



## B<sub>12</sub> and F<sub>430</sub> models: Metal- versus ligand-centered redox in cobalt and nickel tetrahydrocorrin derivatives

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### ABSTRACT

DFT calculations with the well-tested OLYP and B3LYP\* exchange-correlation functionals (along with D3 dispersion corrections and all-electron ZORA STO-TZ2P basis sets) and careful use of group theory have led to significant insights into the question of metal- versus ligand-centered redox in Co and Ni B,C-tetrahydrocorrin complexes. For the cationic complexes, both metals occur in their low-spin M(II) forms. In contrast, the charge-neutral states vary for the two metals: while the Co(I) and Co<sup>II</sup>-TDC<sup>\*2-</sup> state are comparable in energy for cobalt, a low-spin Ni<sup>II</sup>-TDC<sup>\*2-</sup> state is clearly preferred for nickel. The latter behavior stands in sharp contrast to other corrinoids that reportedly stabilize a Ni(I) center.

One of us (AG) has been fortunate in knowing the late F. Ann Walker pretty much all of his professional life. Her many talks on advanced NMR and EPR studies of heme proteins at national American Chemical Society meetings and at Gordon Research Conferences made a profound impact on me and the entire heme protein and model compound community. Her papers, review articles, and book chapters, likewise, survive as exemplars of scholarship. Add to that an exemplary record of service, perhaps most notably as long-time Associate Editor of *JACS*, and mentoring, and you have a rare role model who has inspired multiple generations of bioinorganic chemists. Below are a few first-person reminiscences.

Ann and I crossed paths when we both started studying corroles at the start of this century. She drew on her expertise of heme NMR spectroscopy to conclude that FeCl corroles were best described as Fe<sup>III</sup>Cl-corrole<sup>\*2-</sup> as opposed to Fe<sup>IV</sup>-corrole<sup>3-</sup>. [1–3] We had reached the same conclusion in our laboratory based on DFT calculations. [4,5] The proposal met some resistance but Ann remained steadfast in her views, masterfully summarizing the evidence in a special issue of this *Journal* that I edited [6].

Ann was an avid traveler. Every year, I eagerly awaited her Christmas letter to read about her adventures, often in Latin America, but also in Europe and Africa. I have fond memories of her visit to my laboratory in Arctic Norway. We spent a long day driving around Kvaløya (Whale Island), an island neighboring the city of Tromsø, taking in views of fjords, mountains, and waterfalls and occasionally stopping to whip up

Scandinavian shrimp sandwiches.

As a pioneering woman scientist, she endured the slings and arrows of sexism. Her warmth and optimism, however, never failed and spurred us all.

Compared with metalloporphyrins [7,8] and metallocorroles, [9–12] cobalamin [13–18] and F<sub>430</sub> [19–23] models remain less explored. An important recent development has been the availability of the mono-anionic B,C-tetrahydrocorrin [24–26] ligand and its coordination to cobalt and nickel states (Fig. 1) [27]. Both metals have yielded complexes formally at the M(I) state. In the nickel case, the neutral complex has been fairly conclusively assigned to a Ni<sup>II</sup>-TDC<sup>\*2-</sup> state [27], but the nature of the neutral Co complex is more subtle. A neutral cobalt corrin has been traditionally thought of as a d<sup>8</sup> Co(I) complex; [28–31] however, advanced ab initio calculations have suggested a more multi-configurational description. [32–35] Herein we have examined the low-energy states of C<sub>2</sub>-symmetrized M[TDC] (M = Co, Ni) complexes at the 0 and +/- charge with high-quality density functional theory (DFT) calculations. Symmetrization allowed us to calculate different electron occupancies for the two irreducible representations in question and thereby to determine the relative energetics of metal- versus ligand-centered redox in both the neutral and ionized states of the molecules. Such exercises have a long and successful track record vis-a-vis porphyrin-type molecules and have shed a good deal of light on electronic-structural aspects of manganese porphyrins [36], low-spin ferrihemes, [37,38] cobalt dipyrin-bisphenolates [39], nickel

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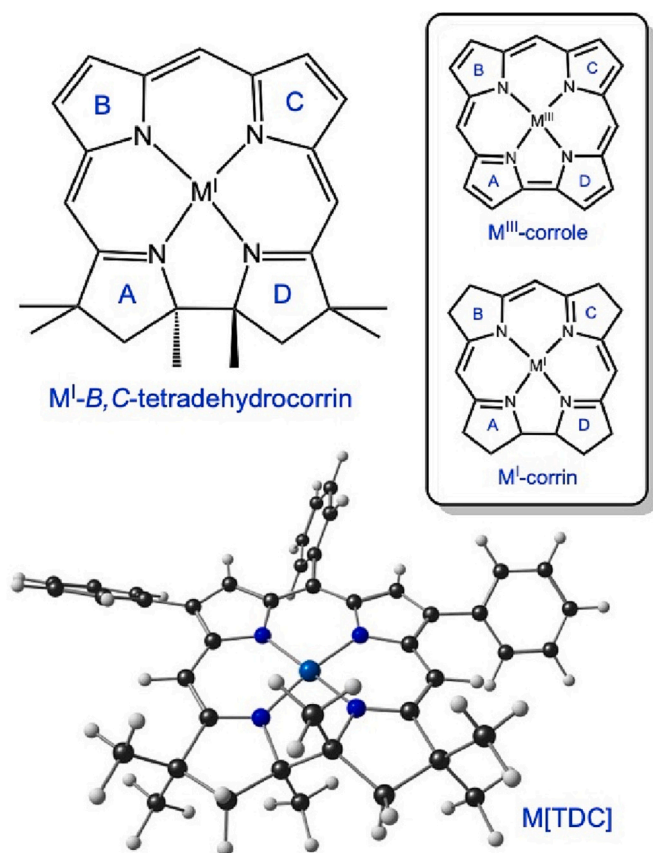
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**Fig. 1.** B,C-tetrahydrocorrin and its relation to corrole and corrin. Bottom: Ball-and-stick diagram of the  $M$ [TDC] complex studied in this paper.

porphyrins [40,41] and hydroporphyrins [42], and metallocorroles [43–45] including metal-metal-bonded metallocorrole dimers, [46–49] as well as on the photoelectron spectra of porphyrins. [50–54] The present exercise allows for greater certainty in the interpretation of redox behavior Co and Ni corrinoids as well as new insights into metal-ligand interactions in these systems.

