Optical Behaviors and Electronic Properties of Mo₂–Mo₂ Mixed-Valence Complexes within or beyond the Class III Regime: Testing the Limits of the Two-State Model

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Abstract

Three symmetric Mo₂ dimers [Mo₂(DAniF)₃](μ-E₂CCE₂)[Mo₂(DAniF)₃] (DAniF = *N*, *N'*-di(*p*-anisyl)formamidinate) with oxalate (E = O) or the thiolated derivatives (E = O or S) as bridging ligands have been synthesized, and the optical properties of the mixed-valence (MV) derivatives obtained by one-electron oxidation studied within the framework of the vibronic two-state model. These Mo₂–Mo₂ systems are effective models for testing electron transfer theories, with the δ electrons of the Mo₂ fragments that are responsible for the redox and optical properties of the MV complex being well isolated from other metal d and ligand π -type orbitals. This in turn gives rise to unique, well-resolved metal to ligand (MLCT) and intervalence charge transfer (IVCT) absorption bands that permit accurate analyses based on band-shape. In the series [Mo₂(DAniF)₃](μ-E₂CCE₂)[Mo₂(DAniF)₃], the extent of electron delocalization between the Mo₂ cores increases with increasing number of sulfur atoms, E, in the bridge. Higher energy IVCT absorption bands are observed for the more strongly coupled complex, but in contrast to the predictions from the two-state model, the IVCT band becomes more symmetric in shape as the electronic coupling constant increases beyond the Class III border and $2H_{ab}/\lambda \gg 1$. Thus, the oxalate-bridged complex (E₂ = O₂) is situated on the Class II-III borderline, while the two thiolated

species are well placed deep into Class III, where novel optical behavior can be observed. The electronic coupling matrix elements (H_{DA}) estimated from the transition energy E_{IT} ($H_{DA} = E_{IT}/2$, 2000 – 2500 cm^{-1}) are in excellent agreement with data (H_{ab} , 2400 – 3000 cm^{-1}) calculated from the modified Mulliken-Hush expression for Class III systems. DFT calculations show that linear combinations of the δ orbitals of the Mo_2 centers generate the HOMO (out-of-phase, $\delta-\delta$) and HOMO-1 (in-phase, $\delta+\delta$), with the energy difference corresponding to the E_{IT} . This study illustrates a systematic transition from strongly coupled MV complex near the Class II-III border, to Class III and to systems in which the underlying ground state is better described in terms of simple delocalized electronic states rather evolving from strongly coupled diabatic states which define Class III.

Introduction

Low dimensional molecules D–B–A, in which an electron donor (D) and an electron acceptor (A) are linked through a central bridging moiety (B) have played crucial role in elucidation of electron transfer (ET) phenomena that is ubiquitous in chemical and biological processes.^{1,2,3,4,5} In 1950s to 60s, the semi-classical theory of ET reactions was constructed mainly through the works of Marcus and Hush and the development of the two-state model.^{6,7,8,9,10} Experimentally, the great advantage of employing mixed-valence (MV) metal complexes M–B–M^+ as the D–B–A model for ET studies is that under the semi-classical formalism, information on the D-A electronic coupling and ET reaction kinetics can be extracted from the shape, energy and intensity of the intervalence charge transfer (IVCT) absorption band.^{1,2,3,4,11} MV compounds are traditionally grouped into one of three major classes according to the scheme proposed by Robin and Day.¹² Class I compounds are those for which there is no electronic coupling between the donor (D or M) and acceptor (A or M^+) sites. For Class II compounds, there is a moderate degree of electronic coupling, and intramolecular ET may occur optically via a diabatic process, leading to the observation of the IVCT band in the electronic spectrum, and thermally by an adiabatic pathway, achieved by vibronic coupling between the donor and acceptor. As

the coupling increases further the thermal barrier between the donor and acceptor sites in the ground state decreases, and the system evolves to Class III when the thermal barrier is completely removed. These three cases are illustrated in Figure 1. Systems on the Class II-III borderline are of particular interest because as coupling increases the vibronic two-state model predicts a low-energy “cut-off” of the IVCT band, leading to an increasingly pronounced asymmetric-shape to the IVCT absorption band.^{11,13,14} For Class III compounds, the charge is fully delocalized and character of the “IVCT” band is changed from a true “charge transfer” transition and is perhaps better described as a “charge resonance” transition.^{11,15} However, whether or not the two-state model, which is based on the coupling of two diabatic states, each describing one of the fully localised electronic situations, is adequate for systems in the truly delocalised regime is a topic of debate.^{16,17,18,19} Resolving this question relies on accessing detailed information on closely related molecular systems which map the “vibronic to electronic” transformation.

