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Dual-Channel-Mediated Spin Coupling for One-Electron-Oxidized Cobalt(II)-Saddled Porphyrin

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Ⓢ *Supporting Information*

ABSTRACT: Saddle-shaped $Co^{II}[OET(p\text{-}R)PP]$ (R = CF_3, H, CH_3) can be readily oxidized with Cl_2, Br_2, and I_2 to the corresponding one-electron-oxidation product $Co[OET(p\text{-}R)PP]X$ (X = Cl, Br, I) with the clear character of a ring cation radical. With the series of ^1H and ^{13}C NMR spectra of these related complexes, both the axial ligand and peripheral substituent of the ring macrocycle are proven to act as a dual channel to tune spin coupling between low-spin Co(II) and a porphyrin π-cation radical. Density functional theory calculations have shown that the antiferromagnetic coupling between spins residing in d_{z^2} and a_{2u} are expected to exist as the ground state. The paramagnetic properties are attributed to an a_{1u}-type ferromagnetic excited triplet state.

The ring-oxidized metalloporphyrin π-cation radicals and their derivatives play crucial roles in various oxidative pathways catalyzed by hemoproteins and also in the electron-transport chain of photosynthetic organisms.[1,2] Different modes of spin coupling between the metal- and ligand-centered unpaired electrons seem to be a subtle mechanism to fine-tune the electronic structures of the heme prosthetic group. Attempts to attribute the mode and magnitude of intramolecular spin−spin coupling between the metal and porphyrin radical to differences in the axial ligation,[3] porphyrin shape (symmetry of the complex), or porphyrin radical symmetry (a_{2u} vs a_{1u})[4] were, however, only partially successful.

Porphyrins deformed into a saddle shape have been noticed to be easily oxidized and form stable π-cation radicals.[5,6] $Cu^{II}(OETPP)$ (OETPP = dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphinato) undergoes one-electron oxidation to form five-coordinated copper(II) π-cation radical $Cu^{II}(OETPP)^+ClO_4^-$ with strong antiferromagnetic coupling between $d_{x^2-y^2}$ and a_{2u}.[7] With a single electron in d_{z^2}, which is the most sensitive to the properties of axial ligands, ring-oxidized five-coordinated $Co^{II}(OETPP)^+X^-$ should provide a unique chance to investigate axial-ligand-controlled spin coupling between metal and porphyrin cation radicals. The $Co^{II}(OETPP)$ complex undergoes clean one-electron oxidation with I_2, Br_2, and Cl_2 in a solution of dichloromethane to the corresponding product $Co^{II}(OETPP)^+X^-$ (X = I, Br, Cl), as evidenced by isosbestic visible absorption spectra (Figures 1 and S1 in the Supporting Information, SI). In all cases, oxidation leads to blue-shifted Soret bands with intensities of about half that of Co(OETPP), a typical characteristic of porphyrin cation radicals.[8,9] Molecular structures of Co(OETPP)X (X = I, Br, Cl) were determined by X-ray crystallography and clearly indicate the five-coordinated nature of the complexes and deformation of the porphyrin macrocycles (Figures S2 and S3 in the SI). Although the out-of-plane displacements of cobalt are similar to each other (0.11 Å), the average $Co-N_p$ bond distances increase as the axial ligand changes, in the order $I^- < Br^- < Cl^-$ (1.928 < 1.932 < 1.935 Å). They are close to 1.929 Å for $Co^{II}(OETPP)$, establishing that oxidation is centered on the porphyrin rather than on the metal.

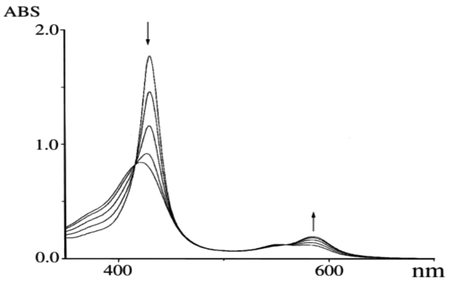

Figure 1. Absorption spectral changes of Co(OETPP) upon one-electron oxidation with I_2 in a solution of dichloromethane at room temperature.

