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Molybdocene Porphyrazines: A Peripheral Dithiolene Metallacycle Fused to a Porphyrinic Core

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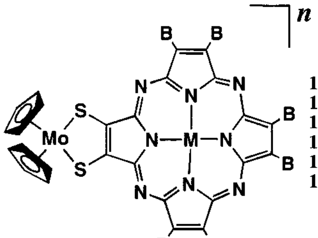
As one of the efforts to synthesize porphyrinic macrocycles with metal ions attached to the periphery,[1−3] we have developed a new family of tetraazaporphyrin (porphyrazine, pz) macrocycles that have metal-binding sulfur,[4] nitrogen,[5] or oxygen atoms[6] attached to the pz periphery. We anticipated that the peripheral metals in these molecules would be strongly coupled with the pz π-system, giving rise to physical properties not seen in the pz or metal fragments alone, and that such systems may prove useful in catalysis,[1] in electron-transfer,[7] and as molecular electronic[3] or magnetic[8] devices. Herein we report the preparation of metallocene porphyrazine complexes $[Cp_2Mo^{IV}][M(pz((S_2^{-});(B_2)_3))]$ (**1a**−**c**), in which a molybdocene unit is covalently attached to a dithiolene binding site[9] on the macrocyclic periphery (Chart 1). These complexes conjoin the metalladithiolene metallacycle, well-known for its extensive bond delocalization and aromatic properties,[10] with the aromatic 18 π-electron pz core.[11,12] The resulting hybrid molecule has properties beyond the sum of the porphyrazine and molybdocene−dithiolene fragments. These include the existence of five reversible redox couples that are related to those of the discrete porphyrazine core and molybdocene−dithiolene fragments but are quite altered by coupling between them. Most dramatic is strong antiferromagnetic exchange between Cu(II) and Mo(V) in **1f**, the one-electron oxidized form of **1c**.

Chart 1



1a: B = *t*-butylphenyl, M = 2H, *n* = 0
1b: B = *n*-propyl, M = 2H, *n* = 0
1c: B = *t*-butylphenyl, M = Cu(II), *n* = 0
1d: B = *t*-butylphenyl, M = 2H, *n* = +1
1e: B = *n*-propyl, M = 2H, *n* = +1
1f: B = *t*-butylphenyl, M = Cu(II), *n* = +1

Compounds **1a** and **1b** were synthesized[13] from the dithioether-substituted porphyrazines $[H_2(pz((S{-}BCB)_2;(B_2)_3))]$ (BCB = 4-(butyloxycarbonyl)benzyl) (**2a**,[14] B = (*tert*-butylphenyl); **2b**,[13] B = (*n*-propyl)), which in turn were prepared from mixed cyclization of the appropriate dinitrile precursors following methods developed in our laboratories.[4] The developments reported here critically depended on the fact that these B groups gave us freely soluble compounds, a common hurdle in porphyrin and phthalocyanine chemistry. The *n*-propyl system, in particular, is reported here for the first time and represents a significant expansion of our dithiolene ligand family. The BCB protecting groups were removed by reductive cleavage with $Na/NH_3(l)$, giving the intermediate porphyrazine dithiolate, followed by quenching of excess sodium with NH_4Cl. Reaction of the dithiolate with Cp_2MoCl_2 was followed by chromatographic purification of **1a** or **1b** over silica gel. Yields were improved by addition of Cs_2CO_3 to ensure that the sulfur atoms of the dithiolate were fully deprotonated. The copper compound **1c**[13] was prepared by reaction of **1a** with $Cu(OAc)_2$ followed by chromatographic purification.

Compound **1a** was crystallized, and X-ray diffraction analysis[15] yielded the structure shown in Figure 1. The structure of **1a** contains two crystallographically independent molecules (A and B) in the asymmetric unit, each with similar gross conformations. The Mo−S [2.472(3)−2.475(3) Å] and Mo−Cp(centroid) [1.96−2.01 Å] distances are consistent with other molybdocene−dithiolene complexes, and the C−S bond lengths [1.71(1)−1.74(1) Å] indicate single bonds between these atoms.[9,16] An interesting difference between the two independent molecules is that in one (B) the Mo atom lies only 0.15 Å out of the plane of the eight porphyrazine N atoms, whereas in the other (A) the Mo atom lies 1.17 Å out of the corresponding N_8 plane. In both cases, however, the five-membered chelate ring is essentially planar.

