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Electronic Structure of High-Valent Transition Metal Corrolazine Complexes. The Young and Innocent?

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Abstract: This is a first quantum chemical study of corrolazine complexes. DFT calculations suggest that despite their extremely contracted central cavities, compared with porphyrins, a variety of corrolazine complexes may be expected to exist as stable compounds. The calculations also indicate that corrolazine complexes may be regarded as strongly electron-deficient analogues of corrole complexes. Thus, the calculated valence ionization potentials of P(V) and Cu(III) corrolazine derivatives are dramatically higher than those of analogous corrole derivatives. In addition, DFT calculations on Fe(IV) and Mn(IV) corrole and corrolazine derivatives suggest that compared with the often noninnocent corrole ligands, corrolazines are electronically more innocent and stabilize "purer" high-valent states of transition metal ions.

I. Introduction

Corrolazine (Figure 1), which may be regarded as a hybrid of a corrole and a porphyrazine, is one of the newest members of the porphyrin-type family of ligands. Although only phosphorus(V) complexes and the free-base form of a β-octaaryl-corrolazine have so far been reported,[1] we wished to explore the possibility that a significant corrolazine-based transition metal chemistry, akin to modern corrole chemistry,[2-5] might emerge in the foreseeable future. This prompted us to undertake an exploratory quantum chemical study, based on density functional theory (DFT) calculations,[6-9] on corrolazine complexes and we present here the results and predictions from this study. Our calculations reveal a number of novel attributes of metallocorrolazines, compared with porphyrazine and corrole derivatives.

The motivations behind this study can be explained in greater detail as follows. Porphyrin (P^{2-}), porphyrazine (Pz^{2-}), corrole(Cor^{3-}), and corrolazine(Cz^{3-}) are a quartet of tetrapyrrolic ligands (Figure 1), related to each other by meso-azasubstitution, ring contraction (i.e. deletion of a meso carbon),
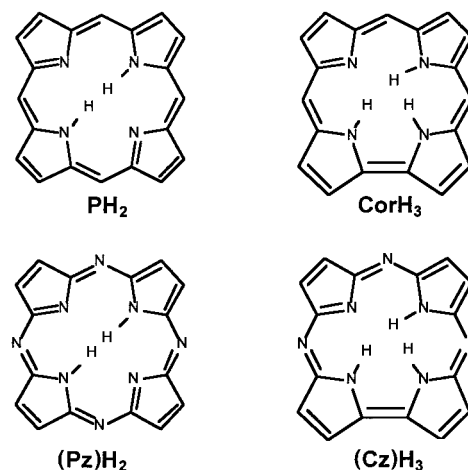

Figure 1. Free-base porphyrin (PH$_2$), porphyrazine (PzH$_2$), corrole (CorH$_3$), and corrolazine (CzH$_3$).

or both. These structural differences are responsible for a number of interesting electronic-structural differences between porphyrins, porphyrazines, and corroles, some highlights of which are as follows.

(a) Both meso-azasubstitution and ring contraction result in a smaller cavity for metal coordination and a stronger square-planar ligand field. Thus, although (OEP)Fe^{III}Cl (OEP^{2-} = octaethylporphyrinato) is a relatively cleanly $S = ^5/_2$ species (neglecting $S = ^5/_2$, $^3/_2$ quantum admixture), the analogous porphyrazine complex, (OEPz)Fe^{III}Cl (OEPz^{2-} = octaethylporphyrazinato) is $S = ^3/_2$, reflecting the stronger square-planar ligand field of the porphyrazine ligand.[10,11]

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(1) Ramdhanie, B.; Stern, C. L.; Goldberg, D. P. *J. Am. Chem Soc.* **2001**, *123*, 9447−9448..
(2) Paolesse, R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 2, Chapter 11, pp 201−232.
(3) Erben, C.; Will, S.; Kadish, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 2, Chapter 12, pp 233−300.
(4) Gross, Z. *J. Biol. Inorg. Chem.* **2001**, *6*, 733−738.
(5) For a collection of reviews on high-valent metalloporphyrins, see: Ghosh, A. *J. Biol. Inorg. Chem.* **2001**, *6*, 726−726.
(6) Ghosh, A. *Acc. Chem. Res.* **1998**, *31*, 189−198.
(7) Ghosh, A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 7, pp 1−38.
(8) Ghosh, A.; Steene, E. *J. Biol. Inorg. Chem.* **2001**, *6*, 733−738.
(9) For a collection of reviews on DFT calculations on metalloporphyrins and related compounds, see: Ghosh, A. *Curr. Opin. Chem. Biol.* **2001**, *5*, 713−714.