^1H NMR data of $Co^{II}[OET(p\text{-}R)PP]^+X^-$ (R = CF_3, H, CH_3; X = I, Br, Cl) are collected in Table 1 and shown in Figures S4 and S5 in the SI. Complete resonance assignments are based on the relative intensities and line widths for the methylene and methyl protons of the ethyl substituents and the coupling patterns and 2D [^1H,^1H] COSY spectrum for the phenyl protons (Figure S6 in the SI). Similar to $Cu^{II}(OETPP)^+ClO_4^-$, Co(OETPP)I exhibits sharp ^1H NMR lines in solution, very close to the corresponding diamagnetic species. ^1H NMR spectra of the series of Co(OETPP)X (X = I, Br, Cl) spread out systematically and significantly into larger range as the axial ligand changes from I^- to Br^- and Cl^-. Likewise, when the axial ligand is fixed at any of the above halide anions and the phenyl para substituent is varied from CF_3 to H and CH_3, magnetic and ring radical properties obviously increase.

For these cases, downfield-shifted *p*-H and upfield-shifted *m*-H refer to negative spin density at *meso*-C atoms.[10,11] This has been

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Table 1. ^{1}H and ^{13}C NMR Data for Co[OET(*p*-R)PP]X Complexes Taken in $CDCl_3$ at Room Temperature

Co[OET(*p*-R)PP]X	*o*-H	*m*-H	*p*-H	CH_2	CH_3	*meso*-C	*α*-C	*β*-C
R = H; X = I	8.04, 8.38	7.60. 7.68	7.68	2.01, 2.06, 2.55, 2.61	0.42, 0.48	122.7	144.9, 154.4	149.1, 150.0
R = H; X = Br	7.25, 8.63	6.95, 7.25	7.74	1.77, 2.45, 3.57, 4.09	0.47, 0.47	89.4	175.9, 187.1	170.6, 171.4
R = H; X = Cl	6.08, 9.90	5.53, 6.42	8.15	0.10, 3.43, 6.28, 7.01	0.22, 0.95	0.6	247.1, 278.1	216.6, 228.3
R = CF_3; X = Cl	6.88, 8.95	6.65, 7.12		1.43, 4.08, 4.33, 5.00	0.53, 0.53	51.0		
R = CH_3; X = Cl	5.57, 11.01	4.56, 5.86	(1.48)	−1.08, 2.77, 8.15, 8.92	−0.09, 1.37	−40.5		
Co(OETPP)	16.13	10.43	10.19	5.28, 7.96	0.21	204.7	135.8	98.9

further confirmed by the upfield-shifted ^{13}C signal of *meso*-C along this same series (Table 1 and Figure S7 in the SI).[12,13] ^{13}C NMR spectra have been assigned unambiguously through ^{13}C enrichment at *meso*-C, and the pattern of ^{1}H- or ^{13}C-coupled signals. Downfield-shifted *α*-C and *β*-C suggest significant positive spin densities at these positions. Contrary to what we would expect from an a_{2u} cation radical, which should have large positive spin density at *meso*-C and small positive spin densities at *α*-C and *β*-C, both ^{1}H and ^{13}C NMR data suggest an a_{1u} cation radical.[14] In addition, Co^{II}[OET(*p*-R)PP] porphyrin *π*-cation radical with strong antiferromagnetic coupling between d_{z^2} and a_{2u} should be a reasonable electronic ground structure. Rigorously speaking, saddled Co[OET(*p*-R)PP]X (R = CF_3, H, CH_3; X = I, Br, Cl) complexes still have sort of Co^{III} character because of d_{z^2}—a_{2u} allowable overlap under C_{2v} symmetry, which is also supported by density functional theory (DFT) calculations, because only the very small partial electron density of Co^{II} will be removed from the a_{2u} molecular orbital through d_{z^2}—a_{2u} interaction (Figure 2). The tunable magnetism induced by saddle deformation is totally different from planar five-coordinated Co(TPP)X (X = Cl, Br, I), for which the ^{1}H NMR spectra are present in the complete diamagnetic range, as shown in Figure S8 in the SI. These NMR data also exclude the possibility of mixing between the low- and high-spin five-coordinated cobalt(III) porphyrinates, in which the diamagnetic low-spin Co^{III} is not influenced that much by the phenyl para substituent (−CF_3 or −CH_3), and a five-coordinated high-spin Co^{III} with the metal out of the plane of the porphyrin N atoms would delocalize the d_{z^2} sizable positive density to the *meso*-C atoms via d_{z^2}—a_{2u} overlap, which is a typical bonding interaction for five-coordinated metalloporphyrin discovered by Cheng et al.,[15] instead of the negative spin density observed.

