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Unusual Molecular Orbital Ordering in Molybdenum−Ruthenium Heterometallic Porphyrin Dimers: Structural and Magnetic Evidence

James P. Collman,* Steven T. Harford, Pascale Maldivi,[†] and Jean-Claude Marchon*,[†]

Department of Chemistry, Stanford University
Stanford, California 94305
Département de Recherche Fondamentale
sur la Matière Condensée/SCIB
CEA-Grenoble, 38054 Grenoble, France

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Our previous communication[1] on the preparation of metalloporphyrin dimers with metal−metal bonds between MoRu and MoOs was the first report of multiple metal−metal bond formation between two transition metal atoms from different triads. These unprecedented dimers exhibit a metal−metal bond composed of 10 electrons, and thus are isoelectronic with the Re_2(porphyrin)$_2$, Ru_2(porphyrin)$_2^{2+}$, and Os_2(porphyrin)$_2^{2+}$ congeners. Interestingly, whereas all three homodimers are diamagnetic,[2] the MoRu and MoOs heterodimers exhibit large, temperature-dependent, paraagnetic shifts in their ^{1}H NMR spectra. Classical molecular orbital schemes[3] imply that even-electron metal−metal bonded systems may exhibit a nonzero spin state when the highest occupied molecular orbitals are degenerate, for example when they have π symmetry.[1] Herein we report the first structural and magnetic studies of a polar, unsupported Mo−Ru bond.

Combined with magnetic susceptibility data (vide infra), the crystal structure of [(OEP)MoRu(TPP)]PF_6, $\mathbf{1}^+PF_6^-$ (OEP = octaethylporphyrin, TPP = tetraphenylporphyrin),[4] provides a wealth of information about the molecular orbital diagram for these hithertofore unstudied *inter*-triad heterometallic multiple bonds. The asymmetric unit contains two distinct metal−metal bonded conformers (Figure 1): one has eclipsed porphyrin macrocycles ($\mathbf{1a}^+$, twist angle = 4.4°, see Figure 2a), whereas the other exhibits two porphyrin ligands staggered at almost exactly 45° ($\mathbf{1b}^+$, see Figure 2b). This unexpected result provides a rare example of deformational isomerism,[5] and represents the first report of a simultaneous structural characterization of two unique metal−metal bonds in a single asymmetric unit.

We suggest that the two conformations found in the crystal structure of $\mathbf{1}^+$ reflect an electronic preference for the eclipsed conformation and a steric preference for the staggered. According to the known angular dependence of metal−metal d_{xy} overlap to form a δ-bond, the interaction energy is maximum in an eclipsed conformation, and decreases to zero as the orbitals rotate to a staggered position. On the other hand, the steric strain between eclipsed porphyrin macrocycles may be relieved by rotation of the porphyrins to the staggered conformation. Indeed, δ-bond strengths in [W(TPP)]$_2$[6] and [Mo(TPP)]$_2$[7] have been estimated as 11.6 and 6.3 kcal/mol, respectively, and are both seen to exhibit a porphyrin−porphyrin twist angle of 18° in the solid state. For these symmetric tetraphenylporphyrin dimers, the minimum energy conformation is a compromise between the two extremes. Our OEP-TPP heterodimer was specifically designed to make intermediate twist angles unfavorably high in steric energy and thus force the dimer into one or the other energy minimum.

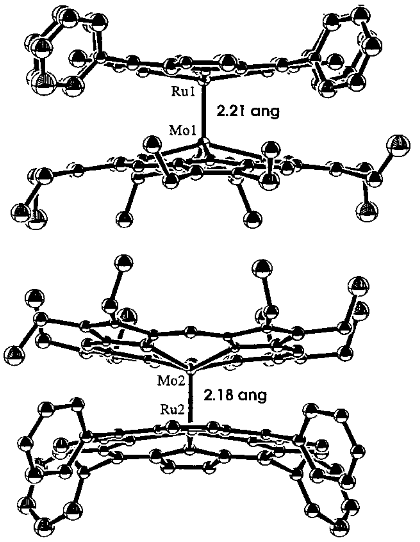

Figure 1. ORTEP plot of [(OEP)MoRu(TPP)]PF_6 illustrating the two separate dimers in the asymmetric unit: (a) Mo1−Ru1 (ligands eclipsed) 2.211(2) Å, (b) Mo2−Ru2 (staggered) 2.181(2) Å.