(10) Fitzgerald, J. P.; Haggerty, B. S.; Rheingold, A. L.; May, L.; Brewer, G. A. *Inorg. Chem.* **1992**, *31*, 2006−2013.
(11) Ghosh, A.; Gonzalez, E.; Vangberg, T.; Taylor, P. *J. Porphyrins Phthalocyanines* **2001**, *5*, 187−189.

(b) Deletion of a meso carbon also entails that while porphyrins are dianionic ligands corroles are trianionic. In turn, this is related to the fact that while many high-valent transition metal porphyrins, such as the Fe(IV)- and Mn(IV)-oxo derivatives, are unstable intermediates, Fe(IV) and Mn(IV) and many other high-valent transition metal derivatives of corroles are stable species under ordinary conditions.[12−15]

(c) Metalloporphyrazines exhibit consistently higher half-wave potentials for oxidation than analogous metalloporphyrins in cyclic voltammetry experiments.[16,17] The a_{2u}-type porphyrin HOMO, which has large amplitudes at the meso positions, is strongly stabilized by meso-azasubstitution. Accordingly, metalloporphyrazines generally have a_{1u}-type HOMOs and Gouterman's four-orbital model[18] does not hold for porphyrazine derivatives.

(d) Metallocorroles also exhibit consistently lower half-wave potentials for oxidation and ionization potentials than similarly substituted metalloporphyrins. With such low half-wave potentials for oxidation, how do corroles stabilize high-valent transition metal ions? As we[15] and others[14] have shown, the corrole ligand in many, but not all, high-valent metallocorroles is noninnocent, i.e., has π-cation radical character.

What do these considerations imply in relation to the electronic structure of the as yet unknown high-valent metallocorrolazines? Qualitatively, one might reason as follows.

(a) One can expect, for example, that meso-triazasubstitution should bring about a significant increase in the half-wave potential for oxidation of a metallocorrolazine, compared with a related metallocorrole. This appears to be the case, although an exact parallel with a corrole derivative is not available. Thus, the first oxidation potential of [{(TBP)$_8$Cz}P^V(OH)]OH (TBP = 4-*tert*-butylphenyl) is rather high, 1.16 V vs Ag/AgCl (which corresponds to an irreversible oxidation), despite the presence of eight electron-donating TBP substituents.[1]

(b) Meso-triazasubstitution of corrole should strongly stabilize the b_1 HOMO of a corrole, which crudely resembles a porphyrin a_{2u} HOMO.[19] We have recently shown that the b_1 corrole HOMO plays a critical role in determining the electronic character of the corrole ligand in high-valent metallocorrole complexes, i.e., whether the metal center is "truly" high-valent or whether the corrole ligand is noninnocent.[15] For example, DFT calculations[15] suggest that the electronic structure of (corrolato)Fe^{IV}Cl, an $S = 1$ species, is best described as involving an $S = \frac{3}{2}$ Fe(III) center antiferromagnetically coupled to a corrole b_1 radical. With the b_1 HOMO of the corrolazine ring strongly stabilized by meso-triazasubstitution, a corrolazine radical would be a more unlikely proposition. Thus we come to the question posed in the title of the paper: Is corrolazine, the newest member of the family of porphyrin-type ligands, a more innocent version of corrole?

(c) A key unknown factor related to the eventual synthesis of a significant range of metallocorrolazine derivatives is whether these complexes will be stable on geometrical and structural grounds. Both porphyrazine and corrole ligands feature significantly contracted core sizes relative to porphyrin and, therefore, the question arises as to whether the core size of corrolazine, a porphyrazine−corrole hybrid, might be too small to sustain a significant range of transition metal complexes. Not surprisingly, the first corrolazine complex reported involves the very small P(V) ion as the central ion.[20,21] Indeed, this small ion was instrumental in promoting the ring contraction of a porphyrazine to generate the corrolazine ring system.[1] We address these issues below.