Our  $M$ [TDC] model is a slightly simplified and symmetrized analogue of the system experimentally studied by Lindsey, Nocera and their associates (Fig. 1) [27]. The simplification consists of merely replacing a *meso-p*-tolyl group with a phenyl group so as to generate a  $C_2$ -symmetric model. Two well-tested exchange-correlation functionals were generally used – OLYP [55,56] and B3LYP\*, [57,58] the latter containing 15% Hartree-Fock exchange relative to B3LYP, [59,60] which contains 20%. Both functionals were augmented with Grimme's D3 [61] dispersion corrections. A spin-unrestricted formalism and all-electron ZORA STO-TZ2P basis sets were used throughout. Appropriately fine meshes for numerical integration of matrix elements were employed, as were suitably tight criteria for geometry optimizations.

For neutral  $Co$ [TDC], B3LYP\*-D3 calculations predicted multiple low-energy states (Table 1 and Fig. 2), including (a) a  $d^8$  Co(I) state, (b) a broken-symmetry, antiferromagnetically coupled  $Co^{II}(d_{22}^1)$ - $TDC^{*2-}$  state, and (c) the corresponding ferromagnetically coupled triplet state. In contrast, OLYP-D3 calculations only predicted a  $d^8$  Co(I) ground state, with no hint of a low-energy broken-symmetry state, and a triplet state some 0.35 eV higher in energy. In other words, as previously observed, the pure functional OLYP exhibits a certain preference for spin-paired states, whereas the hybrid functional B3LYP\*-D3 favors a greater degree of spin decoupling, i.e., classic behavior for the two classes of functionals. [38,57,58,62–69] These results point to a multiconfigurational ground state for  $Co$ [TDC] and indeed for cobalamin and “Co(I)” corrinoids in general, with several low-energy excited states. [32–35]

**Table 1**

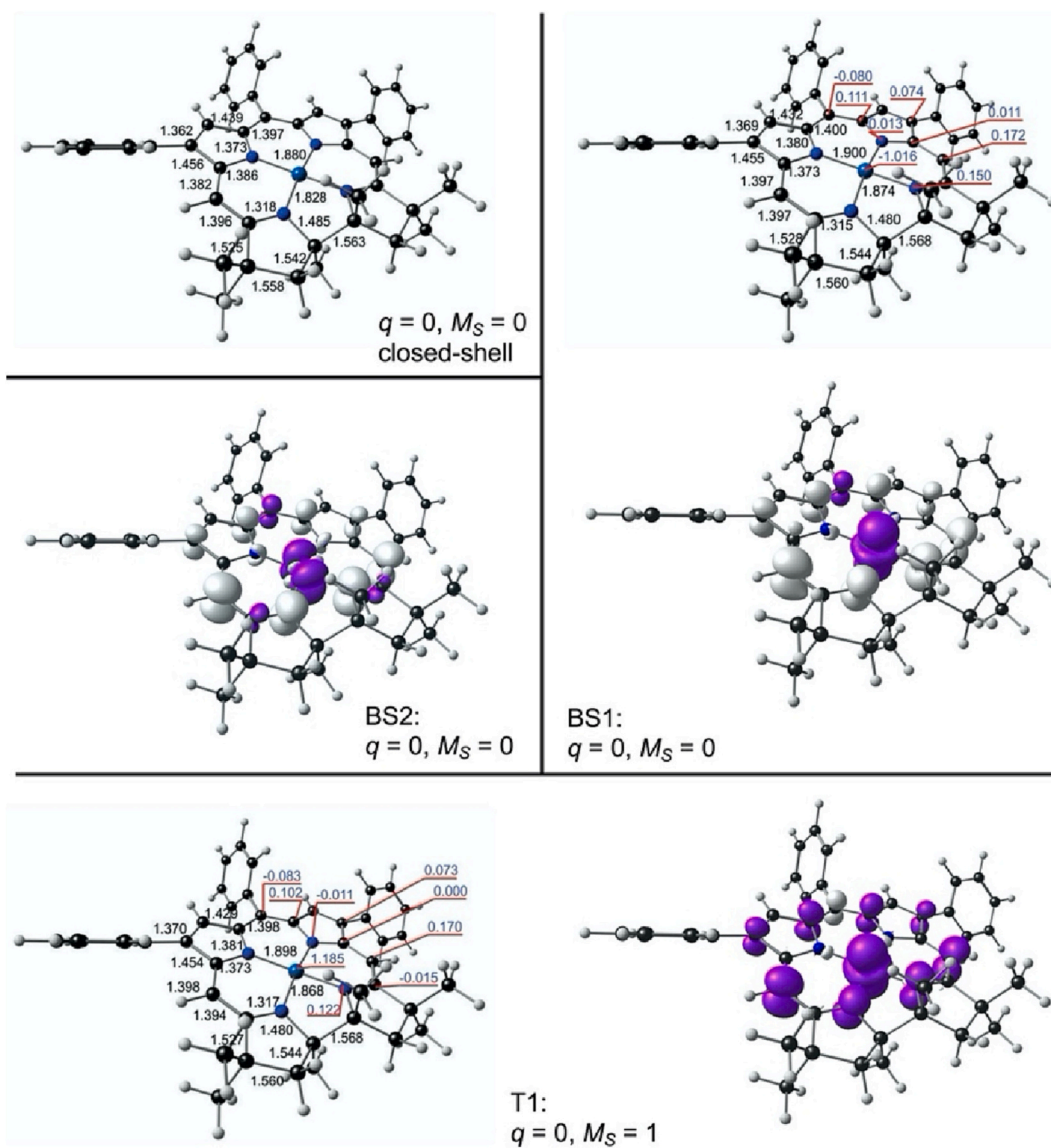
OLYP-D3 and B3LYP\*-D3 energetics (eV) of Co, Ni and K TDC complexes as a function of electron occupancy.