Figure 1. Plots of the free-energies for the initial (left-hand parabola) and final (right-hand parabola) diabatic states (Class I, red lines)) and the lower and upper adiabatic states (Class II, blue lines and Class III, green lines) of a symmetric MV system *vs.* the reaction coordinate. E_{IT} is the IV transition energy for Class I and II and electronic transition energy between the associated molecular orbitals for Class III. H_{ab} is the electronic coupling matrix element between the donor and acceptor.

This significance of the evolution from Class II to Class III arises in part from the distinct characteristics of the low energy electronic transitions in the two MV regimes. For symmetric Class II systems, according to the semi-classical theory, the upper and lower adiabatic potential energy surfaces (PESs) at the transition state are separated by $2H_{ab}$ and the system is characterized by $2H_{ab}/\lambda < 1$,²⁰ where H_{ab} is the electronic coupling matrix element between diabatic states, denoted as ϕ_a and ϕ_b . For Class III, whose ground state PES has one energy minimum, at which the state energy difference ΔE is twice the coupling parameter H_{ab} (Figure 1). Following the traditional nomenclature, ΔE is still termed as intervalance transition energy (E_{IT}), although in the Class III system an averaged valence is found on each of the two redox sites. Thus, an important energetic relationship,

$$E_{IT} = 2H_{ab} \quad (1)$$

is obtained, which has been widely used to estimate the coupling element for strongly coupled systems (Class III) from the IVCT band. The two-state model also indicates that Class III systems should meet the condition $2H_{ab} > \lambda$, while $2H_{ab} = \lambda$ is a quantitative criterion that defines the Class II-III borderline.²⁰ The typical optical behaviors for systems in the three broad Robin-Day classes (Class I $H_{ab} = 0$; Class II $2H_{ab} < \lambda$; Class III $2H_{ab} > \lambda$) predicted from the two-state model and analyzed through application of various derived theories have been observed across a broad cross-section of MV compounds.^{13,21} However, the behavior as $2H_{ab} \gg \lambda$ for very strongly coupled systems has not yet been well explored.

In contrast to the semi-classical two-state model, in a quantum mechanical treatment, an ET reaction is described by mixing of initial and final wave functions of the system, ϕ_a (reactant) and ϕ_b (product). Considering single-electron donor (ϕ_D) and acceptor (ϕ_A) orbitals involved in the electron exchange process, Newton demonstrated that the Hamiltonian (H_{el}) for wave functions on many-electron basis equals that (h) in the effective one-electron system;¹⁵ therefore,

$$H_{ab} = \langle \phi_a | H_{el} | \phi_b \rangle = \langle \phi_D | h | \phi_A \rangle \quad (2)$$

Equation 2 provides a framework through which to describe the adiabatic ET in Class II and electronic transition in Class III as well as the transition from Class II to Class III. Experimental verification of Eq. 2 will provide full endorsements for the contemporary ET and MV theories. However, it is difficult to find appropriate model systems in which the intramolecular electron transfer involves pure one-particle donor and acceptor orbitals. Many of the commonly and intensely studied binuclear d^5-d^6 MV metal complexes, such as bridged diruthenium systems,^{1,2,3,4,11,22} are unfavorable because of uncertainty of the zero-order states ϕ_D and ϕ_A . Furthermore, according to Eq. 2, electronic coupling constant can alternatively be calculated for Class III systems from the energy gap between the electronic states, which can be approximated in the single-electron model as the difference in energy between the molecular orbitals involving the donor and acceptor fragments. However, this relationship holds only for well-defined Class III systems, and analysis requires that the (single) IVCT absorption band can be unambiguously assigned, and that the electronic nature of the transition is clearly established. At present, few systems can convincingly meet these requirements. For most of the reported Class III systems, including the Cruetz-Taube ion,^{23,24,25,26,27,28,29,30,31} and many organic MV systems,³² the low energy transition responsible for the IVCT-derived absorption band exhibits principal vibronic character with substantial charge distributed on the bridge. As a consequence of this bridge involvement, the system cannot be accurately represented by inherent approximations in the two-state model.

In seeking to identify compounds that might permit more thorough exploration of the change in character of the IVCT transition in strongly coupled systems from vibronic to electronic, attention is drawn to covalently bonded dimetal unit (M_2) in which the d orbital degeneracy is removed by the formation of M–M multiple bonds. For example, a quadruply bonded Mo_2 unit has an electronic configuration of $\sigma^2\pi^4\delta^2$; two valence electrons occupy the δ orbital, which is distinct from σ and π orbitals in

terms of both energy and symmetry.³³ Thus, in suitably constructed MV systems,^{34, 35 36 37} $\{[\text{Mo}_2]\text{-bridge-}[\text{Mo}_2]\}^+$, the electronic character and optical behaviors are explicitly and uniquely due to interactions between electrons in δ -orbitals across the bridge. Therefore, the δ orbital can be viewed as effective one-electron orbital for the donor (ϕ_D) and acceptor (ϕ_A). In addition, as shown in Figure 2, when the $[\text{Mo}_2]$ moiety is supported by the common paddlewheel arrangement of auxiliary ligands, the π^* orbital of the chelating groups of the bridging ligand can also be considered as part of the donor (ϕ_D) and acceptor (ϕ_A) orbitals due to the $d(\delta)$ - $p(\pi)$ conjugation, which affects the electron donating (or accepting) ability of the $[\text{Mo}_2]$ unit. For strongly coupled systems, direct interactions between ϕ_D and ϕ_A are expected to generate molecular orbitals associated with the states associated with vertical electron transitions.

