(12) On the basis of extensive experiments using several proteins, Kangawa (Ph.D. Thesis, Osaka University, 1977) has shown that, under the conditions used in the present experiments, the extent of back-exchange in finally separated deuterated histidine peptides is not >3%.

(13) ^{1}H NMR spectra were recorded on a JEOL PS-100 spectrometer operating at 100 MHz in the correlation mode (Y. Arata and H. Ozawa, *J. Magn. Reson.*, 21, 67–76 (1976)).

(14) The His^{198} peak is much broader in line width than the His^{189} peak. In addition, His^{198} has an unusually low pK_a of 4.9. Significance of the results obtained here concerning Bence Jones dimer Ak will be discussed elsewhere.

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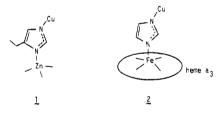*Osaka University School of Medicine, Osaka, Japan*

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Imidazolate Anion Bridged Metalloporphyrins of Relevance to a Model for Cytochrome Oxidase
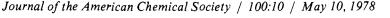
Sir:

There is wide interest in the active site structure and function of metalloproteins with magnetically interacting metal sites[1] and in probing these systems by the model complex approach.[2] We have been particularly intrigued with the metal/imidazolate/metal situation exemplified by the histidine bridged Zn^{2+}/Cu^{2+} couple **1** of bovine superoxide dismutase[3] and

suggested for the ESR inactive Cu^{2+}/heme a$_3$ couple **2** of cytochrome oxidase.[4] The nature of Cu^{2+}/Cu^{2+} magnetic coupling across an imidazolate bridge (Im) has been investigated by ESR in copper-substituted superoxide dismutase derivatives[5] and by magnetic susceptibility measurements on synthetic analogues.[6] Herein we report synthetic, structural, and magnetic data for some interesting, new imidazolate-bridged metalloporphyrins. Our preliminary conclusions for such systems are that (a) metal–metal antiferromagnetic coupling through an imidazolate bridge is weak, (b) the magnitude of the coupling is greatest when the orbitals containing the unpaired electrons have mutual σ symmetry, and (c) it seems unlikely that an imidazolate bridge can account for the very large magnetic coupling observed in the Cu/heme a$_3$ site of cytochrome oxidase.

Stoichiometric treatment of $Mn(OClO_3)(TPP)$[7] with $(Bu_4N)(Im)$ in dry THF gives an insoluble dark green precipitate of polymeric $[Mn(Im)(TPP)·THF]_n$, **3**.[8] Growing single crystals of a polymer is a rarely successful endeavor but by extremely careful layering of methanolic solutions of $NaOCH_3$/imidazole/$Mn(OCH_3)(TPP)$ we were able to isolate solvate-free single crystals of $[Mn(Im)(TPP)]_n$, **4**. The x-ray crystal structure[9] reveals layers of parallel polymeric chains with alternate layers having their quasi-linear chains approximately orthogonal to each other. The molecular structure
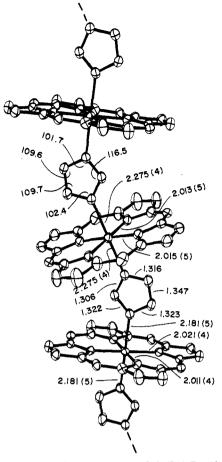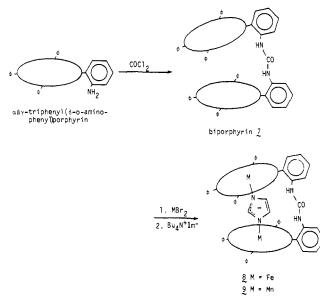

Figure 1. An ORTEP plot of three units of the $[Mn(Im)(TPP)]_n$ polymer, **4.** Each Mn(III) atom is located at an inversion center; the lowest two units (with required C_i symmetry) are the crystallographically unique portion of the polymer. For the sake of clarity, peripheral phenyl groups are omitted. Bond distances in the coordination group and bond distances and angles for the imidazolate anion are entered on the diagram. The dihedral angle between adjacent porphinato planes is 28.5°; the dihedral angles between (Im) and the porphinato planes are 86.3 and 80.4°. The intrachain Mn···Mn distance is 6.54 Å; interchain distances are >11 Å.