Molecule, charge	S	Irrep ( $\alpha/\beta$ )		$\Delta E$ (eV)		Description
		A	B	OLYP-D3	B3LYP*-D3	
<b>Co</b>						
{Co [TDC]} <sup>0</sup>	0 (closed-shell)	92//92	85//85	0.00	0.00	Co <sup>I</sup> -TDC <sup>-</sup>
{Co [TDC]} <sup>0</sup>	0 (BS1)	92//92	85//85	–	0.06	Co <sup>II}(d<sub>22</sub><sup>1</sup>)-TDC<sup>*2-</sup></sup>
{Co [TDC]} <sup>0</sup>	0 (BS2)	93//92	84//85	0.75	0.20	Co <sup>II}(d<sub>xz</sub><sup>1</sup>)-TDC<sup>*2-</sup></sup>
{Co [TDC]} <sup>0</sup>	1 (T1)	93//91	85//85	0.35	–0.02	Co <sup>II}(d<sub>22</sub><sup>1</sup>)-TDC<sup>*2-</sup> (triplet)</sup>
{Co [TDC]} <sup>-</sup>	1/2	93//92	85//85	–1.60	–1.96	Co <sup>II}(d<sub>xy</sub><sup>1</sup>)-TDC<sup>3-</sup></sup>
{Co [TDC]} <sup>+</sup>	1/2 (C1)	92//91	85//85	5.18	4.92	Co <sup>II}(d<sub>22</sub><sup>1</sup>)-TDC<sup>-</sup></sup>
{Co [TDC]} <sup>+</sup>	1/2 (C2)	92//92	85//84	5.35	5.14	Co <sup>II}(d<sub>xz</sub><sup>1</sup>)-TDC<sup>-</sup></sup>
<b>Ni</b>						
{Ni [TDC]} <sup>0</sup>	1/2	93//92	85//85	0.00	0.00	Ni <sup>II</sup> -TDC <sup>*2-</sup>
{Ni [TDC]} <sup>0</sup>	1/2	92//92	86//85	0.83	1.16	Ni <sup>I</sup> -TDC <sup>-</sup>
{Ni [TDC]} <sup>-</sup>	0 (closed-shell)	93//93	85//85	–1.57	–1.73	Ni <sup>II</sup> -TDC <sup>3-</sup>
{Ni [TDC]} <sup>-</sup>	1	93//92	86//85	–1.05	–0.96	Ni <sup>I</sup> -TDC <sup>*2-</sup>
{Ni [TDC]} <sup>+</sup>	0	92//92	85//85	4.81	4.95	Ni <sup>II</sup> -TDC <sup>-</sup>
<b>K</b>						
{K[TDC]} <sup>0</sup>	0	89//89	84//84	0.00	0.00	K <sup>I</sup> -TDC <sup>-</sup>
{K[TDC]} <sup>0</sup>	1	90//89	84//83	0.76	0.76	K <sup>I</sup> -TDC <sup>**</sup> (triplet)
{K[TDC]} <sup>-</sup>	1/2	90//89	84//84	–1.79	–1.88	K <sup>I</sup> -TDC <sup>*2-</sup>
{K[TDC]} <sup>+</sup>	1/2	89//89	84//93	5.62	5.74	K <sup>I</sup> -TDC <sup>0</sup>

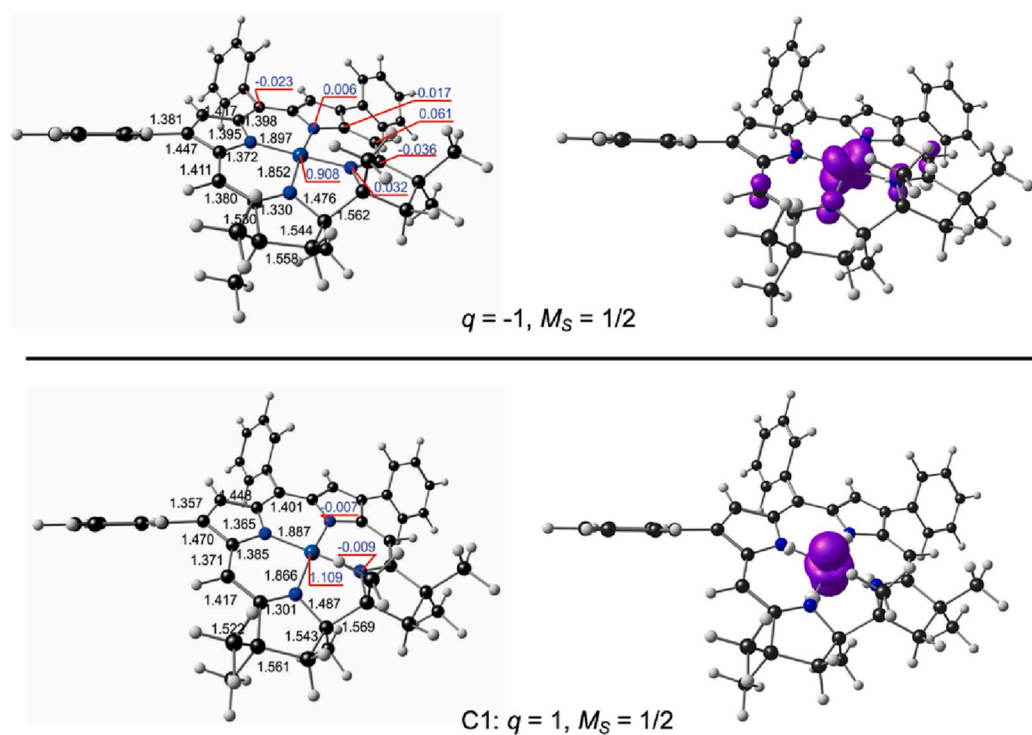
As for why the TDC ligand fails to decisively stabilize a true Co(I) relative to a  $Co^{II}(d_{22}^1)$ - $TDC^{*2-}$  state (in spite of its constricted inner core), we suspected that the reason might have to do with a high electron affinity of the TDC ligand. That indeed appears to be the case. Thus, the adiabatic electron affinity (EA<sub>a</sub>) of K[TDC] (with a redox-inactive K<sup>+</sup> ion at its core) turned out to be 1.9 eV, far higher than that of a typical electronically innocent metalloporphyrin, which typically hover around 1.2–1.3 eV (Table 1) [70].