II. Methods

For all calculations described here, we used the nonlocal PW91 exchange-correlation functional, Slater-type triple-ζ plus polarization basis sets, a fine mesh for numerical integrations of the matrix elements, full geometry optimizations with appropriate symmetry constraints, and tight criteria for geometry optimizations, as implemented in the ADF program system.[22] We have studied the following molecules: (Cor)-P^{V}F$_2$ (C_{2v}, $S = 0$), (Cz)P^{V}F$_2$ (C_{2v}, $S = 0$), (Cor)Cu^{III} (C_{2v}, $S = 0$), (Cz)-Cu^{III} (C_{2v}, $S = 0$), (Cor)Fe^{IV}Cl (C_s, $S = 1$), (Cz)Fe^{IV}Cl (C_s, $S = 1$), (Cor)Mn^{IV}Cl (C_s, $S = \frac{3}{2}$), and (Cz)Mn^{IV}Cl (C_s, $S = \frac{3}{2}$). Closed- and open-shell molecules were studied with spin-restricted and -unrestricted calculations, respectively, in general. Ionization potentials were calculated via a ΔSCF procedure, i.e., by taking the difference in energy between the un-ionized state on one hand and ionized states of different symmetries on the other.[23]

III. Results and Discussion

A. Corrolazine Vis-à-Vis the Gouterman Four-Orbital Model. Both porphyrins and corroles "obey" the Gouterman four-orbital model, according to which (i) the two HOMOs are near-degenerate and so are the two LUMOs, and (ii) these four MOs are energetically well-separated from all other occupied and unoccupied MOs.[18] As mentioned above, meso-azasubstitution is expected to lead to the breakdown of the four-orbital model, as has been observed for porphyrazine. The same may be expected for corrolazine. To check whether this is the case, we have calculated the two lowest vertical one-electron ionization potentials (IPs) for each of the closed-shell molecules we have studied. These are as follows, with symmetries of the ionized final states being indicated: viz. (Cor)P^{V}F$_2$ ($^2A_2$, 7.00 eV; $^2B_1$, 6.82 eV), (Cz)P^{V}F$_2$ ($^2A_2$, 10.28 eV; $^2B_1$, 10.68 eV), (Cor)Cu^{III} ($^2A_2$, 6.84 eV; $^2B_1$, 6.73 eV), (Cz)Cu^{III} ($^2A_2$, 8.18 eV; $^2B_1$, 8.52 eV). Observe that the two lowest IPs are very close to each other for the two corroles, consistent with the four-orbital model, but (perhaps surprisingly) slightly less so for the corrolazines. However, at this point, we have not yet computed IPs beyond the second lowest for the corrolazine derivatives. However, the orbital energy eigenvalue spectra (not shown) of the corrolazine complexes studied show that the second criterion of Gouterman's four-orbital model (see above) does not hold for these complexes, i.e., the two corrolazine HOMOs are not well-separated from other occupied MOs in terms of their orbital energies. The key point illustrated by these results is that

(12) Vogel, E.; Will, S.; Schulze Tilling, A.; Neumann, L.; Lex, J.; Bill, E.; Trautwein, A. X.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 731−735; *Angew. Chem.* **1994**, *106*, 771.
(13) Simkhovich, L.; Gross, Z. *Tetrahedron Lett.* **2001**, *42*, 8089−8092.
(14) Cai, S.; Walker, F. A.; Licoccia, S. *Inorg. Chem.* **2000**, *39*, 3466−3478.
(15) Steene, E.; Wondimagegn, T.; Ghosh, A. *J. Phys. Chem. B* **2001**, *105*, 11406−11413.
(16) Ghosh, A.; Gassman, P. G.; Almlöf, J. *J. Am. Chem. Soc.* **1994**, *116*, 1932−1940.
(17) Ghosh, A.; Fitzgerald, J.; Gassman, P. G.; Almlöf, J. *Inorg. Chem.* **1994**, *33*, 6057−6060.
(18) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3, pp 1−165.
(19) Ghosh, A.; Wondimagegn, T.; Parusel, A. B. J. *J. Am. Chem. Soc.* **2000**, *122*, 5100−5104.

