Norcorrole and Dihydronorcorrole: A Predictive Quantum Chemical Study

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Dedicated to Professor Emeritus Dr. Dr. h. c. Emanuel Vogel

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DFT calculations indicate norcorrole (NCH_2), a 16π-electron doubly contracted porphyrin, to be a promising synthetic target, especially when complexed to a small cation such as Ni^{II}. The relative stability of norcorrole derivatives appears to reflect the fact that they are not antiaromatic, but should rather be viewed as bis(dipyrrins). However, norcorrole (NC) complexes are expected to be prone to reduction and we predict that high-valent transition metal dihydronorcorrole (DHNC) derivatives should exist as reasonably stable substances. Our calculations further predict that both NC and DHNC complexes should exhibit short metal–nitrogen distances and moderate to strong doming of the macrocycle. Overall, a number of calculated results suggest that NC and DHNC derivatives should be of unique electronic-structural interest, as conceptual links between aromatic tetrapyrroles such as porphyrin and corrole on the one hand and open-chain pyrrole-based ligands such as dipyrrins and biliverdines on the other.

The study of porphyrin analogues such as expanded and contracted porphyrins and heteroatom-substituted porphyrins (e. g. porphyrazines and corrolazines) has been a major new direction of porphyrin-related research.[1] In many cases, the new macrocycles have resulted in new metal spin states and novel chemical behavior, relative to the analogous porphyrin complexes. In 2002, Professor Emanuel Vogel encouraged one of us (AG) to investigate by theoretical means the question of stability of the doubly contracted porphyrin shown in Figure 1, for which we have used the trivial name norcorrole (NCH_2; "nor" signifying one fewer carbon than in corrole), as well as its potential as a ligand in coordination chemistry. Given the 16π-electron, possibly antiaromatic, nature of the ring system and the extremely contracted nature of the central N_4 core, we were not optimistic about the prospects. Nonetheless, we undertook a DFT[2] investigation of the problem and have been pleasantly surprised by the results, which seem quite promising, as described below.[3–5]

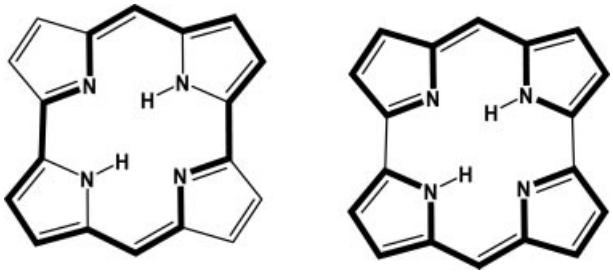

Figure 1. Two views of norcorrole. Left: antiaromatic; right: a bis(dipyrrin) structure.

Despite the small N_4 core size, a geometry optimization indicated an essentially planar, near-C_{2h} geometry for NCH_2, some highlights of which are depicted in Figure 2. Note the compact N_4 core and the short N–H···N hydrogen bonds.[6] Remarkably, the optimized NCH_2 structure does not exhibit the strong bond length alternation for the various skeletal CC and CN bonds that one might expect for

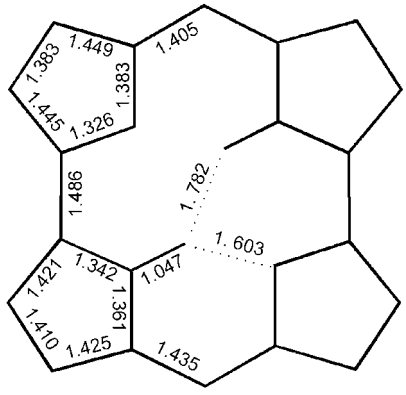

Figure 2. Selected symmetry-unique bond lengths [Å] in free-base norcorrole. Note the crowded core and the short N–H···N hydrogen bond.

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an antiaromatic system. Thus, adjacent C_α–C_{meso} distances differ by only 0.03 Å. The long, nearly single bond-like, C_α–C_α distance of 1.486 Å provided the key insight into this structure, namely that NCH_2 should not be viewed as antiaromatic but rather as a cyclic bis(dipyrrin),[7,8] and indeed as a unique conceptual link between aromatic tetrapyrroles on the one hand and dipyrrins and other open-chain oligopyrroles on the other.[9]