The electronic descriptions of the ionized states of  $Co$ [TDC] appear to much more straightforward relative to that for neutral state (Fig. 3). The lowest-energy cation (denoted C1) is a straightforward low-spin Co (II) species with a  $d_{22}^1$  electronic configuration, with a  $d_{\pi}^1$  state only slightly higher in energy. Both functionals also indicate a relatively high adiabatic IP of ~5 eV for neutral  $Co$ [TDC] (Table 1), comparable to that of an electron-rich porphyrin, which explains the experimentally observed air-stability of the Co(I) state.

For charge-neutral Ni[TDC], both functionals indicate a low-spin Ni (II) TDC<sup>\*2-</sup> description, with the Ni(I) state about 1 eV higher in energy (Fig. 4). In this respect, Ni[TDC] does *not* mimic cofactor F<sub>430</sub> [19,71,72] as well as ligands such as iaobacteriochlorin, [42,73–75] oxaporphyrin [76], and thiaporphyrin, [77–79] which stabilize the Ni(I) state. Remarkably, the B,C-tetrahydrocorrin ligand also appears to differ from Ni corrin [20,22] and other Ni dehydrocorrins, [80,81] which are thought stabilize a Ni(I) state. Our calculations also indicate unambiguous ligand-centered oxidation and reduction. Thus, the {Ni[TDC]}<sup>+</sup>



**Fig. 2.** B3LYP\*-D3 results for selected low-energy states of charge-neutral Co[TDC]. Bond distances (Å) and Mulliken spin populations are indicated in black and blue, respectively; up- and down-spin densities are indicated in purple and ivory, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** B3LYP\*-D3 results for selected low-energy, ionized states of Co[TDC]. Bond distances (Å) and Mulliken spin populations are indicated in black and blue, respectively; up- and down-spin densities are indicated in purple and ivory, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