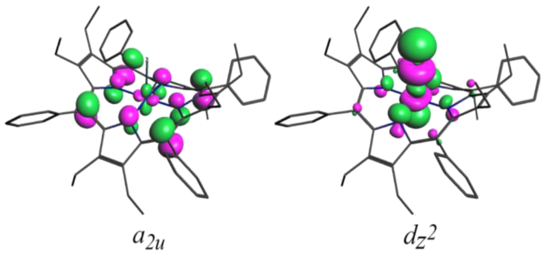


Figure 2. DFT-calculated a_{2u} and d_{z^2} molecular orbitals from the $d_{xy}{}^2d_{xz}{}^2d_{yz}{}^2d_{z^2}{}^1a_{2u}{}^1$ ($S = 0$, $^{1}A_1$) state of Co(OETPP)Cl (H atoms of OETPP omitted for clarity).

Upon careful examination of the paramagnetic shifts of these complexes, cation radicals with a_{1u} character show the significant positive spin densities at *α*,*β*-C atoms and negative spin density at *meso*-C derived from spin polarization of neighboring *α*-C atoms, regardless of the a_{2u} character possessing the same signs with *meso*- and *α*,*β*-C atoms.[12] That is, significant isotropic shifts of both Co[OET(*p*-R)PP]Br and Co[OET(*p*-R)PP]Cl must be ascribed to a ferromagnetically coupled low-spin Co^{II} a_{1u} cation radical. DFT-based molecular orbital calculations for this series of complexes provide further evidence to support our interpretations from experimental data.

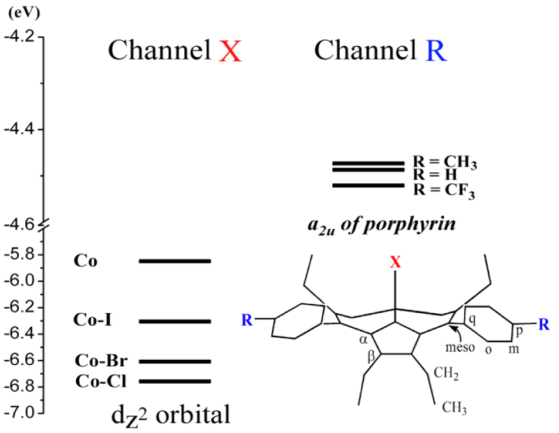
They all have antiferromagnetically coupled ground state $d_{xy}{}^2d_{xz}{}^2d_{yz}{}^2d_{z^2}{}^1a_{2u}{}^1$ ($S = 0$, $^{1}A_1$ state), which presents an apparent bonding interaction between the d_{z^2} and a_{2u} orbitals (Figure 2) and low-lying ferromagnetic coupled excited state $d_{xy}{}^2d_{xz}{}^2d_{yz}{}^2d_{z^2}{}^1a_{1u}{}^1$ ($S = 1$, $^{3}A_2$ state). The energies of the lowest singlet and triplet states for each of the complexes investigated are reported in Table 2. The energy difference between these two states, $\Delta E(^{3}A_2-^{1}A_1)$, decreases in order from Co(OETPP)I to Co(OETPP)Br and then Co(OETPP)Cl. These results can be rationalized through a molecular orbital energy level representation from DFT fragment orbital calculations[15,16] (Scheme 1), which coincides with the effects on the d_{z^2} orbital by axial ligands and on the a_{2u} orbital by the para substituent of the *meso*-phenyl groups (Table 1).

Table 2. Self-Consistent-Field Energies Calculated from BP-DFT for the Low-Lying Electronic Structures of Co(OETPP)X

	X = I	X = Br	X = Cl
$^{3}A_1(d_{z^2}\uparrow a_{2u}\uparrow)$	−18163.19	−18161.94	−18173.97
$^{3}A_2(d_{z^2}\uparrow a_{1u}\uparrow)$	−18166.96	−18166.00	−18178.03
$^{1}A_1(d_{z^2}\uparrow a_{2u}\downarrow)$	−18194.37	−18192.71	−18202.51
$\Delta E(^{3}A_2-^{1}A_1)^a$	27.41	26.71	24.48
$\Delta E(^{3}A_1-^{1}A_1)^a$	31.18	30.77	28.54

^{a}Energy in kcal mol^{-1}.