Electrochemical and EPR measurements show that the properties of the hybrid molybdocene−pz system are far from a simple summation of those of the component fragments. The precursor

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(15) $C_{86}H_{90}MoN_8S_2{\cdot}2.5MeOH$, M = 1475.8, triclinic, space group $P\bar{1}$ (No. 2), a = 17.732(2) Å, b = 23.126(3) Å, c = 23.633(3) Å, α = 107.61(1)°, β = 91.41(1)°, γ = 110.09(1)°, V = 8586(2) Å^3, Z = 4 (there are two crystallographically independent molecules in the asymmetric unit), ρ_{calcd} = 1.142 g cm^{-3}, μ(Cu Kα) = 20.8 cm^{-1}, $F(000)$ = 3124, T = 203 K, R_1 = 0.105, wR_2 = 0.285 (SHELXTL PC, 5.03).

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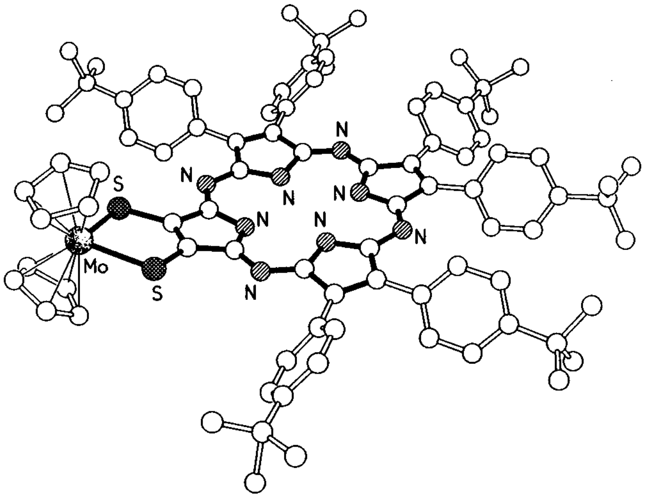

Figure 1. Perspective view of one of the two crystallographically independent molecules present in the structure of **1a**.

pzs **2a,b** show two reversible ring reductions (**2a**, −1.04, −1.38 V; **2b**, −1.24, −1.60 V vs Fc^+/Fc)[17] and one irreversible ring oxidation (~0.7−0.8 V). In contrast, the cyclic voltammograms of **1a,b**[18] show *five* reversible waves: two reductions and three oxidations. The two-ring reductions seen for **2a**,**b** are shifted negative by as much as 250 mV (**1a**, −1.29, −1.54 V; **1b**, −1.31, −1.77 V), consistent with the Cp_2Mo group acting as an electron-donating unit which changes the redox properties of the entire porphyrazine π-system. The first oxidation for **1a**, at −0.132 V, is typical of the Mo^V/Mo^{IV} couple,[9,16] but a reversible Mo^{VI}/Mo^V couple, seen as the second oxidation at 0.522 V, is a rarity for this coordination environment.[9] Finally, the pz^+/pz^0 couple is shifted positive by ~300 mV to 1.06 V by addition of the metallocene unit yet has been made reversible. Thus, the molybdocene group can act *both* as an electron-accepting and electron-donating partner toward the porphyrazine. The redox properties of the molybdocene−pz system are unchanged by insertion of copper(II) into the central cavity to give **1c**.