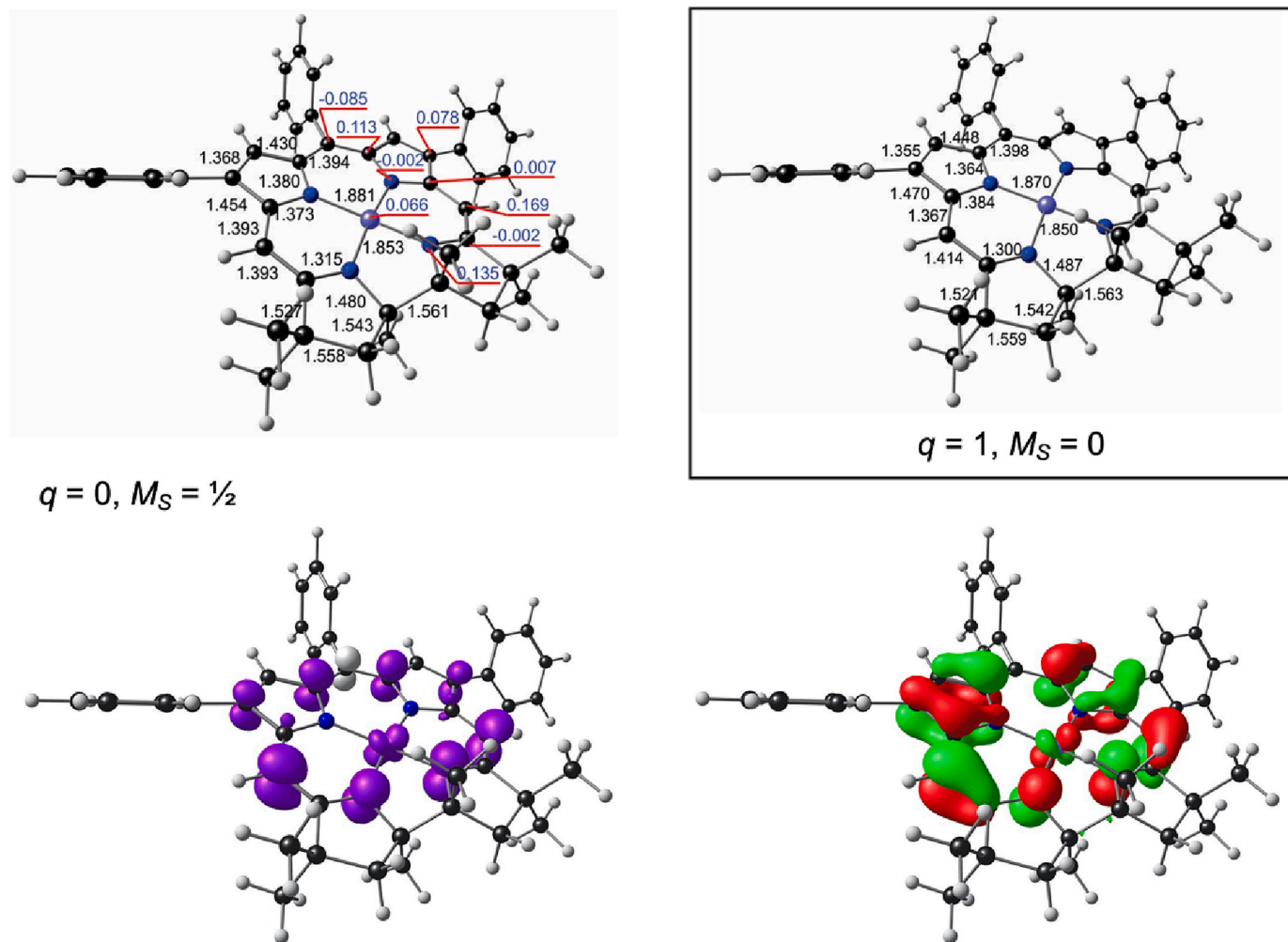


Fig. 4. B3LYP\*-D3 results for neutral and cationic Ni[TDC]. Bond distances (Å) and Mulliken spin populations are indicated in black and blue, respectively. Bottom left: spin density. Bottom right: canonical MO best described as SOMO. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cation is a straightforward, low-spin Ni(II) species, whereas the anion is clearly describable as  $\text{Ni}^{\text{II}}\text{-L}^{3-}$ . For both ionized states, the triplet states are considerably higher in energy relative to the singlet ground states.

In summary, high-quality DFT calculations and judicious use of group theory have led to significant insights into the question of metal-versus ligand-centered redox in Co and Ni tetradehydrocorrin complexes. For the +1 states, both metals occur in their low-spin M(II) forms. In contrast, the charge-neutral states vary for the two metals: while Co(I) and  $\text{Co}^{\text{II}}\text{-TDC}^{2-}$  state are comparable in energy for cobalt, a  $\text{Ni}^{\text{II}}\text{-TDC}^{2-}$  state is clearly preferred for nickel. The latter behavior may be contrasted with other corrinoids that reportedly do stabilize a Ni(I) center.

#### Author statement

Both authors contributed equally to this work.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data required to reproduce our work has been included as supplementary material.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jinorgbio.2023.112199>.

#### References

- [1] S. Cai, F.A. Walker, S. Licoccia, NMR and EPR investigations of iron corrolates: iron (III) corrolate  $\pi$ -cation radicals or iron(IV) corrolates? *Inorg. Chem.* 39 (2000) 3466–3478.
- [2] S. Cai, S. Licoccia, C. D'Ottavi, R. Paolesse, S. Nardis, V. Bulach, B. Zimmer, T. Kh. Shokhireva, F.A. Walker, Chloroiron *meso*-triphenylcorrolates: electronic ground state and spin delocalization, *Inorg. Chim. Acta* 339C (2002) 171–178.
- [3] O. Zakhariyeva, V. Schünemann, M. Gerdan, S. Licoccia, S. Cai, F.A. Walker, A. X. Trautwein, Is the Corrolate macrocycle innocent or noninnocent? *Magnetic*