Might NCH_2 serve as a macrocyclic ligand and exhibit interesting coordination behavior? Given the small size of the low-spin Ni^{II} cation, Ni(NC) (S = 0) seemed like an ideal candidate for a DFT study. A C_2 symmetry-constrained geometry-optimization yielded a near-C_{2v} geometry, the essential symmetry-equivalence of the four pyrrole units once again signifying that the structure is best viewed as a bis(dipyrrin) complex. The optimized geometry, depicted in Figure 3, exhibits a significant doming, but is otherwise quite strain-free. The Ni–N distances of 1.85 Å are short (but not exceptionally so), and the direct C_α-C_α linkages are once again nearly single bond-like in length

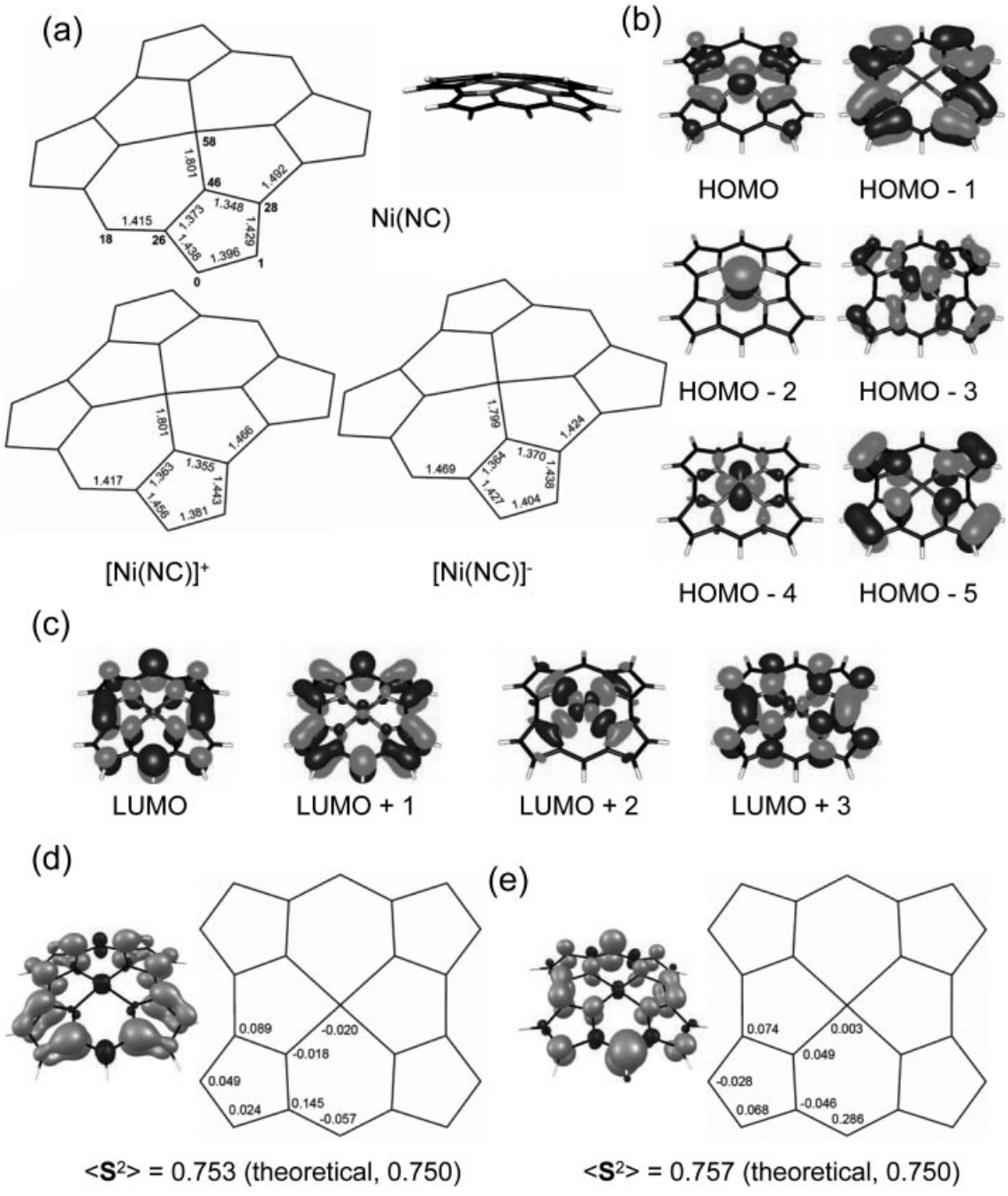


Figure 3. Selected computed results on Ni(NC): (a) Optimized structures [Å], (b) HOMOs, (c) LUMOs, (d) spin density for $[Ni(NC)]^+$, (e) and spin density for $[Ni(NC)]^-$. In part (a), the numbers in bold indicate the "elevation" of the atoms in question in pm "above" the "lowest" β-carbons, to give an estimate of the amount of doming.