The solid-state structural isomerism implies that these limiting conformations are very similar in absolute energies,[8] and thus an estimate of the excess steric strain in the eclipsed conformation is also an estimate of the δ-bonding strength. Atomic coordinates from $\mathbf{1}^+$ were fed into Chem3D[9] and MM2 steric energy computations were then performed as a function of N−Mo−Ru−N dihedral angle. A steric energy minimum was found at an angle of 44.0°, in close agreement with the conformation of $\mathbf{1b}^+$. Rotation of [(OEP)MoRu(TPP)]PF_6 from the eclipsed position to the staggered was found to relieve 5.5 kcal/mol in steric strain. This estimate of the MoRu δ-bonding interaction in $\mathbf{1}^+$ is consistent with our previous unsuccessful attempt to measure the electronic barrier to rotation by dynamic NMR methods.[10]

Two descriptions of the δ-bonding interaction in the d^9 [(OEP)MoRu(TPP)]PF_6 heterodimer are possible. Since 9 *d*-electrons are involved in the metal−metal bond, the magnetic orbital may be either a $\delta^{*/\mathrm{nb}}$ (exponent indicates eclipsed/staggered conformation) or a π^* orbital. In the first case, the molecular orbital diagram is $\sigma^2\pi^4\delta^{(/\mathrm{nb})2}\delta^{(*/\mathrm{nb})1}$ and the calculated excess steric strain of 5.5 kcal/mol would be representative of only one-half of the full δ-bond energy. The alternative molecular orbital description of $\sigma^2\pi^4\delta^{(/\mathrm{nb})2}\pi^{*1}$ would imply that the molecule contains a full δ-bond when in the eclipsed conformation. Since the corresponding configurations of the one-electron reduced (d^{10}) dimer are much more readily distinguishable: $\sigma^2\pi^4\delta^{(/\mathrm{nb})2}\delta^{(*/\mathrm{nb})2}$ ($S = 0$) versus $\sigma^2\pi^4\delta^{(/\mathrm{nb})2}\pi^{*2}$ ($S = 1$), we decided to investigate the solid-

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* Address correspondence to this author at Stanford University.

[†] EA-Grenoble.

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(4) Crystals of [(OEP)MoRu(TPP)]$PF_6\cdot(CH_2Cl_2)(C_6H_6)$ were grown by layering and slow diffusion of benzene into a saturated solution of 2.0 mg/0.1 mL dichloromethane. Space group $P2(1)/n$, with $a = 17.5677(3)$ Å, $b = 42.8491(3)$ Å, $c = 21.0196(3)$ Å, $\beta = 90.613(1)°$, $Z = 8$, $V = 15821.8(3)$ Å^3; structure was solved by direct methods (SHELXS-86) and expanded with Fourier techniques. Anisotropic refinement of the Mo, Ru, P, F, and Cl atoms, isotropic refinement of C and N atoms, with H atoms included at ideal geometries, converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.080$, $R_w=[(\sum w(|F_o| - |F_c|)^2/\sum wF_o2)]^{1/2} = 0.093$ for 27211 unique reflections.

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(9) Version 3.5 (July 1996) from Cambridge Soft Corporation, Cambridge, MA 02139. The outputs for through-space nonbonded interactions were calculated with use of an MM2 force field derived from Allinger's MM2 program (QCPE 395) and Ponder's TINKER system (unpublished).

(10) We have attempted to measure the barrier to rotation for [(OEP)MoRu(TOEP)] by variable-temperature ^{1}H NMR, but were only able to establish an upper limit of 8.0 kcal/mol (see ref 1).