Scheme 1. Schematic Representation of the Axial Ligand Effect (X) and Phenyl Para Substituent Effect (R) on the Relative Energies of the Two Magnetic Orbitals d_{z^2} and a_{2u} of Co[OET(*p*-R)PP]X Based on DFT Calculations



The most electronegative axial ligand (Cl), lowering the d_{z^2} orbital in energy, and the best electron-donating ring macrocycle [OET(p-$\mathrm{CH_3}$)PP], raising the a_{2u} orbital in energy, result in the weakest antiferromagnetic coupling in the Co[OET(p-R)PP]X (R = $\mathrm{CF_3}$, H, $\mathrm{CH_3}$; X = I, Br, Cl) complexes (i.e., the weakest bond formation),[17] which, in turn, will decrease the energy difference between the singlet and triplet states and induce a larger contribution from the ferromagnetic triplet excited state. Thus, the purely diamagnetic Co[OET(p-$\mathrm{CF_3}$)PP]I is rational. Variable-temperature ^{1}H NMR spectra of Co(OETPP)Cl with non-Curie behavior reveals the nature of the excited-state contribution (Figure S9 in the SI).[18]

The collective data from electronic ^{1}H and ^{13}C NMR spectroscopies and from X-ray structure determinations provide unambiguous evidence that the $\mathrm{Co^{II}}$[OET(p-R)PP]$^+$X$^-$ series are cobalt(II) porphyrin π-cation radicals with strong antiferromagnetic coupling. The magnitude of magnetic interactions between cobalt(II) and porphyrin π-cation radicals shows a novel dependence of axial ligands and ring macrocycles. DFT calculations further clarify the nature of the spin coupling between metal and porphyrin macrocycles. On the basis of molecular orbital calculations, all of these complexes have a diamagnetic electronic ground state with obvious bonding interactions between d_{z^2} and an a_{2u}-type ligand-centered orbital (Figure 2). Consistent with NMR analyses, the increasing paramagnetism of this series of complexes should be ascribed to a low-lying ferromagnetically coupled triplet state with spin densities having contributions from both a_{1u} and a_{2u}.

Another novel mechanism that may also induce orbital mixing of a_{1u} and a_{2u} has been reported for distorted porphyrin cation radicals.[19,20] With both saddle- and ruffle-shaped deformation, a five-coordinated $\mathrm{Cu^{II}}$(OETPP)$^+$$\mathrm{ClO_4}^-$ complex at symmetry lower than C_2, a_{1u} and a_{2u} will be of the same character (a) and can therefore be mixed. The pronounced bond alternation of the inner 16-membered ring is a good indication of this ground-state mixing.[7] However, none of our structural data or molecular orbital calculations suggest this ground-state mixing for the $\mathrm{Co^{II}}$(OETPP)$^+$X$^-$ (X = I, Br, Cl) series of complexes.

The cation radicals of heme protein compounds I have been proposed to have contributions from both a_{1u} and a_{2u}.[21,22] On the basis of these more sophisticated model compound studies, there are at least two distinct types of mechanisms for metalloporphyrin π-cation radicals to have contributions from both a_{1u} and a_{2u}. It is crucial to differentiate a ground-state mixing of a_{1u} and a_{2u} from a low-energy excited-state contribution, as suggested by our model system.

As we expected, the ring-oxidized five-coordinated complexes $\mathrm{Co^{II}}$[OET(p-R)PP]$^+$X$^-$ with the metal magnetic orbital of d_{z^2}, which is most sensitive to the properties of axial ligands, and the macrocycle a_{2u} π-cation radical, which is able to be tuned by the ring substituents, turn out to be a novel model for both axial ligand and ring macrocycle, for dual-channel-controlled spin coupling in metalloporphyrin π-cation radicals. The series of $\mathrm{Co^{II}}$[OET(p-R)PP]$^+$X$^-$ with an antiferromagnetically coupled ground state offers a unique chance to elucidate the nature of the first excited state and reveals a distinct mechanism for mixing of a_{1u} and a_{2u} in porphyrin cation radicals.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, Co(OETPP)$^+$X$^-$ (X = I, Br, Cl), physical measurement, crystallography, computational methods, and DFT-calculated Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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