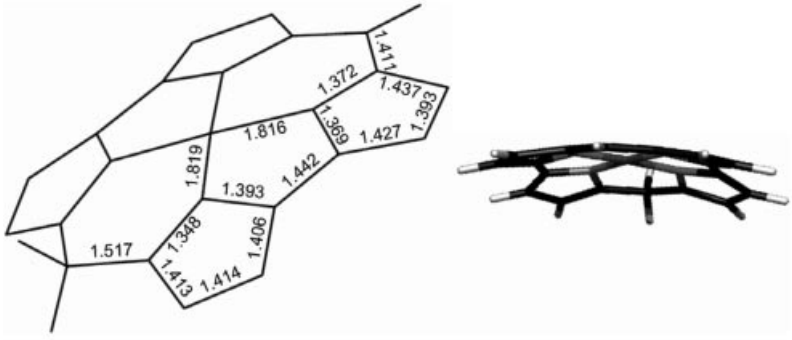
(1.493 Å). Overall, the geometry parameters of Ni(NC) are similar to those of a typical Ni(dipyrrin)$_2$ complex.[7]

Figure 3 also depicts several frontier MOs of Ni(NC), including the HOMO and LUMO, which are both macrocycle-based π MOs, as well as geometrical highlights and spin density profiles for the cationic and anionic states of Ni(NC), for which we also carried out geometry optimizations. Note the strong C_α–C_α bonding interaction in the Ni(NC) LUMO and the shortening of these bonds ($d_{C\alpha-C\alpha}$ = 1.469 Å) in the Ni(NC)$^-$ anion. The calculations on the ionized states yielded an adiabatic ionization potential of 6.91 eV and an adiabatic electron affinity of 2.47 eV for Ni(NC). The ionization potential is roughly comparable to that of a typical metalloporphyrin (e. g. zinc porphyrin[4a,10]), indicating that Ni(NC) should not be particularly sensitive to oxidative degradation. However, the electron affinity is extremely high (compared to about 1.2–1.5 eV for typical porphyrins[4a,11]), suggesting that norcorrole derivatives should be very prone to reduction. The high amplitude of the LUMO at the *meso* positions suggests that either of these positions is a plausible site of nucleophilic attack. We therefore carried out some exploratory DFT studies on dihydronorcorrole (DHNC) complexes, featuring one *meso* CH_2 unit.

By analogy with the corroles and biliverdines,[12,13] we suspected that the trianionic DHNC^{3-} ligand might form highly oxidized transition-metal complexes and our calculations suggest that it indeed should do so. Figure 4 depicts the optimized geometry Cu(DHNC), which exhibits a clear singlet "Cu^{III}" ground state, the lowest S = 1 Cu^{II} π-cation radical state being at least several tenths of an eV higher in energy. Clearly, the highly contracted N_4 core favors the smaller Cu^{III} ion ($d_{CuN} \approx 1.82$ Å, Figure 4) over the significantly larger Cu^{II} ion. The optimized structure of Cu(DHNC) exhibits the same kind of strain-free doming as Ni(NC), but note that the C_α-C_α linkages are significantly shorter (1.44 Å) than in Ni(NC), indicating reasonably effective conjugation across the entire π-system.

The extreme stabilization of the Cu^{III} state in Cu(DHNC) is probably most reminiscent of Cu^{III} corrolazines, where Goldberg[14] and co-workers have experimentally shown that a Cu^{III} ground state is also clearly favored over a Cu^{II} ligand π-cation radical state.[15] In contrast, using temperature-dependent NMR measurements (as well as DFT calculations[4]), we[16,17] and others[18,19] have shown that the Cu^{III} and the Cu^{II} ligand π-cation radical states are essentially isoenergetic for corroles, whereas Cu biliverdines clearly exhibit Cu^{II} ligand π-cation radical ground states. As in the DHNC case, the stability of the Cu^{III} state for corrolazines seems readily ascribable to their significantly tighter N_4 cores, compared with corroles. Interestingly, DFT calculations predict that Cu isocorroles, whose central cavities are expected to be only slightly smaller relative to Cu corroles, should also exhibit clear Cu^{III} ground states.[20]

We have carried out DFT calculations for a number of additional high-valent DHNC complexes, namely Fe(DHNC)Cl (Figure 5), Mn(DHNC)Cl (Figure 6),