(20) Zheng, J. Y.; Konishi, K.; Aida, T. *Inorg. Chem.* **1998**, *37*, 2591.
(21) Vangberg, T.; Ghosh, A. *J. Am. Chem. Soc.* **1999**, *121*, 12154−12160.
(22) The ADF program is obtainable from the following: Scientific Computing and Modelling, Department of Chemistry, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands.
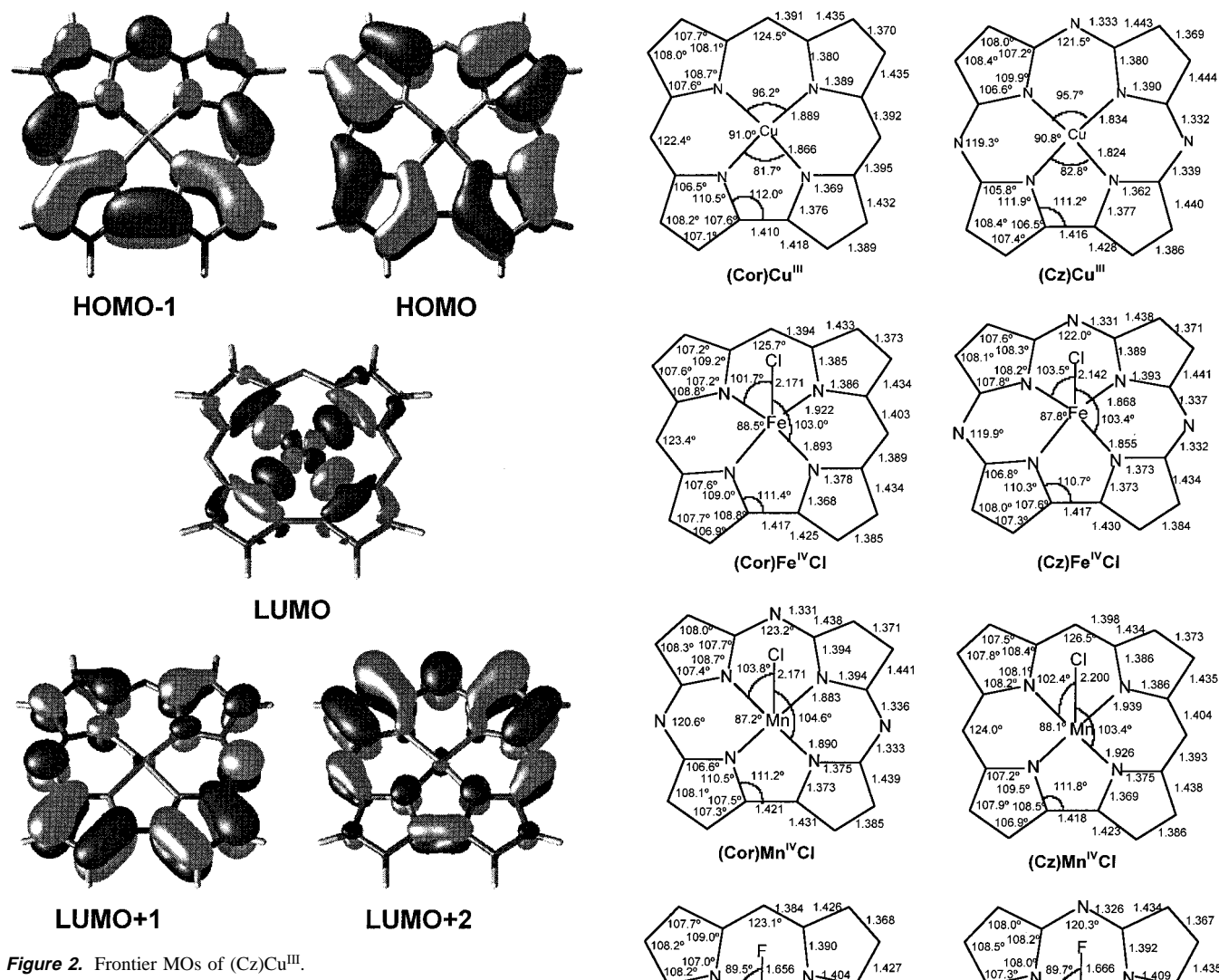(23) Ghosh, A.; Vangberg, T. *Theor. Chem. Acc.* **1997**, *97*, 143−149.

Figure 2. Frontier MOs of (Cz)Cu^{III}.

Figure 3. Selected optimized geometry parameters (Å, deg).

corrolazine complexes are far more difficult to ionize than analogous corrole complexes.