(Figure 1) shows the expected six-coordinate manganese stereochemistry but is unusual in that a long–long/short–short alternation of axial Mn–N$_{Im}$ bond lengths occurs. A most reasonable explanation[10] lies in a high-spin/low-spin alternation of the d^4 Mn(III) atoms. The longer pair at 2.275 (4) Å is close to that of the known high-spin monomer $[Mn(1-MeIm)_2(TPP)]ClO_4$, **5**, where Mn–N$_{Im}$ is 2.308 (3).[11] There are no suitable low-spin manganese(III) porphyrin complexes for comparison with the shorter Mn–N$_{Im}$ pair at 2.181 (5) Å, but the shortening of ~0.1 Å is typical of a high to low spin-state change where an electron is transferred from an antibonding to a nonbonding d orbital.[12] Consistent with these spin-state assignments, the room temperature magnetic moment of the polymer **3** has a value expected of an $S = 2/S = 1$ mixture (found, $\mu_{eff} = 4.2$; calcd spin only, $\mu_s = 4.02$ μ_B). The monomer **5** has $\mu_{eff} = 5.3$ μ_B, typical of a pure $S = 2$ species.

To look for possible antiferromagnetic coupling in the polymer **3** magnetic susceptibilities were measured over the range 4.2–300 K.[13] The essential linearity of the Curie plot ($1/\chi_M$ versus T in Figure 2a) down to 10 K shows that **3** also behaves like an uncoupled $S = 1/S = 2$ system. The small but real curvature toward 0 K at very low temperatures is suggestive of very weak antiferromagnetic coupling and/or zero-field splitting. Application of theory to a mixed-spin linear chain is nontrivial, but that[14] for an $S = 1/S = 2$ dimer places an upper limit on the exchange coupling constant, $-J \leqslant 8$

Scheme I

aßγ-triphenyl(δ-o-amino-
phenyl)porphyrin

biporphyrin 7

1. MBr$_2$
2. Bu$_4$N$^+$Im$^-$

8 M = Fe
9 M = Mn

cm^{-1}. However, since in the polymeric chain each Mn atom has two interacting neighbors the value of J per Mn/Im/Mn dimer must be ≪8 cm^{-1}. A magnetic investigation of the presumably isostructural, previously reported,[15] low-spin Fe(III) polymer [Fe(Im)(TPP)·THF]$_n$, 6, which we prepared from Fe(OClO$_3$)(TPP)[16] and (Bu$_4$N)(Im) in THF,[17] reveals a similar Curie plot (Figure 2a). An upper limit $-J < 2$ cm^{-1} can be placed on 6 and it has been argued that antiferromagnetism is nonexistent.[15] Thus, antiferromagnetic coupling in these polymers is weak or negligible and, although they are useful for arguments regarding the orbital coupling mechanism (vide infra), better estimates of $-J$ for metal/Im/metal systems and commentary on possible biological situations can be made only by studying discrete dimers.

Adaption of a reported[2a] face-to-face porphyrin synthesis leads to a new biporphyrin 7 (Scheme I). The synthetic strategy was to favor entropically imidazolate bridging by employing a urea linkage whose planarity and dimensions favor a "clamshell" configuration but which also retains enough flexibility to allow canting of the porphyrin rings to readily accommodate the five-membered ring. We find that the iron(II) and manganese(II) imidazolate bridged dimers 8 and 9 are synthetically accessible by straightforward procedures and they were isolated as well-characterized purple crystals.[18] Five coordination in 8 and 9 is expected[19,20] to give rise to high-spin states and their 300 K magnetic moments (μ_{eff} = 5.2 for 8; μ_{eff} = 6.1 for 9) are close to the uncoupled values of their respective monomers Fe(2-MeHIm)(TPP)·C$_2$H$_5$OH, 10 (μ_{eff} = 5.4) and (Bu$_4$N)[Mn(Im)(TPP)] (μ_{eff} = 6.4). The Curie plots of the iron S = 2 dimer 8 and its analogous monomer 10 are compared in Figure 2b; the minimum for 8 identifies it as an antiferromagnet. The more familiar χ_M vs. T plot in Figure 3 shows T_{max} at 22 K and to a good approximation[21] the relationship of T_{max} to the coupling constant gives $-J = 8 \pm 2$ cm^{-1}. The $S = {}^5/_2$ manganese(II) dimer 9 behaves similarly with T_{max} at 10 K and $-J = 8 \pm 2$ cm^{-1}.