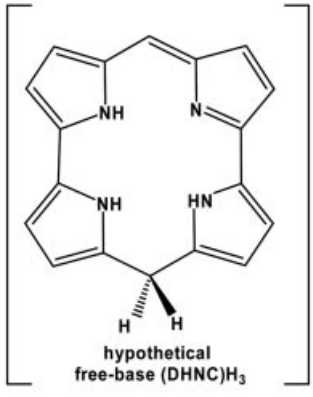


Figure 4. Highlights [Å] of the optimized structure of Cu(DHNC). For clarity, only the *meso* C–H bonds are explicitly shown in the diagram to the left. Note the structure of the hypothetical free-base dihydronorcorrole.

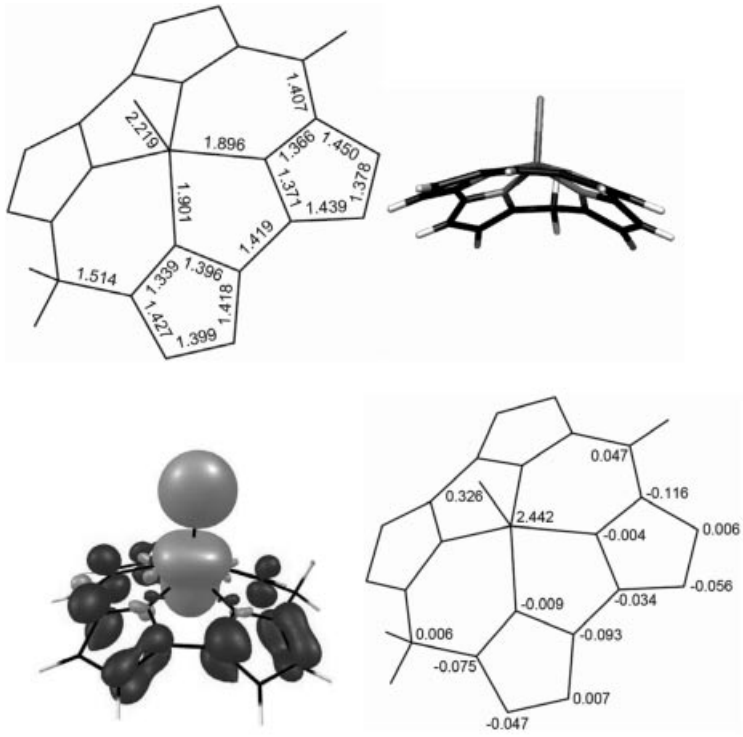


Figure 5. Selected computed results on Fe(DHNC)Cl; top: optimized geometry [Å], bottom: spin density and populations.

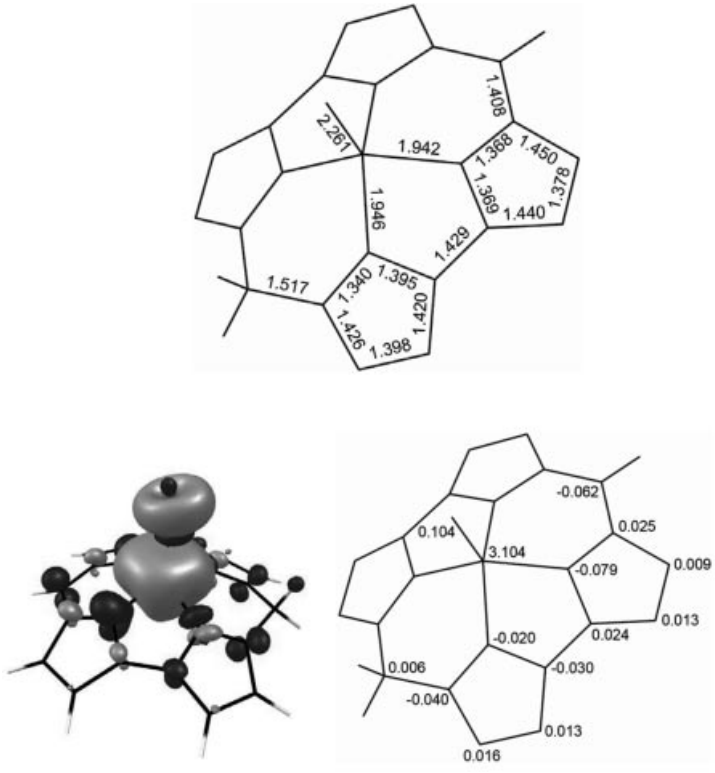


Figure 6. Selected computed results on Mn(DHNC)Cl; top: optimized geometry [Å], bottom: spin density and populations.

