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Mixed Valency in Hydrogen Bonded 'Dimers of Dimers'

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Supporting Information

ABSTRACT: Dimolybdenum quadruply bonded compounds containing a pendant lactam functional group form self-complementary hydrogen bonded 'dimers of dimers' in the solid-state and CH_2Cl_2 solutions. Electrochemical studies in CH_2Cl_2 show two consecutive one-electron redox processes corresponding to oxidation of the Mo_2^{4+} cores. Spectroelectrochemical studies on the 'dimers of dimers' show no evidence of intervalence charge transfer bands in the mixed valence radical cations formed by one-electron oxidation, indicating that they are examples of proton-coupled mixed valency.

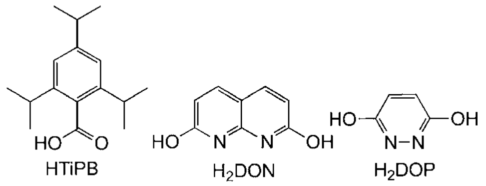
Intramolecular electron transfer (ET) processes are ubiquitous in nature as they play a vital role in a plethora of energy transduction processes.[1] Mixed valence compounds contain two redox active sites, which act as donor and acceptor, and are identical apart from their oxidation state, covalently linked by a symmetric conjugated ligand.[2] This class of compound has proven valuable as models to elucidate the mechanism, rate constant and activation barriers for ET processes relevant to biological systems.[3]

As well as covalently linked systems, it is also conceivable that hydrogen bond bridges could be used to link redox centers in mixed valence systems.[4] Given the experimental insight that these models would provide to electron transfer processes in DNA and other biological systems, it is surprising that only a handful of examples have been reported.[5] A recent investigation by Goeltz and Kubiak on an oxo-centered triruthenium cluster having a pyridine-4-carboxylic acid ligand found that it formed a hydrogen bonded dicarboxylic acid dimer upon one-electron reduction to the mixed valence form.[6] The mixed-valence state was stabilized by a combination of electronic coupling through overlap of the donor-bridge-acceptor orbitals, and hydrogen bonding. The authors used the term proton-coupled mixed valency to describe compounds such as this, in which electron transfer is dependent on the proton coordinate.

Previous studies by Chisholm and Cotton on dicarboxylate bridged 'dimers of dimers' of form $[(L)_3M_2\text{-}(\mu\text{-}O_2C\text{-}R\text{-}CO_2)\text{-}M_2(L)_3]$ (M = Mo or W; L = $^-O_2C^tBu$ or *N*,*N*-diphenylformamidinate; R = conjugated spacer) have demonstrated that metal−metal quadruply bonded compounds are particularly suited to the study of mixed valency as the M_2^{4+} core is redox-active and the HOMO (M_2-δ) interacts strongly with the bridge-π orbitals.[7] This study investigates mixed-valency through hydrogen bonds in dimolybdenum 'dimers of dimers' formed by self-complementary hydrogen bond interactions.

The compounds $[Mo_2(TiPB)_3(HDON)]$ (**1**; TiPB = 2,4,6-triisopropylbenzoate; H_2DON = 2,7-dihydroxy-naphthyridine, see Scheme 1) and $[Mo_2(TiPB)_3(HDOP)]$ (H_2DOP = 3,6-dihydroxypyridazine) (**2**) were prepared by reaction of $Mo_2(TiPB)_4$ with H_2DON or H_2DOP. One of the TiPB ligands in **1** could be substituted by reaction with 1 equiv of HO_2CCF_3 to generate $[Mo_2(TiPB)_2(O_2CCF_3)(HDON)]$ (**3**).