- susceptibility, Mössbauer,  $^1\text{H}$  NMR, and DFT investigations of Chloro- and Phenyliron Corrolates, *J. Am. Chem. Soc.* 124 (2002) 6636–6648.
- [4] E. Steene, T. Wondimagegn, A. Ghosh, Electrochemical and electronic absorption spectroscopic studies of substituent effects in iron(IV) and manganese(IV) corroles. Do the compounds feature high-valent metal centers or noninnocent corrole ligands? Implications for Peroxidase Compound I and II Intermediates, *J. Phys. Chem. B* 105 (2001) 11406–11413. Addition/correction: *J. Phys. Chem. B* 106 (2002) 5312–5312.
- [5] E. Steene, A. Dey, A. Ghosh,  $\beta$ -Octafluorocorroles, *J. Am. Chem. Soc.* 125 (2003) 16300–16309.
- [6] F.A. Walker, S. Licoccia, R. Paolesse, Iron Corrolates: unambiguous Chloroiron(III) (Corrolate) $^{2-}$   $\pi$ -cation radicals, *J. Inorg. Biochem.* 100 (2006) 810–837.
- [7] F.A. Walker, NMR and EPR spectroscopy of paramagnetic metalloporphyrins and heme proteins, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), *Handbook of Porphyrin Science* vol. 6, World Scientific, Singapore, 2010, pp. 1–337 (Chapter 29).
- [8] A. Ghosh, E. Steene, High-valent transition metal centers and noninnocent ligands in Metalloporphyrins and related molecules: a broad overview based on quantum chemical calculations, *J. Biol. Inorg. Chem.* 6 (2001) 739–752.
- [9] A. Ghosh, Electronic structure of Corrole derivatives: insights from molecular structures, spectroscopy, electrochemistry, and quantum chemical calculations, *Chem. Rev.* 117 (2017) 3798–3881.
- [10] R.K. Hocking, S.D. George, Z. Gross, F.A. Walker, K.O. Hodgson, B. Hedman, E. I. Solomon, Fe L- and K-edge XAS of low-spin ferric Corrole: bonding and reactivity relative to low-spin ferric porphyrin, *Inorg. Chem.* 48 (2009) 1678–1688.
- [11] A.B. Alemayehu, K.E. Thomas, R.F. Einrem, A. Ghosh, The Story of 5d Metalloporroles: From Metal–Ligand Misfits to New Building Blocks for Cancer Phototherapeutics, *Acc. Chem. Res.* 54 (2021) 3095–3107.
- [12] S. Nardis, F. Mandoj, M. Stefanelli, R. Paolesse, Metal complexes of corrole, *Coord. Chem. Rev.* 388 (2019) 360–405.
- [13] G.N. Schrauzer, New developments in the field of vitamin B $_{12}$ : reactions of the cobalt atom in corrins and in vitamin B $_{12}$  model compounds, *Angew. Chem. Int. Ed. Engl.* 15 (1976) 417–426.
- [14] B. Kräutler, Biological organometallic chemistry of vitamin B $_{12}$ -derivatives, in: T. Hirao, T. Moriuchi (Eds.), *Advances in Bioorganometallic Chemistry*, Elsevier, Amsterdam, 2019, pp. 399–430.
- [15] B. Kräutler, Antivitamins B $_{12}$  – some inaugural milestones, *Chem. Eur. J.* 26 (2020) 15438–15445.
- [16] D. Osman, A. Cooke, T.R. Young, E. Deery, N.J. Robinson, M.J. Warren, The requirement for cobalt in vitamin B $_{12}$ : a paradigm for protein metalation, *Biochim. Biophys. Acta, Mol. Cell Res.* 1868 (2021), 118896.
- [17] Y. Mathur, A.B. Hazra, Methylations in vitamin B $_{12}$  biosynthesis and catalysis, *Curr. Opin. Struct. Biol.* 77 (2022), 102490.
- [18] M. Giedyk, D. Gryko, Vitamin B $_{12}$ : an efficient cobalt catalyst for sustainable generation of radical species, *Chem Cataly.* 2 (2022) 1534–1548.
- [19] R.K. Thauer, Methyl (alkyl)-coenzyme M reductases: nickel F-430-containing enzymes involved in anaerobic methane formation and in anaerobic oxidation of methane or of short chain alkanes, *Biochemistry.* 58 (2019) 5198–5220.
- [20] C. Brenig, L. Prieto, R. Oetterli, F. Zelder, A nickel (II)-containing vitamin B $_{12}$  derivative with a cofactor-F430-type  $\pi$ -system, *Angew. Chem. Int. Ed.* 57 (2018) 16308–16312.
- [21] C. Kieninger, K. Wurst, M. Podewitz, M. Stanley, E. Deery, A.D. Lawrence, K. R. Liedl, M.J. Warren, B. Kräutler, Replacement of the cobalt center of vitamin B $_{12}$  by nickel: nibalamin and nibracyc acid prepared from metal-free B $_{12}$  ligands hydrogenobalamin and hydrogenobyric acid, *Angew. Chem. Int. Ed.* 59 (2020) 20129–20136.
- [22] C. Brenig, L. Mosberger, O. Blacque, R. Kissner, F. Zelder, Reversible metal-centered reduction empowers a Ni-Corrin to mimic F430, *Chem. Commun.* 57 (2021) 7260–7263.
- [23] Y. Miyazaki, K. Oohora, T. Hayashi, Focusing on a nickel hydrocorphinoid in a protein matrix: methane generation by methyl-coenzyme M reductase with F430 cofactor and its models, *Chem. Soc. Rev.* 51 (2022) 1629–1639.
- [24] A.W. Johnson, Synthesis of corrins and related macrocycles based on pyrrolic intermediates, *Philos. Trans. R. Soc. London, Ser. B* 273 (1976) 319–326.
- [25] S. Zhang, M.N. Reddy, O. Mass, H.-J. Kim, G. Hu, J.S. Lindsey, Synthesis of tailored hydrodipyrroles and their examination in directed routes to bacteriochlorins and tetrahydrocorrins, *New J. Chem.* 41 (2017) 11170–11189.
- [26] R.M. Deans, O. Mass, J.R. Diers, D.F. Bocian, J.S. Lindsey, Serendipitous synthetic entrée to tetrahydro analogues of cobalamins, *New J. Chem.* 37 (2013) 3964–3975.
- [27] R. Sun, M. Liu, P. Wang, Y. Qin, C. Schnedermann, A.G. Maher, S.-L. Zheng, S. Liu, B. Chen, S. Zhang, D.K. Dogutan, J.S. Lindsey, D.G. Nocera, Syntheses and properties of Metalated Tetrahydrocorrins, *Inorg. Chem.* 61 (2022) 12308–12317.
- [28] G.N. Schrauzer, E. Deutsch, Reactions of cobalt (I) supernucleophiles. The alkylation of vitamin B $_{12}$ , cobaloximes(I), and related compounds, *J. Am. Chem. Soc.* 91 (1969) 3341–3350.
- [29] G.N. Schrauzer, Organocobalt chemistry of vitamin B $_{12}$  model compounds (cobaloximes), *Acc. Chem. Res.* 1 (1968) 97–103.
- [30] M.D. Wirt, I. Sagi, M.R. Chance, Formation of a square-planar co (I) B $_{12}$  intermediate. Implications for enzyme catalysis, *Biophys. J.* 63 (1992) 412–417.
- [31] M.D. Liptak, T.C. Brunold, Spectroscopic and computational studies of Co $^{1+}$  cobalamin: spectral and electronic properties of the “superreduced” B $_{12}$  cofactor, *J. Am. Chem. Soc.* 128 (2006) 9144–9156.