Figure 2. Pseudo-“one-electron” orbitals for $[\text{Mo}_2]$ donor (ϕ_D) and acceptor (ϕ_A), and the orbital interactions between ϕ_D and ϕ_A along the charge transfer axis for the strongly delocalized $[\text{Mo}_2]\text{-}[\text{Mo}_2]$ systems, which gives rise to the electronic states relevant to the “IV” electronic transition.

In this work, the dimolybdenum dimers, $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-OSCCOS})$ (**[OS-OS]**), and $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-S}_2\text{CCS}_2)$ (**[SS-SS]**), where $\text{DAniF} = N, N'$ -di(p-anisyl)formamidinate, have been synthesized by assembling two

$[\text{Mo}_2(\text{DAniF})_3]^+$ building blocks with dithiooxalate (dto) and tetrathiooxalate (tto) bridging ligands, respectively and characterized by single-crystal X-ray diffraction. Together with the oxalate (oxa) analogue $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-O}_2\text{CCO}_2)$ (**[OO–OO]**),³⁸ the three-membered family (Figure 3) permits a detailed examination of the electronic interactions between the two $[\text{Mo}_2]$ units. Most importantly, for these *dimers of dimers*, the linking of two paddlewheel complex units through ligands such as oxalate to give bridges comprising no more than a single bond and thereby avoiding the issues of the bridge localization of charge that can perturb analysis within the two-state framework. One-electron oxidation of the three compounds yielded the corresponding mixed-valence radical cations **[OO–OO]⁺**, **[OS–OS]⁺** and **[SS–SS]⁺** which are shown by magnetic and spectroscopic analyses to be delocalized systems. The low energy (IVCT) bands in the Near-IR spectra correspond to the electronic transitions between the metal-based molecular orbitals, e.g., HOMO-1→SOMO, but the band shape becomes *more* symmetrical with increasing electronic coupling, in contrast with the predicated from the two-state model for Class III complexes. Experimental and theoretical results demonstrate the transformation from vibronic to electronic states accompanying the system transition from strongly coupled **[OO–OO]⁺** to very strongly coupled **[OS–OS]⁺** and **[SS–SS]⁺**.

Figure 3. The common molecular scaffold for the complex systems under investigation.

Results and Discussion

Molecular Structures. Single crystals of [OS–OS] and [SS–SS] were obtained by diffusion of ethanol to the corresponding CH₂Cl₂ solutions. The structures are characterized by X-ray diffraction, as shown in Figure 4 and Table S1. The crystal structure of the oxalate-bridged complex [OO–OO] was reported earlier.³⁸ These three Mo₂ dimers share a common molecular scaffold which may be viewed as two complex units [Mo₂(DAniF)₃(E₂C)] (E = O or S), or [Mo₂], linked through a C–C single bond. Small geometric differences between the members of the series arise from the O/S variation of the donor atoms on the bridging ligand. The Mo–Mo bonds in the dimeric motif are lengthened as a result of introducing S atoms to the bridging ligands (see Table S2), in a manner similar to that found for the phenylene-bridged series, [Mo₂](μ-1,4-C₆H₄)[Mo₂].³⁵ For the same reason, the shortest (6.953(2) Å) and longest (7.881(6) Å) [Mo₂]⋯[Mo₂] separations, as measured from the centroids of the dimetal units, are found for [OO–OO] and [SS–SS], respectively, while in [OS–OS] this distance falls in between these extremes (7.354(7) Å). For the oxalate (oxa) and dithiooxalate (dto) derivatives, [OO–OO] and [OS–OS], the bridging ligands are essentially coplanar with the two Mo–Mo vectors. For the tetrathiooxalate (tto) analogue, [SS–SS], however, there exists a dihedral angle (ca. 22°) between the two linked chelating rings. In the crystal structure of [OS–OS], the molecule resides in a special position of *P*₁; thus the O and S atoms are arranged in the *trans* positions. In the three molecular structures, the C(1)–C(2) bond that connect the two [Mo₂] units decreases in length as the chelating O atoms are replaced by S atoms, being 1.508(2) Å for [OO–OO], 1.476(8) Å for [OS–OS] and 1.454(7) Å for [SS–SS]. Notably, these C–C bond distances are appreciably shorter than those in the acid or anion of the bridging ligands, for example, 1.544(5) Å in oxalic acid,³⁹ 1.516(4) Å in K₂dto⁴⁰ and 1.516(6) Å in (Et₄N)₂tto.⁴¹ The C–C bond contraction is consistent with increasing electron delocalization along the charge transfer axis.