Taken together with the literature values of $-J$ for Cu^{2+}/Im/Cu^{2+} systems (26–90 cm^{-1}),[6] a pattern seems to be emerging. Significant antiferromagnetic coupling ($-J$ in the range 8–90 cm^{-1}) occurs only in systems where the d orbitals containing the unpaired electrons have mutual σ symmetry, i.e., (d$_{z^2}$)^1 and/or (d$_{x^2-y^2}$)^1 occupation. This includes the Cu^{2+}/Cu^{2+}, the high-spin Fe^{2+}/Fe^{2+}, and the high-spin Mn^{2+}/Mn^{2+} systems but not those of the low-spin Fe^{3+}/Fe^{3+} or high-spin Mn^{3+}/low-spin Mn^{3+} polymers. These latter
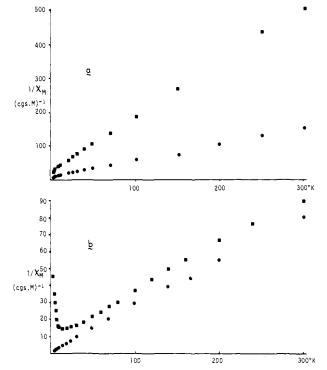

Figure 2. (a) Curie plots of the polymers [Mn(Im)(TPP)·THF]$_n$, 3 (●), and [Fe(Im)(TPP)·THF]$_n$, 6 (■). (b) Curie plots of the magnetically normal monomer Fe(2-MeHIm)(TPP)·C$_2$H$_5$OH, 10 (●), and the antiferromagnetically coupled Fe(II) dimer 8 (■). The data for 8 have been corrected for paramagnetic impurities (<7% if high-spin Fe(III)) by fitting the very low temperature data to a Curie–Weiss law and correcting in the usual way.[22]
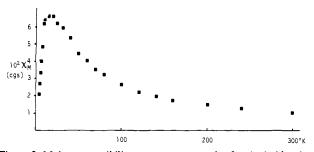

Figure 3. Molar suspectibility vs. temperature plot for the imidazolate bridged iron(II) dimer 8 showing the Neel temperature T_{max} at 22 K.

systems have $-J \ll 8$ cm^{-1} and have only π overlap opportunities.[23] The implication for the superexchange mechanism is that orbital overlap via the σ bonding system of imidazolate may be more important than π.[24] However, since π effects should be dependent upon orientation,[6] several detailed structural investigations will be necessary to establish the exchange pathway.

Again taken altogether, the presently known metal/Im/metal systems scan several different d^n configurations of first-row transition metals and set the range of $-J$ at ∼0–90 cm^{-1}. We suspect therefore that a Cu^{2+}/Im/Fe^{3+} heme system, such as that proposed for the heme a$_3$ site of cytochrome oxidase,[4] will have $-J$ within, or close to, this range;[25] the synthetic analogue approach is uniquely suited to further testing this proposal. Since the coupling in oxidase ($-J \gg 200$ cm^{-1})[26] falls well outside this range a bridging ligand which brings the copper and heme centers in closer proximity may be present.[27]

perature magnetic capability. This work was supported by the National Science Foundation (CHE 75-03648) and the National Institutes of Health (HL-15627).

References and Notes

(1) Examples included the following. (a) Hemocyanin, tyrosinase, and laccase: E. I. Solomon, D. M. Dooley, R.-H. Wang, H. B. Gray, M. Cerdonio, F. Mogno, and G. L. Romani, *J. Am. Chem. Soc.*, **98**, 1029 (1976); J. A. Fee, *Struct. Bond. (Berlin)*, **23**, 1 (1975). (b) Hemerythrin: M. Y. Okamura and I. M. Klotz in "Inorganic Biochemistry", G. I. Eichhorn, Ed., Elsevier, Amsterdam, 1975, Chapter 11. (c) Cytochrome oxidase: D. C. Wharton in ref 1b, Chapter 27.

(2) Recent examples include (a) J. P. Collman, C. M. Elliott, T. R. Halbert, and B. S. Tovrog, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 18 (1977); (b) J. E. Bulkowski, P. L. Burk, M.-F. Ludmann, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 498 (1977); (c) D.-H. Chin, J. Del Gaudio, G. N. La Mar, and A. L. Balch, *J. Am. Chem. Soc.*, **99**, 5486 (1977); (d) J. S. DeCourcy, T. N. Waters, and N. F. Curtis, *J. Chem. Soc., Chem. Commun.*, 572 (1977); (e) T. G. Traylor, Y. Tatsuno, D. W. Powell, and J. B. Cannon, *ibid.*, 732 (1977).