The orbital energy eigenvalue spectrum (not shown) of (Cz)Cu^{III} reveals another interesting feature: the LUMO is not a ligand π MO, but has predominant Cu $d_{x^2-y^2}$ character, the various frontier MOs being shown in Figure 2. This is a feature that the (Cz)Cu^{III} shares with its corrole analogue, (Cor)Cu^{III}.[8,24] Elsewhere,[8,15,24] we have shown that high-valent transition metal corroles, but not the corresponding free-base derivatives, exhibit uniquely substituent-sensitive Soret absorption maxima. With support from quantum chemical calculations,[24] we ascribed these to ligand-to-metal charge transfer (LMCT) transitions. Although the corrole studies featured only variable meso substituents, we anticipate that β-substituents too should exert a significant impact on the absorption maxima of both high-valent metallocorroles and metallocorrolazines by tuning the energies of the LMCT transitions.

B. Molecular Geometries. Figure 3 depicts the DFT(PW91/ TZP) optimized geometries of the molecules studied. The optimized P–N distances and other corrolazine ligand metrical parameters in (Cz)P^{V}F$_2$ are in good agreement with those experimentally determined for [(TBP)$_8$Cz] P^V(OCH$_3$)$_2$. For each
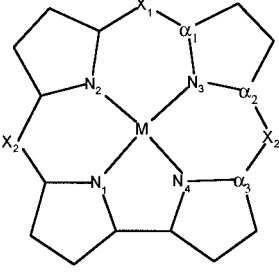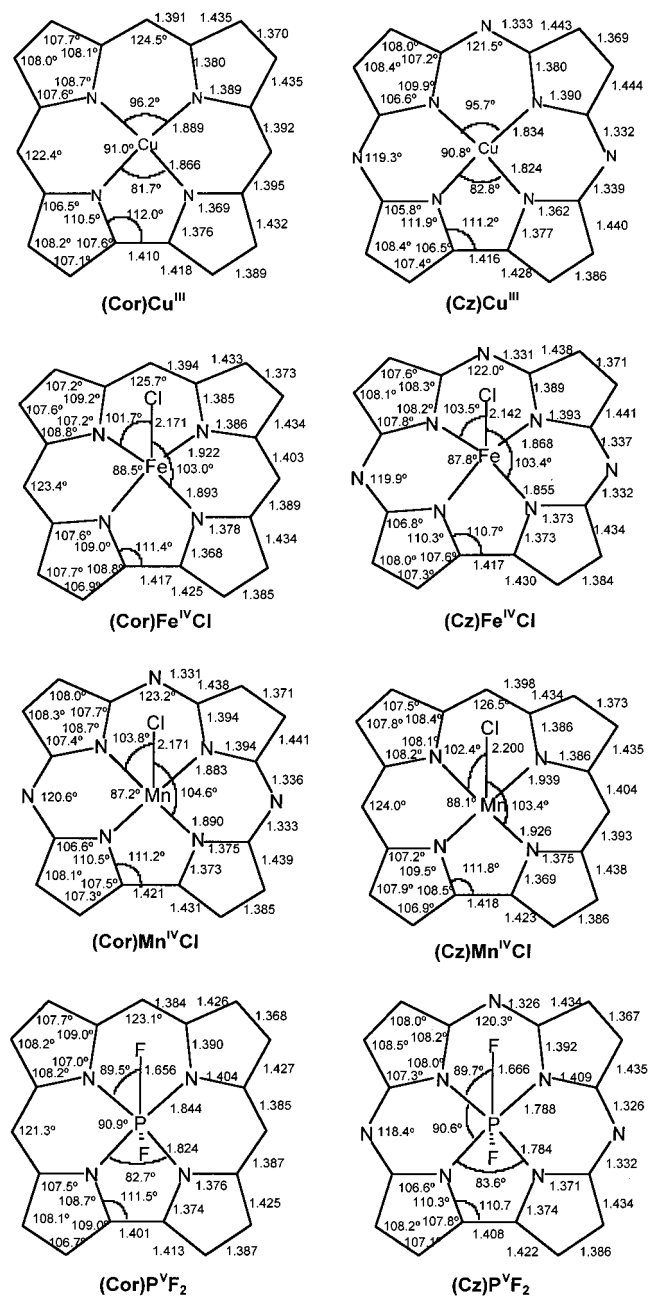
(24) Halvorsen, I.; Wondimagegn, T.; Ghosh, A. *J. Am. Chem. Soc.* **2002**, *124*, 8104.