Figure 4. Crystal structures for [OS-OS] and [SS-SS]. Displacement ellipsoids are drawn at the 30% probability level. All the hydrogen atoms have been omitted for clarity.

Electrochemical Studies. Electrochemical measurements of the complexes were carried out in CH_2Cl_2 solutions with potentials reported vs the Ag/AgCl reference electrode. In our experimental system, the ferrocene/ferrocenium couple is found at 0.46 V. The [OS-OS] and [SS-SS] complexes present two well-separated redox couples in the cyclic voltammograms (CVs) (Figure 5, Table 1), corresponding to the sequential one-electron oxidation of each of the Mo_2^{4+} ions which gives a potential separation $\Delta E_{1/2}$. For [SS-SS], the redox couple at ~ 1.0 V is partially masked by the oxidation of the tto ligand which occurs at a similar potential. In prior work, a two-electron oxidation at 1.07 V was observed for the tetrathiotetraphthalate analogue, illustrating the redox activity of this family of tetrathiolated bridging ligands.⁴² Thus,

the data given in Table 1 was extracted following simulation and fitting of the CV parameters.

In earlier work, the oxalate-bridged complex **[OO–OO]** ($\Delta E_{1/2} = 212$ mV) and a similar oxalate-bridged complex, $[\text{Mo}_2(\text{tBuCO}_2)_3]_2(\mu\text{-O}_2\text{CCO}_2)$ ($\Delta E_{1/2} = 280$ mV), were determined to be examples of strongly coupled (Class III) $[\text{Mo}_2]\text{--}[\text{Mo}_2]$ compounds.^{34,43,44,45,46,47} The $\Delta E_{1/2}$ values increase with increasing S content of the bridging ligand, and values of $\Delta E_{1/2}$ for **[OS–OS]** and **[SS–SS]** were determined to be 480 mV and 572 mV, respectively. Indeed, of all the symmetrical Mo_2 dimers studied to date, **[SS–SS]** shows the largest $\Delta E_{1/2}$ value. Examination of the redox potentials in Table 1 indicates that the coordinating atoms of the bis(chelate) ligand play a role in both the first oxidation potential, with the lower electron-donating ability of sulfur compared with oxygen causing a relatively small anodic shift in the first electrode potential, and also causing a more significant shift in the second redox potential, likely a consequence of additional stabilisation of the MV state brought about by increased delocalization.

Figure 5. Cyclic voltammograms for **[OS–OS]** (top) and **[SS–SS]** (bottom). The high energy redox couple for **[SS–SS]** is simulated as shown by the profile (dashed line) because it is masked by the followed redox event occurring on the bridging ligand. Electrochemical measurements were carried out in CH_2Cl_2 .

Table 1. Electrochemical measurements and the derived thermodynamic parameters for the comproportionation equilibria.

complex	$E_{1/2}(1)$ (mV)	$E_{1/2}(2)$ (mV)	$\Delta E_{1/2}$ (mV)	K_C	ΔG°_C (cm ⁻¹)
[OO–OO] ^a	260	472	212	3.8×10^3	–1709
[OS–OS]	354	788	434	2.2×10^7	–3500
[SS–SS]	393	965	572	4.7×10^9	–4611

^a Data cited from ref. 38

For these Mo₂ dimers, the comproportionation equilibria in solution can be expressed as follows,

$$K_C = \exp[(\Delta E_{1/2})/25.69] \text{ (at 298 K)}$$

$$\Delta G^\circ_C = -RT \ln K_C$$

The comproportionation constant (K_C) and associated free energy change of the comproportionation reaction (ΔG°_C) may be derived from the electrochemical data (Table 3).⁴⁸ The large free energy change ($-\Delta G^\circ_C > 10^3 \text{ cm}^{-1}$) for the series shifts the equilibrium toward the singly oxidized form $\{[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-E}_2\text{CCE}_2)\}^+$, due to the high thermodynamic stability of the MV species in solution. In general, the free energy change ΔG°_C can be divided into non-resonance ($\Delta G^\circ_{\text{nr}}$) and resonance ($\Delta G^\circ_{\text{r}}$) terms, but only the latter is indicative of the extent of electron delocalization. $\Delta G^\circ_{\text{nr}}$ includes statistical factor of 4, intramolecular electrostatic interactions, metal to ligand back bonding effects, etc.⁴⁹ Across the series [OO–OO], [OS–OS] and [SS–SS], these non-resonant terms are likely similar, and hence differences in the overall free energy change ΔG°_C in the series can be attributed to resonance factors and the

increasing $\Delta E_{1/2}$ reflects an increasing electronic interaction between the $[\text{Mo}_2]$ moieties. On this basis, the electronic coupling is expected to increase $[\text{OO-OO}]^+ < [\text{OS-OS}]^+ < [\text{SS-SS}]^+$.