Consistent with the electrochemical data, **1a**−**c** are oxidized by $FcPF_6$ (Fc = ferrocenium) to give the cationic Mo(V) species, $\{[Cp_2Mo^V][M(pz((S_2^-);(B_2)_3))]^+\}$ (Chart 1, **1d**−**f**). This oxidation is fully chemically reversible as shown by regeneration of the Mo(IV) species upon reduction with cobaltocene. The fluid-solution (298 K) X-band EPR spectra of the 2H compounds **1d** (Figure 2) and **1e** (data not shown) exhibit a singlet centered at $g = 2.012$ due to those complexes with spinless ^{96}Mo ($I = 0$; 74.5%), and two pairs of smaller, outer peaks from the sextet produced by hyperfine coupling to $^{95,97}Mo$ ($I = {}^5/_2$; 25.5% total) nuclei. Although one might have expected the dithiolato−pz ligand to behave much like a benzenedithiolato ligand, the isotropic hyperfine coupling constant for $^{95,97}Mo$ is $a_{iso} = 22$ MHz for **1d** and **1e**, more than 2-fold lower than $a_{iso} = 55$ MHz for $[Cp_2Mo(tdt)]^+$ (tdt = 3,4-toluenedithiolato),[19] indicating that the dithiolato−porphyrazine supports much more extensive delocalization from the molybdocene moiety. The pz optical spectra of the Mo(V) complexes differ appreciably from those of the parents (data not shown), further indicating that the pz macrocycle is strongly coupled to the peripheral moiety.

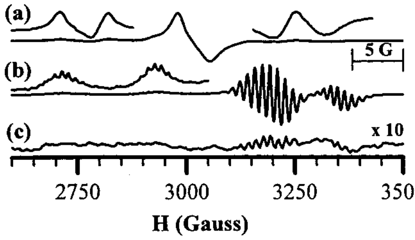

Figure 2. X-band EPR spectra for (a) **1d** at 298 K in CH_2Cl_2, (b) **1c** at 77 K in CH_2Cl_2/*i*-PrOH, and (c) **1f** at 77 K in CH_2Cl_2/*i*-PrOH, generated by oxidation of **1c**.

The Cu^{II}/Mo^{IV} compound, **1c**, gives both fluid- and frozen-solution (Figure 2) EPR spectra typical of Cu(II) incorporated into the pz ring. The electrochemical data shows that one-electron oxidation of **1c** occurs at Mo, and thus **1f** contains two paramagnetic centers, Cu(II) ($S = {}^1/_2$) and Mo(V) ($S = {}^1/_2$). However, both in methylene chloride and methylene chloride/2-propanol (1/3 v:v) solution **1f** shows *no* detectable EPR signal in fluid solution at 298 K *or* in frozen glass at 77 K (Figure 2). The loss of the room-temperature signal shows that the two spins of the oxidized species interact. The absence of a signal at 77 K implies that the two spins are antiferromagnetically coupled, with a diamagnetic $S = 0$ ground state and negligible thermal population of the corresponding triplet excited state. This result requires that the exchange coupling between the Cu(II) ($S = {}^1/_2$) and Mo(V) ($S = {}^1/_2$) centers be extremely strong ($J \sim 100$ cm^{-1}; $H = 2JS_1{\cdot}S_2$).[20]

The dithiolato−porphyrazines constitute a novel class of ligands that support significant interactions between the pz core and a chelated exocyclic metal center, with strong magnetic exchange between central and peripheral metal ions. The preparation and characterization of spin-coupled systems with different central-metal ions (e.g. Mn^{3+}, $S = 2$),[21] multiple ($n = 2−4$) peripheral redox centers, and polymacrocyclic arrays is in progress.

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Supporting Information Available: X-ray structural details for compound **1a** and characterization data for compounds **1a**−**c** and **2b** (22 pages). Ordering information is given on any current masthead page.

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(17) Cyclic voltammograms (V vs ferrocenium/ferrocene) were measured in CH_2Cl_2, 0.1 M Bu_4NPF_6 supporting electrolyte, Pt disc working electrode, Ag/AgCl reference electrode, and Ag wire auxiliary electrode. Scan rate 110 mV/s.

(18) Conditions are the same as in ref 17. The couples for **1a** are given in the text, and for **1b** are ($E_{1/2}$, V vs Fc^+/Fc (ΔE, mV)) pz^+/pz^0, 1.06 (194); Mo^{VI}/Mo^V, 0.460 (108); Mo^V/Mo^{IV}, −0.158 (80); pz^0/pz^-, −1.31 (76); pz^-/pz^{2-}, −1.77 (102).

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(20) A conservative estimate of J can be obtained from the partition function for a singlet/triplet system, if we assume that an excited-state signal would be detectable if as few as 10% of the ions were thermally excited to the triplet state.

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