(3) J. S. Richardson, K. A. Thomas, B. H. Rubin, and D. C. Richardson, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1349 (1975).

(4) G. Palmer, G. T. Babcock, and L. E. Vickery, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 2206 (1976);

(5) J. A. Fee and R. G. Briggs, *Biochim. Biophys. Acta*, **400**, 439 (1975).

(6) G. Kolks and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 5804 (1977).

(7) Abbreviations: TPP = dianion of *meso*-tetraphenylporphyrin; Bu$_4$N = tetra-*n*-butylammonium; Im = imidazolate anion, C$_3$N$_2$H$_3$$^-$; 1-MeIm = 1-methylimidazole; 2-MeHIm = 2-methylimidazole; THF = tetrahydrofuran.

(8) Anal. Calcd for C$_{51}$H$_{39}$N$_6$OMn: C, 75.92; H, 4.67; N, 10.42; Found: C, 75.60; H, 4.86; N, 9.93. NMR integration solvate analysis from acid decomposition: calcd for THF, 8.9; found, 9.8.

(9) Crystal data and refinement results: [Mn(N$_4$C$_{44}$H$_{28}$)(C$_3$N$_2$H$_3$)]$_n$; monoclinic; a = 20.033 (3), b = 16.851 (3), and c = 22.545 (5) Å; β = 104.36 (2)°; space group C2/c; Z = 8; ρ_{calcd} = 1.324, ρ_{obsd} = 1.32 g/cm^3; R_1 = 0.090, R_2 = 0.089; 4320 unique observed data (F_o > 3σ(F_o), 2θ < 55°, Mo Kα radiation).

(10) Another explanation, albeit less likely, is that a Jahn Teller or Peirls distortion causes a symmetry lowering alternation of Mn–N$_{Im}$ bond lengths. The pseudo S = $^3/_2$ spin state would then have to be rationalized by an all high-spin complex with complete coupling of one unpaired electron per Mn(III) atom by overlap of the d$_{z^2}$ orbitals via the σ bonding system of imidazolate.

(11) H. K. Chun, J. L. Hoard, and C. A. Reed, Abstracts of the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 13–17, 1978, INORG 15. The slight shortening by 0.033 Å in **4** is very reasonably ascribed to the charge attraction of the imidazolate anion to Mn(III) when compared with the neutral 1-methylimidazole. Charge attraction is also the rationale for low-spin configuration of every other Mn(III) atom.

(12) For example, comparison of low-spin Fe(1-MeIm)$_2$(TPP) to high spin Fe(2-MeIm)(TPP) reveals differences of 0.09 and 0.15 Å in Fe–N$_{Porph}$ and Fe–N$_{Im}$, respectively. No significant difference in Mn–N$_{Porph}$ is expected between high- and low-spin Mn(III) since in both states d$_{x^2-y^2}$ is unoccupied. W. R. Scheidt, *Acc. Chem. Res.*, **10**, 339 (1977).

(13) Effective magnetic moments are corrected for diamagnetism. Measurements were made at 300 K on a Cahn 7600 Faraday balance and at lower temperatures on a SCT "Squid" system.

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(15) I. A. Cohen and D. Ostfeld, *ACS Symp. Ser.*, No. 5, 221 (1974).

(16) M. E. Kastner, W. R. Scheidt, T. Mashiko, and C. A. Reed, *J. Am. Chem. Soc.*, **100**, 666 (1978).

(17) Excess imidazolate gives isolable crystalline low-spin salts of [Fe(Im)$_2$(TPP)]$^-$ which we have characterized. The existence of such compounds in solution has recently been reported: M. Nappa, J. S. Valentine, and P. A. Snyder, *J. Am. Chem. Soc.*, **99**, 5799 (1977).

(18) Anal. Calcd for C$_{108}$H$_{95}$N$_{13}$OFe$_2$·3THF, **8**: C, 75.08; H, 6.25; N, 9.50; Found: C, 74.98; H, 6.52; N, 9.27. GLC solvate analysis: calcd, 11.2; found, 10.5. UV: λ_{max} (THF) 611 (w), 570 (m), 535 (w), 437 nm (vs). Calcd for C$_{108}$H$_{95}$N$_{13}$OMn$_2$·2THF, **9**: C, 75.49; H, 6.50; N, 9.86; Found: C, 75.68; H, 6.46; N, 9.52. UV: λ_{max} 621 (m), 580 (m), 538 (w), 444 nm (vs).

