will be observed for metallocorroles, which should greatly assist in the determination of different valence tautomeric electronic states that are possible for the molecules being studied.

Conclusions

The main conclusions are as follows.

1. The valence orbital energy spectra and the calculated electronic absorption spectrum of a prototype non-transition-metal corrole, (Cor)Ga, are qualitatively similar to those of a metalloporphyrin such as zinc porphyrin. The four-orbital model

holds well for corroles. The a₂ and b₁ HOMOs of (Cor)Ga are crude analogues of the well-known a_{1u} and a_{2u} porphyrin HOMOs. Thus, as in the case of porphyrins, there are two nearly equienergetic π -cation radical states for corroles.

2. The ground state of (Cor)Cu is a diamagnetic d⁸ Cu(III) state, with Cu(II) π -cation radical states only slightly higher in energy, which faithfully mirrors the experimental scenario. In contrast, there are no known Cu(III) porphyrin complexes.

3. For (Cor)Ni, low-spin Ni(II) π -cation radical states are significantly lower in energy than a Ni(III) state, again consistent with experiment, reflecting the favorable energetics of d⁸ square-planar complexes.

4. The optimized geometries reveal significant, characteristic structural changes accompanying the formation of A₂- and B₁-type π -cation radicals. We predict that resonance Raman spectra of metallocorroles should reflect these structural features and, thereby, provide valuable information on the electronic states of transition-metal corrole complexes with multiple valence tautomers.

Overall, we have clarified some of the basic electronic structural issues of corrole chemistry. We have also studied the stabilization of high-valent transition metals and the possibility of ligand noninnocence, two recurring themes in metallocorrole chemistry. We plan to continue using the methods employed here, density functional theory and its excited-state implementations, to study a variety of additional transition-metal complexes of corroles.

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