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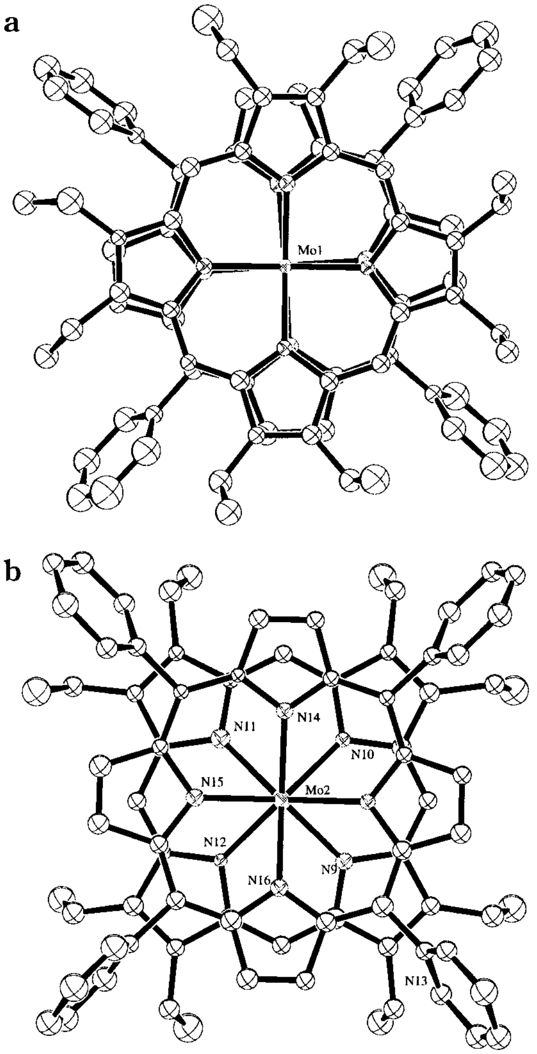

Figure 2. (a) ORTEP plot of **1a**$^+$ as viewed down the Mo1−Ru1 bond axis: porphyrin cores are rotated 4.4°, $N_4-N_4' = 3.106$ (4) Å, $Mo1-N_4 = 0.562$ (2) Å, $Ru1-N'_4 = 0.334$ (2) Å. (b) ORTEP plot of **1b**$^+$ as viewed down the Mo2−Ru2 bond axis: porphyrin cores are rotated 43.5°, $N_4-N_4' = 3.054$ (4) Å, $Mo2-N_4 = 0.578$ (2) Å, $Ru2-N'_4 = 0.295$ (2) Å.

state magnetic susceptibility of [(OEP)MoRu(OEP)], **2**, in the temperature range 2−300 K.

Plots of χ vs T and μ_{eff} vs T for **2** are shown in Figure 3. The magnetic moment of the dimer is 0.44 μ_B at 2 K, and as the temperature is raised to 300 K ($\mu_{\mathrm{eff}} = 2.31\ \mu_B$) it tends to the value expected for an $S = 1$ spin state ($\mu_{\mathrm{eff}} = 2.83\ \mu_B$). This behavior is similar to that we reported recently in Ru and Os doubly bonded homodimers.[11] Curve-fitting analysis of the data for **2** using an adequate model (eq 1 in ref 11) confirmed the spin triplet ground state ($^3A_2$, $S = 1$), and it provided reasonable values for the parameters that were varied[12] and a lower limit for the zero-field splitting parameter ($D \approx 600-800\ \mathrm{cm}^{-1}$). Successful curve fitting by the $^3A_2$-ZFS model (Figure 3) indicates that $MoRu(Por)_2$ dimers are accurately described by the $\sigma^2\pi^4\delta^{(/\mathrm{nb})2}\pi^{*2}$ molecular orbital diagram.[13] This relative ordering $\delta < \pi^* < \delta^*$ has not been previously observed in any metalloporphyrin dimer, and is likely a result of the polarity inherent to an *inter*-triad metal−metal bond. Analogous studies of multiple Mo−Ru bonds with ligand systems other than porphyrins may very well exhibit a similarly perturbed MO diagram.[14]