Fe(DHNC)Ph (Figure 7), Mn(DHNC)Ph (Figure 8), and Co(DHNC)Ph (Figure 9). The corrole analogues of these complexes have also been studied by DFT and, in some cases, also experimentally, which allows us to make some interesting comparisons.[4–6] Our main findings on these molecules are as follows.

All the five-coordinate DHNC complexes exhibit short metal–nitrogen distances, which are shorter than those in

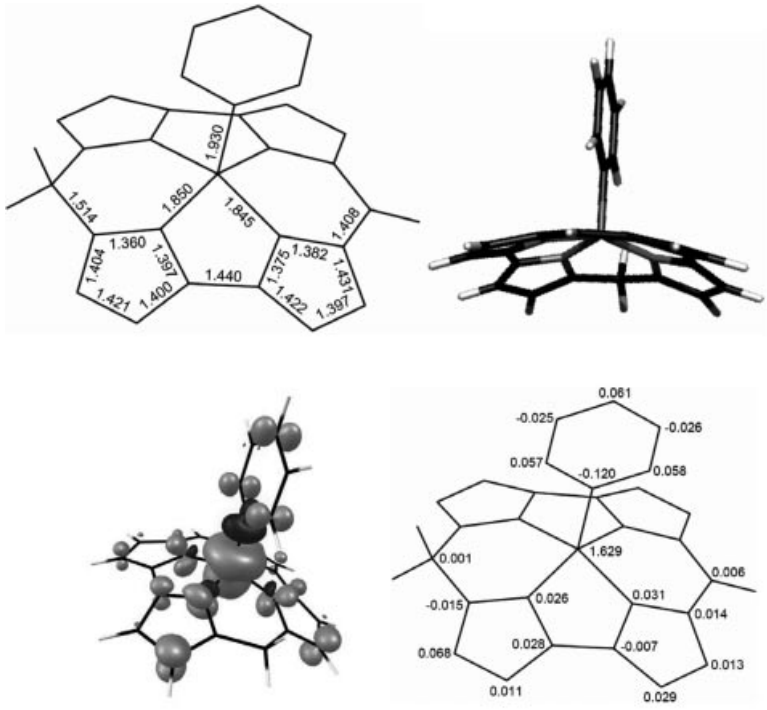


Figure 7. Selected computed results on Fe(DHNC)Ph; top: optimized geometry [Å], bottom: spin density and populations.

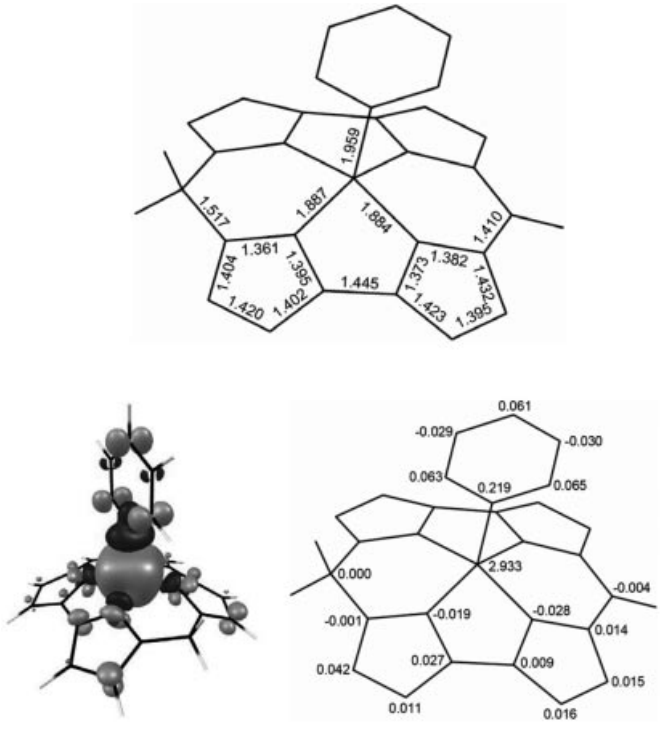


Figure 8. Selected computed results on Mn(DHNC)Ph; top: optimized geometry [Å], bottom: spin density and populations.

corroles, and considerable doming, which is more pronounced than in Ni(NC) and Cu(DHNC). Thus, the metal atom in Fe(DHNC)Cl, Mn(DHNC)Cl, Fe(DHNC)Ph, and Mn(DHNC)Ph is above the DHNC N_4 plane by 0.590, 0.650, 0.400, and 0.444 Å, respectively.