Scheme 1. Ligands Employed in This Study



Despite numerous attempts, we were unable to obtain crystals of **1**, but we were able to obtain crystals of **2** from slow diffusion of water into a DMSO solution. The structure of **2**$(DMSO)_2\cdot$2DMSO is shown in the Supporting Information (SI) and displays the expected paddlewheel arrangement of the ligands about a dimolybdenum core. The short C=O bond length of the unsubstituted amide (1.245(9) Å) indicates that the lactam tautomer is adopted in the solid state,[8] which hydrogen bonds to DMSO solvate molecules. Crystals of $[\mathbf{3}]_2\cdot$2THF were grown from a THF solution. The structure (Figure 1) reveals that a hydrogen bonded 'dimer of dimers' is formed between the lactam functional groups of the HDON ligand, which are coplanar with one another. The C42−O8 bond length of 1.221(1) Å is consistent with a keto tautomer for the HDON ligand.[8] The dimerization results in an axial contact between the metal and ligand (Mo1···O8′ = 2.476(5) Å), which is comparable in length to the relatively weak $Mo\cdots O_{THF}$ interactions (2.478(3) Å) found in $[Mo_2(O_2CCF_3)_4(THF)_2]$.[9] The other axial position (Mo2) is involved in oxygen bridge bonding with an adjacent molecule of $[\mathbf{3}]_2$, propagating the formation of an infinite chain of the dimers in the solid state.

The structure of **2** in solution was probed using diffusion-ordered ^1H NMR spectroscopy. A hydrodynamic volume 3271 Å^3 was obtained in a CD_2Cl_2 solution (0.8 mL). Addition of DMSO-d_6 (20 μL) to the sample resulted in the hydrodynamic volume approximately halving to 1686 Å^3. This demonstrates that the hydrogen bonded dimer $[\mathbf{2}]_2$ (Figure 2) persists in CH_2Cl_2 solutions, but addition of DMSO disrupts the hydrogen bonds to yield the monomer **2**.

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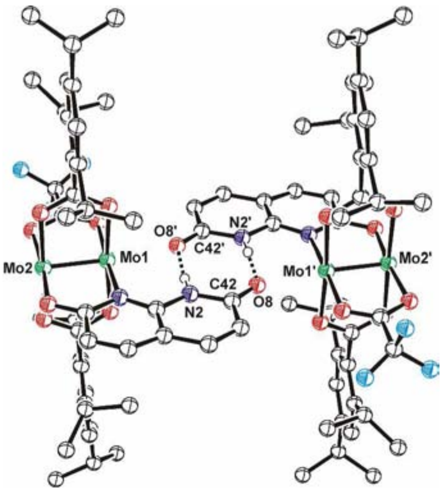

Figure 1. Crystal structure of $[Mo_2(TiPB)_2(O_2CCF_3)(HDON)]_2$, $[\mathbf{3}]_2$. Anisotropic displacement parameters are drawn at the 50% level and all hydrogen atoms, with the exception of those in the bridging hydrogen bonds, have been omitted for clarity. Symmetry equivalent atoms generated using the symmetry operation $-x$, $-y$, $-z$. Selected bond lengths (Å) and angles (°): Mo1−Mo2 = 2.1060(8), C42−O8 = 1.221(10), Mo1···O8′ = 2.476(5), Mo1···Mo1′ = 7.2285(8), Mo1−Mo2−O8 = 169.83(12).

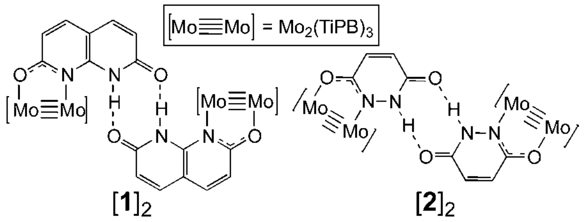

Figure 2. Hydrogen bonded structures of $[\mathbf{1}]_2$ and $[\mathbf{2}]_2$.