- [32] K.P. Jensen, Electronic structure of cob (I) alamin: the story of an unusual nucleophile, *J. Phys. Chem. B* 109 (2005) 10505–10512.
- [33] K.P. Jensen, U. Ryde, Cobalamins uncovered by modern electronic structure calculations, *Coord. Chem. Rev.* 253 (2009) 769–778.
- [34] K. Kornobis, K. Ruud, P.M. Kozłowski, Cob(I)alamin: insight into the nature of electronically excited states elucidated via quantum chemical computations and analysis of absorption, CD and MCD data, *J. Phys. Chem. A* 117 (2013) 863–876.
- [35] M. Kumar, P.M. Kozłowski, Electronic and structural properties of cob(I)alamin: ramifications for B $_{12}$ -dependent processes, *Coord. Chem. Rev.* 333 (2017) (2017) 71–81.
- [36] A. Ghosh, E. Gonzalez, Theoretical studies on high-valent manganese porphyrins: toward a deeper understanding of the energetics, electron distributions, and structural features of the reactive intermediates of enzymatic and synthetic manganese-catalyzed oxidative processes, *Israel J. Chem.* 40 (2000) 1–8.
- [37] A. Ghosh, E. Gonzalez, T. Vangberg, Theoretical studies of low-spin six-coordinate iron (III) porphyrins relevant to cytochromes b: variable electronic configurations, ligand noninnocence, and macrocycle ruffling, *J. Phys. Chem. B* 103 (1999) 1363–1367.
- [38] M.M. Conradie, J. Conradie, A. Ghosh, Capturing the spin state diversity of Iron (III)-aryl porphyrins: OLYP is better than TPSSH, *J. Inorg. Biochem.* 105 (2011) 84–91.
- [39] W. Shan, N. Desbois, S. Pacquelet, S. Brandès, Y. Rousselin, J. Conradie, A. Ghosh, C.P. Gros, K.M. Kadish, Ligand noninnocence in cobalt Dipyrrin–bisphenols: spectroscopic, electrochemical, and theoretical insights indicating an emerging analogy with Corroles, *Inorg. Chem.* 58 (2019) 7677–7689.
- [40] A. Ghosh, T. Wondimagegn, E. Gonzalez, I. Halvorsen, Valence tautomerism and macrocycle ruffling in nickel (III) porphyrins, *J. Inorg. Biochem.* 78 (2000) 79–82.
- [41] J. Conradie, T. Wondimagegn, A. Ghosh, Spin states at a tipping point: what determines the  $d_{22}$  ground state of nickel (III) tetra( $t$ -butyl)porphyrin Dicyanide? *J. Phys. Chem. B* 112 (2008) 1053–1056.
- [42] H. Ryeng, E. Gonzalez, A. Ghosh, DFT at its best: metal-versus ligand-centered reduction in nickel Hydroporphyrins, *J. Phys. Chem. B* 112 (2008) 15158–15173.
- [43] A. Ghosh, T. Wondimagegn, A.B. Parusel, Electronic structure of gallium, copper, and nickel complexes of corrole. High-valent transition metal centers versus noninnocent ligands, *J. Am. Chem. Soc.* 122 (2000) 5100–5104.
- [44] I. Wasbotten, A. Ghosh, Theoretical evidence favoring true iron (V)-oxo corrole and corrolazine intermediates, *Inorg. Chem.* 45 (2006) 4910–4913.
- [45] K.E. Thomas, H. Vazquez-Lima, Y. Fang, Y. Song, K.J. Gagnon, C.M. Beavers, K. M. Kadish, A. Ghosh, Ligand noninnocence in coinage metal corroles: a silver knife-edge, *Chem. Eur. J.* 21 (2015) 16839–16847.
- [46] A.B. Alemayehu, L.J. McCormick, H. Vazquez-Lima, A. Ghosh, Relativistic effects on a metal–metal bond: osmium corrole dimers, *Inorg. Chem.* 58 (2019) 2798–2806.
- [47] A.B. Alemayehu, L.J. McCormick-McPherson, J. Conradie, A. Ghosh, Rhenium Corrole dimers: electrochemical insights into the nature of the metal–metal quadruple bond, *Inorg. Chem.* 60 (2021) 8315–8321.
- [48] J. Conradie, H. Vazquez-Lima, A.B. Alemayehu, A. Ghosh, Comparing isoelectronic, quadruple-bonded Metalloporphyrin and Metalloporrole dimers: scalar-relativistic DFT calculations predict a  $> 1$ -eV range for ionization potential and electron affinity, *ACS Phys. Chem.* Au 2 (2021) 70–78.
- [49] W.R. Osterloh, J. Conradie, A.B. Alemayehu, A. Ghosh, K.M. Kadish, The Question of the Redox Site in Metal–Metal Multiple-Bonded Metalloporrole Dimers, *ACS Org. Inorg. Au* 3 (2023) 35–40.
- [50] A. Ghosh, J. Almlöf, The ultraviolet photoelectron spectrum of free-base porphyrin revisited. The performance of local density functional theory, *Chem. Phys. Lett.* 213 (1993) 519–521.
- [51] A. Ghosh, Substituent effects on valence ionization potentials of free base porphyrins: a local density functional study, *J. Am. Chem. Soc.* 117 (1995) 4691–4699.
- [52] A. Ghosh, Theoretical comparative study of Free Base porphyrin, Chlorin, bacteriochlorin, and isobacteriochlorin: evaluation of the potential roles of ab initio Hartree–Fock and density functional theories in Hydroporphyrin chemistry, *J. Phys. Chem. B* 101 (1997) 3290–3297.
- [53] A. Ghosh, T. Vangberg, Valence ionization potentials and cation radicals of prototype porphyrins. The remarkable performance of nonlocal density functional theory, *Theor. Chem. Accounts* 97 (1997) 143–149.
- [54] A. Ghosh, First-principles quantum chemical studies of porphyrins, *Acc. Chem. Res.* 31 (1998) 189–198.
- [55] N.C. Handy, A.J. Cohen, Left-right correlation energy, *Mol. Phys.* 99 (2001) 403–412.
- [56] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (1988) 785–789.
- [57] M. Reiher, O. Salomon, B.A. Hess, Reparameterization of hybrid functionals based on energy differences of states of different multiplicity, *Theor. Chem. Accounts* 107 (2001) 48–55.
- [58] O. Salomon, M. Reiher, B.A. Hess, Assertion and validation of the performance of the B3LYP\* functional for the first transition metal row and the G2 test set, *J. Chem. Phys.* 117 (2002) 4729–4737.
- [59] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behaviour, *Phys. Rev. A* 38 (1988) 3098–3100.
- [60] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr, *Chem. Phys. Lett.* 157 (1989) 200–206.
- [61] S. Grimme, J. Anthony, S. Ehrlich, H.A. Krieg, Consistent and accurate ab initio parameterization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu, *J. Chem. Phys.* 132 (2010), 154104.
- [62] A. Ghosh, T. Vangberg, E. Gonzalez, P. Taylor, Molecular structures and electron distributions of higher-valent iron and manganese porphyrins. Density functional