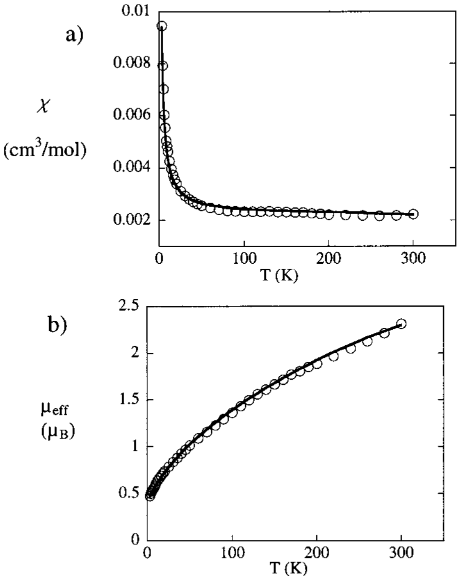

Figure 3. Data points and adjusted curves for the (a) magnetic susceptibility and (b) the magnetic moment of [(OEP)MoRu(OEP)]. The fits were obtained with a value of $D = 800\ \mathrm{cm}^{-1}$, see ref 12.

From the solid-state magnetic susceptibility of the neutral heterodimer **2**, we have assigned molecular orbital descriptions and bond orders to the two torsional isomers seen in the crystal structure of **1**. We propose that the eclipsed molecule in Figure 2 has a MO description $\sigma^2\pi^4\delta^2\pi^{*1}$ and a metal−metal bond order of 3.5 while the staggered dimer demonstrates a $\sigma^2\pi^4\delta^{\mathrm{nb}2}\pi^{*1}$ electronic configuration and a lower metal−metal bond order of 2.5. Interestingly, the metal−metal bond of order 2.5 has a length of 2.181(2) Å while the higher order bond is slightly longer, 2.211(2) Å. Furthermore, the Ru atom in the staggered molecule is displaced only 0.295 Å from the N_4 plane while the corresponding Ru atom in the eclipsed dimer is displaced by 0.334 Å. We attribute the longer Mo−Ru bond and larger $Ru-N_4$ separation to increased porphyrin−porphyrin steric strain in the eclipsed conformation. An increase in strain is consistent with the observed lengthening of the N_4-N_4' distance from 3.054 Å in the staggered dimer to 3.106 Å in the eclipsed dimer. Although the metal−metal bond is also forced to elongate, loss of σ and π overlap are apparently compensated for by the gain in δ overlap. Whether one or the other conformation exhibits a stronger metal−metal bond is an interesting question. It seems likely that the σ and π components of the shorter, 2.5 bond order are stronger than those same components of the slightly longer, 3.5 bond order; but how this difference relates to the δ-bond strength is still a matter of debate.

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Supporting Information Available: Electronic spectra and tables of experimental details and structural parameters (43 pages, print/PDF). See any current masthead page for ordering and Web access instructions.

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[11] Godwin, H. A.; Collman, J. P.; Marchon, J.-C.; Maldivi, P.; Yee, G. T.; Conklin, B. J. *Inorg Chem.* **1997**, *36*, 3499−3502 and references 1a−j cited therein.

[12] $g_{\parallel} = 2.0 \pm 0.2$; $g_{\perp} = 2.2 \pm 0.2$; fraction of impurity 0.019 ± 0.001; g of impurity 2.1 ± 0.1; $\mathrm{TIP} = (4 \pm 1) \times 10^{-5}$. The value given for D is only a lower limit, as good fits were obtained with any value of D in the range $600-1000\ \mathrm{cm}^{-1}$.

[13] Our main text does not discuss the possibility of a magnetically equivalent $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^2$ (^3E) ground state, arising as a result of accidental degeneracy of the δ^* and π^* orbitals. Such a situation has been observed for Os_2^{6+} dimers; see: (a) Miskowski, V. M.; Gray, H. B. *Top. Curr. Chem.* **1997**, *191*, 41−57. (b) Cotton, F. A.; Ren, T.; Eglin, J. L. *Inorg. Chem.* **1991**, *30*, 2552−2558. However, 15−200K magnetic susceptibility data for molecules with the $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^2$ ground electronic configuration are not accurately described by the $^3A_2$-ZFS model.

[14] An analogous destabilization of the δ^* relative to the π^* orbitals has also been seen for $Ru_2(O_2C_2R_3)_4^+$: Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2 ed.; Clarendon Press: Oxford, 1993; pp 400−408.