The cyclic voltammogram of $[\mathbf{1}]_2$ in a 0.1 M NBu_4PF_6/CH_2Cl_2 solution is displayed in Figure 3 and shows two reversible oxidation processes at −0.182 and −0.042 V (vs Fc/Fc^+) corresponding to successive oxidations of the Mo_2^{4+} cores. The thermodynamic stability of the mixed-valence compound with respect to its neutral and doubly oxidized form can be estimated from the comproportionation constant, K_c, determined from the separation between the first and second oxidation potential ($\Delta E_{1/2}$) using the equation K_c = exp($F\Delta E_{1/2}/RT$).[10] This results in K_c = 233 for $[\mathbf{1}]_2^+$. Included in Figure 3 is the voltammogram resulting from the addition of small amount of DMSO (100 μL) to the electrochemical cell (4 mL). The DMSO disrupts the hydrogen bonding resulting in the formation of the monomer **1**, which has a single reversible oxidation at −0.131 V with twice the current response of each single oxidation process in $[\mathbf{1}]_2$. The cyclic voltammogram of $[\mathbf{2}]_2$ in dichloromethane (Figure 4) also shows two reversible single electron oxidations at 0.203 and 0.362 V,resulting in a K_c value of 487. Again, addition of DMSO disrupts the hydrogen bonding motif resulting in the observation of a single reversible oxidation process at −0.117 V. The large cathodic shift for **2** by comparison to $[\mathbf{2}]_2$ is due to axial coordination of the DMSO solvent. Compound $[\mathbf{3}]_2$ displays two irreversible oxidations at 0.408 and 0.573 V. The irreversible nature of these redox processes precludes determination of K_c values, and subsequent discussion will focus on $[\mathbf{1}]_2$ and $[\mathbf{2}]_2$.

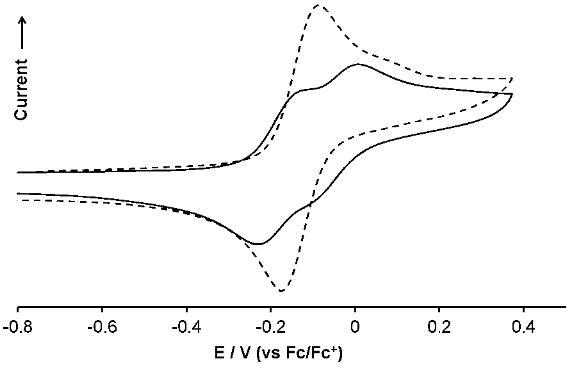

Figure 3. Cyclic voltammogram of a 5 mM solution of $[\mathbf{1}]_2$ in 0.1 M NBu_4PF_6/CH_2Cl_2 before (solid) and after (dotted) addition of DMSO (100 μL) to the cell.

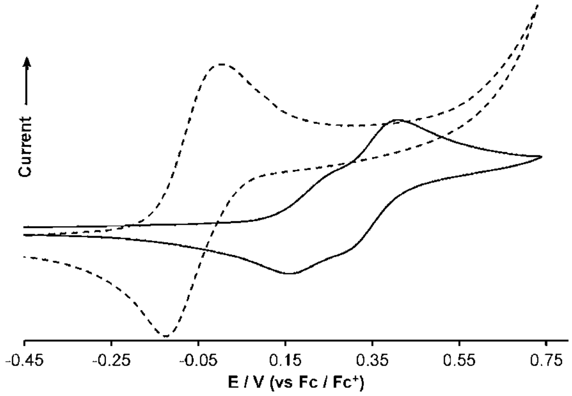

Figure 4. Cyclic voltammogram of a 5 mM solution of $[\mathbf{2}]_2$ in 0.1 M NBu_4PF_6/CH_2Cl_2 before (solid) and after (hashed) addition of DMSO (100 μL) to the cell.

It is important to remember that K_c is an equilibrium constant, and not a direct measure of electronic coupling, as has been highlighted in a number of studies.[11] Nonetheless, the K_c values for $[\mathbf{1}]_2^+$ and $[\mathbf{2}]_2^+$ are relatively modest by comparison to mononuclear M-B-M systems, where Class III (fully delocalized) behavior is often observed when $K_c > 10^6$. However, Class III behavior has been observed in covalently bonded M_2-B-M_2 systems with K_c values as low as 510,[12] due to the more diffuse nature of the charge in the M_2^{5+} radical cation, as discussed previously by Chisholm and co-workers.[13] Therefore, by comparison to other M_2-B-M_2 systems,[14] the K_c values for $[\mathbf{1}]_2$ and $[\mathbf{2}]_2$ suggest significant stabilization of the mixed-valence state formed upon one electron oxidation.