- theory calculations and some preliminary open-shell coupled-cluster results, *J. Porphyrins Phthalocyanines* 5 (2001) 345–356.
- [63] A. Ghosh, B.J. Persson, P.R. Taylor, Ab initio multiconfiguration reference perturbation theory calculations on the energetics of low-energy spin states of iron (III) porphyrins, *J. Biol. Inorg. Chem.* 8 (2003) 507–511.
- [64] A. Ghosh, P.R. Taylor, High-level ab initio calculations on the energetics of low-lying spin states of biologically relevant transition metal complexes: a first progress report, *Curr. Opin. Chem. Biol.* 7 (2003) 113–124.
- [65] A. Ghosh, Transition metal spin state energetics and noninnocent systems: challenges for DFT in the bioinorganic arena, *J. Biol. Inorg. Chem.* 11 (2006) 712–724.
- [66] I.H. Wasbotten, A. Ghosh, Spin-state energetics and spin-crossover behavior of Pseudotetrahedral cobalt(III)–Imido complexes. The role of the Tripodal supporting ligand, *Inorg. Chem.* 46 (2007) 7890–7898.
- [67] J. Conradie, A. Ghosh, DFT calculations on the spin-crossover complex Fe (salen) (NO): a quest for the best functional, *J. Phys. Chem. B* 111 (2007) 12621–12624.
- [68] F. Aquilante, P.Å. Malmqvist, T.B. Pedersen, A. Ghosh, B.O. Roos, Cholesky decomposition-based multiconfiguration second-order perturbation theory (CD-CASPT2): application to the spin-state energetics of Co<sup>III</sup>(diiminato)(NPh), *J. Chem. Theory Comput.* 4 (2008) 694–702.
- [69] E. Gonzalez, P.J. Brothers, A. Ghosh, Density functional theory calculations on ruthenium (IV) Bis (amido) porphyrins: search for a broader perspective of Heme protein compound II intermediates, *J. Phys. Chem. B* 114 (2010) 15380–15388.
- [70] H.L. Chen, P.E. Ellis Jr., T. Wijesekera, T.E. Hagan, S.E. Groh, J.E. Lyons, D. P. Ridge, Correlation between gas-phase electron affinities, electrode potentials, and catalytic activities of halogenated metalloporphyrins, *J. Am. Chem. Soc.* 116 (1994) 1086–1089.
- [71] J. Telser, Y.-C. Fann, M. Renner, J. Fajer, S. Wang, H. Zhang, R.A. Scott, B. M. Hoffman, Investigation by EPR and ENDOR spectroscopy of the nickel(I) form of cofactor F<sub>430</sub> of *Methanobacterium thermoautotrophicum* and of nickel(I) Octaethylisobacteriochlorin, *J. Am. Chem. Soc.* 1997 (119) (1997) 733–743.
- [72] T. Wondimagegn, A. Ghosh, A first-principles quantum chemical study of coenzyme F430: interplay of skeletal stereoisomerism and conformation in the stabilization of nickel (I), *J. Am. Chem. Soc.* 122 (2000) 6375–6381.
- [73] L.R. Furenliid, M.W. Renner, K.M. Smith, J. Fajer, Structural consequences of nickel versus macrocycle reductions in F430 models: EXAFS studies of a Ni(I) anion and Ni(II)  $\pi$ -anion radicals, *J. Am. Chem. Soc.* 112 (1990) 1634–1635.
- [74] M.W. Renner, L.R. Furenliid, K.M. Barkigia, A. Forman, H.K. Shim, D.J. Simpson, K. M. Smith, J. Fajer, Models of factor 430. Structural and spectroscopic studies of nickel(II) and nickel(I) hydroporphyrins, *J. Am. Chem. Soc.* 113 (1991) 6891–6898.
- [75] A.G. Maher, M. Liu, D.G. Nocera, Ligand noninnocence in nickel porphyrins: nickel isobacteriochlorin formation under hydrogen evolution conditions, *Inorg. Chem.* 58 (2019) 7958–7968.
- [76] P.J. Chmielewski, L. Latos-Grażyński, M.M. Olmstead, A.L. Balch, Nickel complexes of 21-Oxaporphyrin and 21, 23-Dioxaporphyrin, *Chem. Eur. J.* 3 (1997) 268–278.
- [77] L. Latos-Grazynski, M.M. Olmstead, A.L. Balch, The first structural characterization of a nickel (I) macrocyclic system: structure of nickel (I) diphenyldi-p-toyl-21-thiaporphyrin, *Inorg. Chem.* 28 (1989) 4065–4066.
- [78] P. Chmielewski, M. Grzeszczuk, L. Latos-Grazynski, J. Lisowski, Studies of the reduction of the nickel(II) complex of 5, 10, 15, 20-tetraphenyl-21-thiaporphyrin to form corresponding nickel(I) complexes, *Inorg. Chem.* 28 (1989) 3546–3552.
- [79] A. Ghosh, T. Wondimagegn, H. Ryeng, Deconstructing F430: quantum chemical perspectives of biological methanogenesis, *Curr. Opin. Chem. Biol.* 5 (2001) 744–750.
- [80] K. Oohora, Y. Miyazaki, T. Hayashi, Myoglobin reconstituted with Ni Tetrahydrocorrin as a methane-generating model of methyl-coenzyme M reductase, *Angew. Chem. Int. Ed.* 58 (2019) 13813–13817.
- [81] Y. Miyazaki, K. Oohora, T. Hayashi, Methane generation and reductive debromination of benzylic position by reconstituted myoglobin containing nickel tetrahydrocorrin as a model of methyl-coenzyme M reductase, *Inorg. Chem.* 59 (2020) 11995–12004.