central ion considered, M = P(V), Cu(III), Fe(IV), and Mn(IV), the corrolazine core is consistently more contracted than the corrole core. Note that there are two distinct M–N bond distances in each compound. As shown in Figure 3 and in Table 1, the longer M–N distance in each corrolazine complex is about 0.05–0.06 Å shorter than the corresponding distance in the analogous corrole complex; the shorter M–N distance in each corrolazine complex is about 0.03–0.05 Å shorter than the corresponding distance in the analogous corrole complex. As expected for five-coordinate square-pyramidal complexes, the Fe(IV) and Mn(IV) ions are significantly displaced above the ligand N$_4$ planes. These displacements are on the order of 0.4 Å and are slightly greater for the corrolazine derivatives than for the corrole derivatives. The M–Cl distances in the five-coordinate corrolazine complexes are slightly shorter than those in the analogous corrole complexes.

Table 1. Selected Optimized Distances (Å), M−N$_4$ Being the Displacement of the Central Atom from the N$_4$-Plane

Compound	Corrolazine				Corrole			
M	Cu^{III}	Fe^{IV}Cl	Mn^{IV}Cl	P^{V}F$_2$	Cu^{III}	Fe^{IV}Cl	Mn^{IV}Cl	P^{V}F$_2$
M−N$_2$	1.834 Å	1.868 Å	1.883 Å	1.788 Å	1.889 Å	1.922 Å	1.939 Å	1.844 Å
M−N$_1$	1.824 Å	1.855 Å	1.890 Å	1.784 Å	1.866 Å	1.893 Å	1.926 Å	1.824 Å
C$_1$−X$_1$	1.333 Å	1.331 Å	1.331 Å	1.326 Å	1.391 Å	1.394 Å	1.398 Å	1.384 Å
C$_2$−X$_2$	1.332 Å	1.337 Å	1.336 Å	1.326 Å	1.392 Å	1.403 Å	1.404 Å	1.385 Å
C$_3$−X$_2$	1.339 Å	1.332 Å	1.333 Å	1.332 Å	1.395 Å	1.389 Å	1.393 Å	1.387 Å
M−L$_{axial}$	−	2.142 Å	2.171 Å	1.666 Å	−	2.171 Å	2.200 Å	1.656 Å
M−N$_4$	−	0.443 Å	0.461 Å	−	−	0.407 Å	0.431 Å	−
N$_2$−N$_4$	3.652 Å	3.616 Å	3.652 Å	3.568 Å	3.747 Å	3.720 Å	3.758 Å	3.662 Å
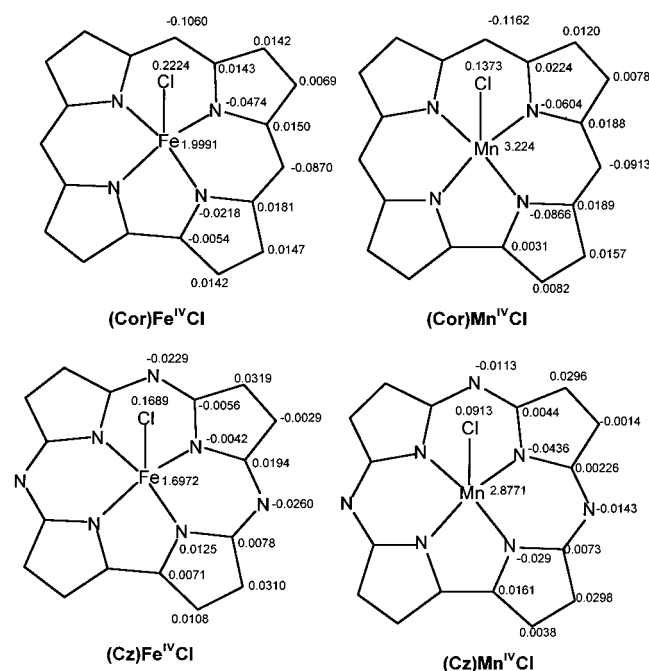
Figure 4. Calculated gross atomic spin populations.