Spectroscopic and Magnetic Properties. Compounds in the series are different in color, being red for $[\text{OO-OO}]$, blue for $[\text{OS-OS}]$ and green for $[\text{SS-SS}]$, and exhibit relatively simple electronic spectra. The electronic spectrum of the complex $[\text{OO-OO}]$ is characterized by a metal (δ) to ligand (π^*) charge transfer (MLCT) absorption band at 460 nm with a rather low extinction coefficient ϵ_{ML} 13027 $\text{M}^{-1}\text{cm}^{-1}$ (Figure S5). In contrast, much more intense, lower energy MLCT bands are observed for the two thiolate complexes $[\text{OS-OS}]$ (733 nm, ϵ_{ML} 24200 $\text{M}^{-1}\text{cm}^{-1}$) and $[\text{SS-SS}]$ (885 nm, ϵ_{ML} 38025 $\text{M}^{-1}\text{cm}^{-1}$) (Figure S6 and Figure S7). For $[\text{OS-OS}]$, a weak $\delta \rightarrow \delta^*$ transition is also apparent at 460 nm, but for $[\text{OO-OO}]$ and $[\text{SS-SS}]$ this band is masked by high energy absorptions.

The mixed-valence complexes $[\text{OO-OO}]^+$, $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$ were generated by chemical oxidation of the corresponding neutral compounds using one equivalent of ferrocenium hexafluorophosphate in CH_2Cl_2 solution. Subsequent magnetic and spectroscopic measurements were carried out *in situ* at 110 K. In the X-band electron paramagnetic resonance (EPR) spectra (Figure S4), each complex cation shows an isotropic peak, with g values, 1.945, 1.944 and 1.942 for $[\text{OO-OO}]^+$, $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$, respectively. Chisholm reported the EPR spectrum for the carboxylate-supported analogue $\{[\text{Mo}_2(\text{tBuCO}_2)_3]_2(\mu\text{-O}_2\text{CCO}_2)\}^+$, which shows a g value of 1.937 and well-resolved hyperfine structures ($A_{\text{iso}} = 14.8$ G).⁴⁴ The g values from these *dimer-of-dimer* complexes are less than the value of 2.0023 expected for an organic radical, and indicates that the odd electron resides essentially on a metal-based δ orbital.

The UV-Vis spectra for the MV complexes are similar to those of the corresponding neutral precursors. For $[\text{OO-OO}]^+$ and $[\text{SS-SS}]^+$, the MLCT absorption band energies remain essentially the same as those for the neutral complexes (Figure S5 and Figure S7), whilst the MLCT band for $[\text{OS-OS}]^+$ is red shifted by only about 20

nm (Figure 6 and Figure S5). It is interesting that here only $[\text{OO-OO}]^+$ shows two bridging ligand (π) to metal (δ) charge transfer (LMCT) absorption bands at 610 and 684 nm (Figure 6 and Figure S5). The appearance of a LMCT bands in the spectrum is indicative of hole hopping from the acceptor to the bridging ligand in superexchange formalism,^{15,50} and is known to occur in $\{[\text{Mo}_2]\text{-bridge-}[\text{Mo}_2]\}^+$ complexes of Class II and Class II-III systems.^{51,52} The absence of this band for $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$ implies that these two complexes have electronic structures significantly different from that of the $[\text{OO-OO}]^+$ analogue.

Figure 6. UV-Vis-Near-IR spectra of radical cations $[\text{OO-OO}]^+$ (black line), $[\text{OS-OS}]^+$ (blue line) and $[\text{SS-SS}]^+$ (red line) in CH_2Cl_2 . The IVCT bands in the low energy region are shown in the inset for clarity.

The most striking difference between the spectra of the MV complexes and the neutral precursors is the exhibition of a new absorption band in the near-infrared spectrum in each case (Figure 6). In terms of the classical two-state model this band would be assigned as the IVCT transition. In contrast to the MLCT bands, the IVCT band energies (E_{IT}) for the three species vary over a relatively narrow range, increasing from 4077 cm^{-1} ($[\text{OO-OO}]^+$) to 4149 cm^{-1} ($[\text{OS-OS}]^+$) to 4926 cm^{-1} ($[\text{SS-SS}]^+$). The E_{IT} value for $[\text{OO-OO}]^+$ is similar to that for $\{[\text{Mo}_2(\text{}^t\text{BuCO}_2)_3]_2(\mu\text{-O}_2\text{CCO}_2)\}^+$ (4085 cm^{-1}).⁴⁷ Given the similarity in molecular

structures, the differences in E_{IT} reflect directly the differences in the strength of electronic coupling (Eq. 1). It was observed that in the more localized Class II $\{[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-E}_2\text{C-1,4-C}_6\text{H}_4\text{-CE}_2)\}^+$ series, the IVCT band energy decreases with increasing electronic coupling such that the most strongly coupled example, $\{[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-S}_2\text{C-1,4-C}_6\text{H}_4\text{-CS}_2)\}^+$, which lies at the Class II-III borderline, has the lowest IVCT band energy ($E_{IT} = 2640 \text{ cm}^{-1}$). In contrast, here the IVCT band energy increases as the electronic coupling increases.