It is conceivable that through-space Coulombic interactions in the hydrogen-bonded dimers could account for the observed separation of oxidation potentials. However, this can be ruled out as the closest intranuclear $Mo_2 \cdots Mo_2$ separation for $[\mathbf{2}]_2^+$ (8.38 Å), which has the larger K_c, is greater than that of $[\mathbf{1}]_2^+$ (7.29 Å) as determined by DFT calculations (vide infra). Stabilization of the mixed-valence state must therefore occur via electronic coupling through the hydrogen bonding motif, which would involve the overlap of ligand π orbitals on either side of the hydrogen bond, or via proton-coupled mixed valency, in which coupling is related to the bridge proton coordinates, or via a combination of both these mechanisms. If an electronic coupling mechanism predominates, an intervalence charge transfer band (IVCT) should be observed in the NIR region of the absorption spectrum. Conversely, the absence of an IVCT transition is anticipated for proton-coupled mixed valency.[5b]

Changes in the electronic absorption spectra of $[\mathbf{1}]_2$ and $[\mathbf{2}]_2$ in CH_2Cl_2 upon oxidation were monitored spectroelectrochemically; the results for $[\mathbf{2}]_2$ are displayed in Figure 5. Both compounds show a red-shift of the MLCT transition in the visible region upon electrochemical oxidation. A weak transition appears at 800 nm as $[\mathbf{2}]_2$ is oxidized. This is not an IVCT transition as the intensity continues to increase as $[\mathbf{2}]_2^{2+}$ is generated, and is likely to correspond a HDOP(π)-to-Mo_2(δ) LMCT transition. For both $[\mathbf{1}]_2^+$ and $[\mathbf{2}]_2^+$, no low energy absorptions were observed which could correspond to IVCT transitions. On the basis of the splittings observed in the electrochemistry, a clear IVCT transition would be observed in the NIR region if electronic coupling is responsible for stabilization of the mixed-valence state. Therefore, the spectroelectrochemical data suggests that proton-coupled mixed valency is solely responsible for stabilization of $[\mathbf{1}]_2^+$ and $[\mathbf{2}]_2^+$.

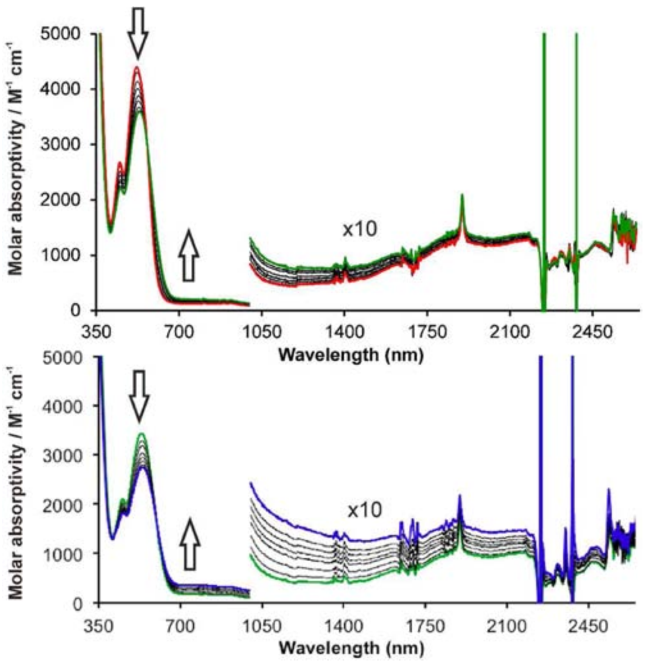

Figure 5. UV/vis/NIR spectroelectrochemistry on a 1.3 mM solution of $[\mathbf{2}]_2$ in 0.1 M NBu_4PF_6/CH_2Cl_2 at −20 °C. Spectroscopic changes from $[\mathbf{2}]_2$ (red) → $[\mathbf{2}]_2^+$ (green) are shown on top, and from $[\mathbf{2}]_2^+ \rightarrow [\mathbf{2}]_2^{2+}$ (blue) on the bottom. The region 1000−2650 has been magnified by a factor of 10; the spectral features at 2243 and 2380 nm correspond to sample cell glass absorptions.