(19) J. P. Collman and C. A. Reed, *J. Am. Chem. Soc.*, **95**, 2048 (1973).

(20) J. F. Kirner, C. A. Reed, and W. R. Scheidt, *J. Am. Chem. Soc.*, **99**, 2557 (1977).

(21) We have attempted to calculate the usual least-squares best fit of our χ_M data to the Van Vleck equations for interacting d^n systems.^{14,22} The fit is barely satisfactory (up to 8.6% discrepancy for some data points), possibly because the Heisenburg approximation is inadequate for anisotropic metalloporphyrin configurations and possibly because of some inadequacies in the data; the complex is extremely air sensitive. We had to assume that as much as 7% magnetic impurity was present and unfortunately iron porphyrin complexes are notorious for having paramagnetic impurities. We are vigorously pursuing cleaner syntheses and a satisfactory fit of the theory. However, we stress that the uncertainty in $-J$ cannot be more than a few reciprocal centimeters and that the qualitative conclusions of this paper are therefore valid.

(22) A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, **4**, 45 (1971).

(23) For low-spin Fe(III) we are assuming an $(xy)^2(xz, yz)^3$ configuration as has been widely accepted in ESR studies: J. S. Griffith, *Mol. Phys.*, **21**, 135 (1971). For high-spin Mn(III) an $(xy)^1(xz, yz)^2(z^2)^1$ configuration can be safely assumed.^{11}

(24) Support for this mechanism comes from theoretical work: P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Amer. Chem. Soc.*, **97**, 4884 (1975).

(25) We note that the high-spin Mn(II) center in **9** is d^5 and therefore isoelectronic with high-spin Fe(III) heme a$_3$.

(26) T. Tzudzuki and K. Okunuki, *J. Biochem.*, **69**, 909 (1971).

(27) There is some ESR evidence^{28} implicating a nitrogen donor as the axial ligand to heme a$_3$ so that a deprotonated lysine or peptide would seem a reasonable suggestion.

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(29) Alfred P. Sloan Fellow, 1976–78; Camille and Henry Dreyfus Teacher-Scholar Awardee, 1976–1981.

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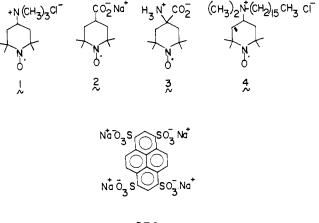*Department of Chemistry, University of Notre Dame*
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Fluorescence Quenching by Nitroxyl Radicals in Micellar Environments. A Useful Probe for Studying Micelle–Substrate Interactions

Sir:

Although it is now well established that micelles can catalyze or inhibit chemical reactions in aqueous solutions,[1] detailed descriptions of these effects are lacking. With the goal of elucidating such mechanisms, we have been investigating the fluorescence quenching of pyrene and pyrene derivatives by nitroxyl radicals in micelle environments.[2]

Previously, we showed that di-*tert*-butylnitroxide (a stable radical) quenches the fluorescence from a series of aromatic hydrocarbons at, or near, the diffusion limit with an interaction distance of 5–7 Å.[3] We find that this reaction is equally as efficient in aqueous media. If the mechanism does not change in going from nonpolar to aqueous solutions,[4] quenching still occurs over collisional distances so that *the relative quenching efficiencies will reflect relative encounter frequencies between the excited fluorophors and quenchers*. In this paper we show that the encounter frequency is strongly influenced by the micelle surface charge and that examples of both micelle-catalyzed and micelle-inhibited fluorescence quenching reactions can be realized.

The quenching of the fluorescence from 1.0×10^{-5} M tetrasodium pyrenetetrasulfonate (PTS)[6] by nitroxyl radicals **1**,[7] **2**,[8] **3**,[9] and **4**[10] was studied in aqueous solutions in the ab-

PTS

sence and presence of cetyltrimethylammonium chloride (CTAC) and sodium dodecylsulfate (SDS) micelles. The apparent k_Q's in Table I were calculated from the essentially linear Stern–Volmer slopes observed between 1.0×10^{-4} M