For delocalized systems, $\Delta G^\circ_{\text{nr}}$ is small or negligible ($\Delta G^\circ_{\text{C}} \approx \Delta G^\circ_{\text{r}}$). Brunschwig and Sutin suggested the use of $\Delta E_{1/2}:E_{IT}$ ratio to differentiate strongly coupled systems from very strongly coupled systems;⁴⁹ that is, $\Delta E_{1/2}:E_{IT} \approx 0.5$ ($-\Delta G^\circ_{\text{r}} \approx E_{IT}/2$) for complexes near to the Class II-III borderline and $\Delta E_{1/2}:E_{IT} \approx 1.0$ ($-\Delta G^\circ_{\text{r}} \rightarrow E_{IT}$) for more well-defined Class III compounds. The $\Delta E_{1/2}:E_{IT}$ criteria are practically useful because the electrochemical and spectroscopic parameters are both readily obtained experimentally. In prior work, we evaluated the strength of coupling for $[\text{N}(\text{H})\text{O}-\text{N}(\text{H})\text{O}]^+$ ($\Delta E_{1/2}:E_{IT} \approx 0.56$) and $[\text{N}(\text{H})\text{S}-\text{N}(\text{H})\text{S}]^+$ ($\Delta E_{1/2}:E_{IT} \approx 0.86$) finding both to lie within the Class III regime.⁵³ In the present study, the $\Delta E_{1/2}:E_{IT}$ ratio for $[\text{OO}-\text{OO}]^+$, $[\text{OS}-\text{OS}]^+$ and $[\text{SS}-\text{SS}]^+$ are determined to be 0.42, 0.84 and 0.94, respectively. Evidently, the oxa-bridged complex $[\text{OO}-\text{OO}]^+$ is on the Class II-III borderline, while the dto and tto derivatives $[\text{OS}-\text{OS}]^+$ and $[\text{SS}-\text{SS}]^+$ should be assigned more definitively to Class III. As will be discussed below, with the largest $\Delta E_{1/2}:E_{IT}$ value, and assuming Koopmans' Theorem holds,^{15,19,54} $[\text{SS}-\text{SS}]^+$ has reached the extreme of electronic coupling, a case of which is rarely seen.

Electronic Coupling Matrix Elements and Reorganization Energies. By treating the spectroscopic parameters of the IVCT band for each of the three complexes by Eq. 1, the coupling parameters, denoted as H_{DA} to distinguish from H_{ab} in the Hush formalism, are determined to be 2039 cm^{-1} ($[\text{OO}-\text{OO}]^+$), 2075 cm^{-1} ($[\text{OS}-\text{OS}]^+$) and 2463 cm^{-1} ($[\text{SS}-\text{SS}]^+$). The H_{DA} values are 5–7 fold larger than those for the Class II $\{[\text{Mo}_2](\mu\text{-E}_2\text{C-1,4-C}_6\text{H}_4\text{-CE}_2)[\text{Mo}_2]\}^+$ systems.^{35,36,37} Alternatively, the Mulliken-Hush expression (Eq. 4), which holds for the calculation of H_{ab} for Class II

systems,⁵⁵ may be modified according to the work of Brunschwig, Creutz and Sutin to extend its application to Class III systems (Eq 5),²⁰

$$H_{ab} = \frac{0.0206 \times \sqrt{\epsilon_{\max} E_{IT} \Delta \nu_{1/2}}}{r_{ab}} \quad (4)$$

$$H_{ab} = \frac{0.0206 \times \left\{ \nu_{\max} \epsilon_{\max} \sqrt{4 \ln(2) \lambda RT} [1 - \text{erf}(z)] \right\}^{1/2}}{r_{ab}} \quad (5)$$