While the rate constants for the transfer of a proton and electron can often be fairly large,[15] they will still be slower than the femtosecond time scale of electronic absorption. For proton-coupled mixed valency, we would therefore expect to see a single isosbestic point for the $[\mathbf{2}]_2 \rightarrow [\mathbf{2}]_2^+ \rightarrow [\mathbf{2}]_2^{2+}$ processes, as the spectrum for the MV compound $[\mathbf{2}]_2^+$ should be a superposition of the neutral and doubly oxidized species. Two isosbestic points are actually observed during the electrochemical oxidation of $[\mathbf{1}]_2$ and $[\mathbf{2}]_2$, a consequence of the pK_a change upon oxidation of one-half of the molecule due to a decrease in Mo_2(δ)-to-ligand(π^*) backbonding, which will slightly affect the hydrogen bond strength. A spectroelectrochemical study on **1** in a CH_2Cl_2/DMSO solution has also been performed; as expected a single isosbestic point and red shift of the MLCT transition was observed.

DFT calculations (M06/6-311G(d,p) and SDD) were performed using the Gaussian 09 suite of programs to provide insight into the electronic structure of $[\mathbf{1}]_2^+$ and $[\mathbf{2}]_2^+$. Geometry optimizations using a PCM solvation model (CH_2Cl_2) were performed on the model compounds $[(HCO_2)_3Mo_2(HDON)]_2^+$, $[\mathbf{1}']_2^+$, and $[(HCO_2)_3Mo_2(HDOP)]_2^+$, $[\mathbf{2}']_2^+$, in which the bulky TiPB ligands have been replaced by formate to reduce computational time. The lactam tautomers of $[\mathbf{1}']_2^+$ and $[\mathbf{2}']_2^+$ were calculated to be the most stable ground state tautomers. No delocalization of the charge between the dimetal units was calculated, as reflected in the calculated Mo−Mo bond distances of 2.116 and 2.177 Å for $[\mathbf{1}]_2^+$, and 2.116 and 2.170 Å for $[\mathbf{2}]_2^+$. The SOMO and SOMO-1 are localized on separate monomers (see SI) demonstrating that the charge is localized on one Mo_2 unit. This is consistent with proton-coupled mixed valency, as opposed to electronic coupling, being responsible for stabilization of the MV state.

In conclusion, the hydrogen bonded 'dimers of dimers' $[\mathbf{1}]_2$ and $[\mathbf{2}]_2$ are shown to form in CH_2Cl_2 solutions. Cyclic voltammetry experiments show the formation of the mixed-valence compounds $[\mathbf{1}]_2^+$ and $[\mathbf{2}]_2^+$. The lack of IVCT transitions in the electronic absorption spectra of these species suggests that they are examples of proton-coupled mixed valency. This is the first time this has been observed through hydrogen bonded lactam dimers, and these compounds are promising models for interstrand electron transfer processes in DNA. Clearly, further studies are required to confirm the mechanism by which the mixed valence state is stabilized, and the effect of solvent dependence, deuteration of the bridging ligand and modifying the pK_a of the bridge by adding electron withdrawing and donating groups is currently being investigated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details for synthesis, crystallographic studies and DFT calculations. Frontier MO plots for $[\mathbf{1}']_2^+$ and $[\mathbf{2}']_2^+$ and spectroelectrochemical data for $[\mathbf{1}]_2$ and **1**. 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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