C. Molecular Spin Density Profiles. Figure 4 depicts the gross atomic spin populations for the open-shell Fe(IV) and Mn(IV) complexes studied. For both metal ions, there are some systematic differences between the corrolazine versus the corrole derivatives. Thus, the metal and Cl spin populations are somewhat lower in the corrolazines than the analogous corroles. However, the main difference between the corrolazine and corrole complexes lies in the spin populations of the meso atoms and the central nitrogens. These atoms carry large negative (i.e. minority) spin populations in the case of (Cor)Fe^{IV}Cl and (Cor)Mn^{IV}Cl, but near-zero or small negative spin populations in the case of (Cz)Fe^{IV}Cl and (Cz)Mn^{IV}Cl. As we have discussed elsewhere,[15] the large negative spin populations in the case the Fe(IV) and Mn(IV) corrole complexes are localized exactly where the macrocycle b$_1$ HOMO has large amplitudes. Thus, the electronic structures of (Cor)Fe^{IV}Cl and (Cor)Mn^{IV}Cl

appear to be best described as involving $S = {}^3/_2$ Fe(III) and Mn(III) centers, respectively, antiferromagnetically coupled to corrole b$_1$-type radicals, the specific metal orbital involved in the antiferromagnetic coupling being (as discussed elsewhere) the metal 3d$_{z^2}$ orbital.[14,15] The small spin populations, positive or negative, on the corrolazine ligands in (Cz)Fe^{IV}Cl and (Cz)Mn^{IV}Cl indicate a relatively innocent macrocyclic ligand and purer high-valent Fe(IV) and Mn(IV) centers, compared with (Cor)Fe^{IV}Cl and (Cor)Mn^{IV}Cl.

D. Relevance to a Current Controversy Vis-à-Vis Ligand Noninnocence in Metallocorroles. These results appear to be relevant to a current debate on the nature of high-valent metallocorroles.[25] On the basis of NMR studies, Walker and co-workers[14] proposed a description involving an intermediate spin Fe(III) center antiferromagnetically coupled to a corrole radical for (octamethylcorrolato)Fe^{IV}Cl.[14] On the basis of electrochemical studies on various formally Fe(IV) and Mn-(IV) *meso*-triarylcorrole complexes and supporting DFT calculations, we[15] also reached the same conclusion as Walker and co-workers. In contrast, Gross has favored a clean Fe(IV) description for the Fe(IV)Cl complex of *meso*-tris(pentafluorophenyl)corrole.[4] In what appears to be a resolution of this controversy, this study suggests that *both* descriptions may be appropriate for metallocorroles for *different* corrole ligands. Like corrolazine, the highly electron-deficient *meso*-tris(pentafluorophenyl)corrole ligand presumably does not support a ligand-centered radical, favoring a relatively "pure" Fe(IV) center. The more-electron-rich metallocorroles studied by Walker and co-workers[14] and by Ghosh and co-workers[8,15] presumably feature a (partial) corrole ligand radical. Obviously, there are degrees of ligand noninnocence and, in any given case, the real electronic structure corresponds to some point on the continuum between the two extreme scenarios. This point has been further discussed in ref 24. We are addressing this issue in greater detail via additional DFT calculations on peripherally substituted metallocorroles and Mössbauer spectroscopy.

Finally, should the transition metal corrolazine derivatives studied actually exist as stable compounds? The geometry

(25) Ghosh, A.; Steene, E. *J. Inorg. Biochem.* in press.

parameters in the optimized molecular geometries are all reasonable so we suspect no particular instability on structural grounds. While the stability of four-coordinate Cu(III) corrolazine complexes appears relatively assured, the strongly electron-deficient character of the corrolazine ligand does raise the possibility that Fe(IV) and Mn(IV) corrolazine complexes may be prone to reduction to the metal(III) oxidation level.

IV. Conclusion

DFT geometry optimizations suggest that despite their extremely contracted central cavities, compared with porphyrins, a variety of corrolazine complexes should be experimentally accessible as stable compounds. DFT calculations also indicate that corrolazine complexes may be regarded as strongly electron-deficient analogues of corrole complexes. Thus, the calculated valence ionization potentials of P(V) and Cu(III) corrolazine derivatives are dramatically higher than those of analogous corrole derivatives. In addition, DFT calculations on Fe(IV) and Mn(IV) corrole and corrolazine derivatives suggest that compared with the often noninnocent corrole ligands, corrolazines are electronically more innocent and stabilize "purer" high-valent states of transition metal ions.

Supporting Information Available: Complete sets of optimized Cartesian coordinates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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