where $\text{erf}(z)$ is the “error function”, $z = (2H_{ab} - \lambda) / \sqrt{4\lambda RT}$, introduced to correct the expression for strongly coupled systems beyond the Class II limit. As is well known, using the geometrical separation between the donor and acceptor as the electron transfer distance (r_{ab}) results in a significant under-estimation of H_{ab} calculated from Eq. 4 because r_{ab} is likely very much shorter than this geometric distance due to convolution of the donor-bridge a bridge-acceptor electronic characters.^{56,57} Accurate determination of r_{ab} can be achieved from electroabsorption spectroscopic methods (Stark effect),⁵⁸ which measures the dipole moment change for electron transfer. In the absence of such data, in the current *dimer-of-dimer* systems, for the purposes of evaluation of H_{ab} from Eq. 5, the C–C bond lengths likely serve as reasonable approximations of the ET distances (r_{ab}) in considering the d(δ)–p(π) conjugation within a [Mo₂] unit; calculations from Eq. 5 yield the H_{ab} values, 2376 cm^{–1} for [OO–OO]⁺, 2726 cm^{–1} for [OS–OS]⁺ and 2950 cm^{–1} for [SS–SS]⁺. Thus, the coupling parameters derived from the two different methods (Eq. 1 and Eq. 5) are very close (Table 2). By satisfying $2H_{ab} = E_{IT}$ and $E_{IT} \Delta E_{1/2} \approx 0.5$, [OO–OO]⁺ is located at the Class II-III limit, while [OS–OS]⁺ and [SS–SS]⁺ may be considered to be very strongly coupled Class III systems. The excellent consistency between values of H_{DA} (from Eq. 1) and H_{ab} (from Eq. 5) also validates the consistency of the related theories.

A general condition for assignment of a compound to Class III is $2H_{ab}/\lambda \geq 1$.²⁰ The magnitude of λ is determined by two terms: λ_v for internal molecular vibrational frequency adjustment; and λ_s for outer-sphere type solvent molecule rearrangements. Both terms must be considered in a general description of an ET reaction. While λ_s

can be calculated according to Marcus' dielectric continuum model,^{6,7,59,60} there is no experimental method to determine λ_v . However, for strongly coupled D–B–A systems, the λ_v term is generally small.⁶¹ In addition, the differences in λ_v between these complexes are minimized by their structural similarities. Therefore, for the series of Mo₂ dimers under examination here, the influence of λ_v on the differences in electronic coupling is negligible and it is assumed that $\lambda \approx \lambda_s$. According to Brunschwig and Sutin,⁴⁹ for Class III, the free energy change from the resonance effects (ΔG°_r) is related to the IVCT transition energy E_{IT} by

$$-\Delta G_r = 2(H_{ab} - \lambda/4) = E_{IT} - \lambda/2 \quad (6)$$

Considering $-\Delta G_r \approx \Delta E_{1/2}$ for strong coupling system, the total reorganization energy can be estimated by

$$\lambda = 2(E_{IT} - \Delta E_{1/2}) \quad (7)$$

Thus, the reorganization energies, 4734 cm⁻¹ ([**OO–OO**]⁺), 1296 cm⁻¹ ([**OS–OS**]⁺) and 624 cm⁻¹ ([**SS–SS**]⁺), are calculated from Eq. 7. For [**OO–OO**]⁺, the calculated λ is close to, but larger than E_{IT} (4080 cm⁻¹) (Table 2), as expected for compounds at the Class II-III borderline ($2H_{ab}/\lambda = 1$) and at the Class III limit. The difference between the two values is understandable as the non-resonance contribution to ΔG°_c that is not taken into account in the calculation are expected to be most significant for less strongly coupled complexes. These results verify our assignment of [**OO–OO**]⁺ at the Class II-III borderline or Class III limit, and support the approach taken in arriving at the calculated λ value. In contrast, the very small λ for [**SS–SS**]⁺ is in accord with the description of this system in terms of almost perfect electronic delocalization.

The Near-IR spectra were also recorded in more polar solvents, THF, DMF and MeCN, in order to examine the solvent dependence of the IVCT absorption bands (Figure 7, Figures S8 – S10). The IVCT band in complex [**OO–OO**]⁺ exhibits a solvent dependence quite distinct from that of [**OS–OS**]⁺ and [**SS–SS**]⁺, consistent with the distinctions in electronic structure between [**OO–OO**]⁺ and the other two complexes in this series inferred from the other data discussed above. In the case of [**OO–OO**]⁺, the IVCT transition energies E_{IT} , 6540 cm⁻¹ (THF), 13684 cm⁻¹ (MeCN)

and 15526 cm^{-1} (DMF), increase with increasing the solvent polarity. In the more

Table 2. Near-IR spectral data and calculated H_{ab} parameters and reorganization energies (λ) for the MV complexes.

complex	$E_{IT}(\text{cm}^{-1})$	$\varepsilon_{IT}(\text{M}^{-1}\text{cm}^{-1})$	$\lambda(\text{cm}^{-1})^a$	H_{DA}^b	H_{ab}^c	$\Delta E_{1/2}/E_{IT}$	$2H_{ab}/\lambda$
[OO–OO] ⁺	4077	7680	4734	2039	2376	0.42	1
[OS–OS] ⁺	4149	20100	1296	2075	2726	0.84	4.2
[SS–SS] ⁺	4926	9900	624	2463	2950	0.94	9.5