As shown in Figure 5, the Fe(DHNC)Cl results show considerable spatial separation of the majority and minority spin densities. In other words, the calculations suggest that electronic structure might best be described as involving an $S = 3/2$ Fe^{III} center antiferromagnetically coupled to a

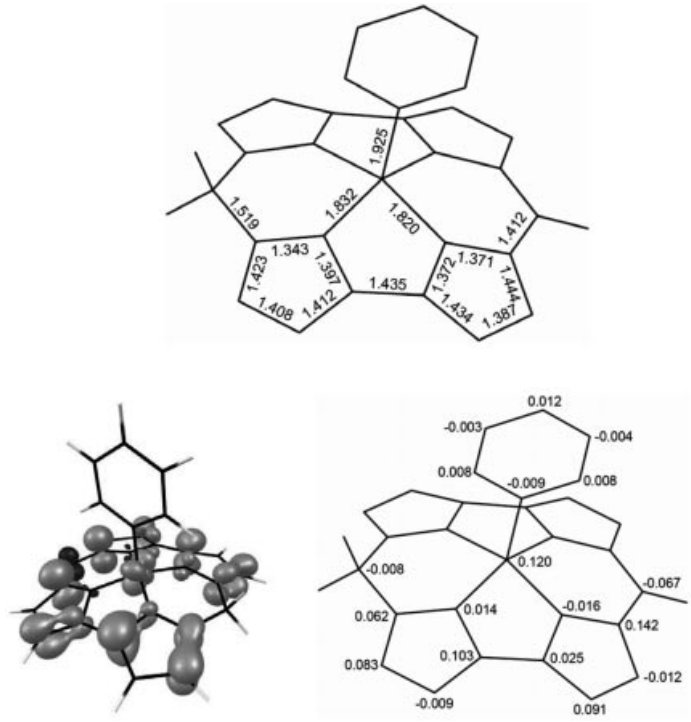


Figure 9. Selected computed results on Co(DHNC)Ph; top: optimized geometry [Å], bottom: the spin density.

$DHNC^{2-\cdot}$ radical. A similar electronic-structural description has also been found for FeCl corrole derivatives on the basis of ^1H NMR spectroscopy and DFT calculations.[5,6,21,22]

Compared to Fe(DHNC)Cl, we found only small amounts of minority spin on the DHNC ligand in Mn(DHNC)Cl (Figure 6). According to our calculations, Mn(DHNC)Cl therefore seems best viewed as a "true" Mn^{IV} complex. In contrast, we found approximately the same amount of ligand radical character (noninnocence) for MnCl corrole as we did for FeCl corrole.[4] In other words, there are both qualitative similarities and intriguing differences between the ways ligand noninnocence plays out in corroles vs. DHNC derivatives.

The spin density profiles of Fe(DHNC)Ph (Figure 7) and Mn(DHNC)Ph (Figure 8) are similar to those of Fe(Cor)Ph and Mn(Cor)Ph, respectively, in the following way.[23] Unlike Fe(DHNC)Cl and Fe(Cor)Cl, Fe(DHNC)Ph and Fe(Cor)Ph do not exhibit significant spatial separation of majority and minority spin densities; in both cases, 80–90% of the majority spin is localized on the Fe, the remainder being distributed over selected sites on both the macrocycle and the phenyl group. In contrast, Co(DHNC)Ph exhibits only a small spin population on the metal but almost pure majority-spin radical character for the DHNC ligand. In other words, the Co compound is best viewed as made up of a $Co^{III}Ph$ center and a $DHN^{2-\cdot}$ ligand.[20] Overall, all the phenyl complexes exhibit very close to the theoretically expected values of $<\mathbf{S}^2>$.

In conclusion, our calculations clearly point to norcorrole as a promising synthetic target, especially when complexed to a small cation such as Ni^{II}. However, NC complexes should be prone to reduction and we predict that high-valent metal-DHNC complexes should exist as reasonably stable substances. However, the successful preparation of NC and DHNC derivatives is likely to be much more than a synthetic exercise: These molecules may be viewed as conceptual links between aromatic tetrapyrroles such as porphyrin and corrole on the one hand and open-chain pyrrole-based ligands such as dipyrrins and biliverdines on the other and detailed studies of their electronic structure is likely to be of unusual interest.

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