^a Data determined by $\lambda = 2(E_{IT} - \Delta E_{1/2})$ (Eq 7). ^b Data determined by $H_{DA} = E_{IT}/2$ (Eq 1). ^c Data determined by modified Mulliken-Hush expression (Eq 5).

polar solvents, the IVCT band for this complex becomes very weak, broad and symmetrical in shape, thereby showing typical Class II behavior (Figure 7). Solvent-controlled system transitions from delocalized to localized electronic structures have also been reported in organic dinitroaromatic radical anions.^{61,62} The solvent dependence of $[\text{OO-OO}]^+$ is in contrast to the solvent-independent IVCT band observed for Cruetz-Taube ion, $[(\text{NH}_3)_5\text{Ru}(\text{pyridine})\text{Ru}(\text{NH}_3)_5]^{5+}$, which shows the properties of both Class II and Class III and is proposed to be in Class II-III.¹¹ Our results indicate that Class II-III does not necessitate solvent-independence that is considered to be an experimental criterion for Class II-III.^{11,63} Contrarily, for $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$, the IVCT transition energy (E_{IT}) and bandwidth $\Delta\nu_{1/2}(\text{exp})$ are essentially solvent independent, although the band intensity is significantly reduced in polar solvents (Figure 9). The constant E_{IT} values for $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$ in different solvents imply the very small reorganization energy with respect to the transition energy ($\lambda \ll E_{\text{IT}}$), as estimated from the electrochemical and optical data (Table 2). For $[\text{OO-OO}]^+$, the large solvent effect is indicative of the large solvent reorganization energy (λ_s), which makes a major contribution to the total reorganization energy $\lambda (= E_{\text{IT}})$. Therefore, for this system the solvent dipoles are able to control the charge localization, promoting the transition from the Class II-III borderline in less polar solvents, to weakly coupled Class II in more polar solvents that better support charge localization.

Figure 7. Near-IR spectra of the $[\text{OO-OO}]^+$, $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$ in four different solvents.

DFT Calculations and Electronic Structures. DFT calculations were carried out on simplified models generated by replacing the anisyl groups of the compounds with hydrogen (H) atoms. As there is little orbital mixing from the anisyl groups on the

supporting ligands, this substitution permits more rapid computational investigation without significant loss of relevance to the experimental results. As the compounds under investigation are largely delocalized, the common B3LYP functional has been adopted in the interests of computational expense. Although the structure of [SS–SS] does not reproduce the torsion angle of the solid state structure, in general the calculated geometries are in good agreement with the structural data obtained crystallographically (Table 3), giving confidence in the appropriateness of the computational models to the experimental systems. The three frontier molecular orbitals (MOs), LUMO, HOMO and HOMO-1, are constructed through interactions between the Mo₂ (δ) and bridging ligand (π) orbitals (Figure 8). The LUMO is composed primarily of orbitals on the bridging ligand. In- ($\delta+\delta$) and out- ($\delta-\delta$) of-phase combinations of δ orbitals, with some involvement of bridging ligand π orbitals, result in the HOMO (antisymmetric) and HOMO-1 (symmetric), respectively. For each of the compounds [OO–OO], [OS–OS] and [SS–SS], the calculated energy gaps ($\Delta E_{\text{H-L}}$) between the HOMOs and LUMOs correspond to the observed MLCT band energies (E_{MLCT}) with acceptable consistency ($\Delta E_{\text{H-L}}/E_{\text{MLCT}} = 1.1\text{--}1.2$), proving further evidence for the appropriateness of the approximations made in the computational work (Table 3).

Figure 8. Molecular orbital and energy diagram showing the energy and symmetry of the key MOs for the computational models of [OO–OO], [OS–OS] and [SS–SS].

Table 3. The calculated bond distances and energy gaps between the selected frontier MOs, in comparison with the charge transfer bands.

Models	Bond distance(Å)		Single point				TD-DFT	
			MLCT (cm ⁻¹)		IVCT (cm ⁻¹)		E_{ex} (cm ⁻¹)	$H_{\text{DA}}(\text{cal})/H_{\text{ab}}$ (cm ⁻¹)
	Mo–Mo	C–C	$\Delta E_{\text{H-L}}$	E_{ML}	$\Delta E_{\text{H-L-S}}$	E_{IT}		
[OO–OO]	2.130	1.519	24062	21739	/	/	/	/
[OO–OO] ⁺	2.149	1.503	26779	21779	2285	4077	6038	3019/2376
[OS–OS]	2.138	1.490	17613	13642	/	/	/	/
[OS–OS] ⁺	2.158	1.464	22135	12500	3905	4149	7094	3547/2726
[SS–SS]	2.142	1.470	14120	11236	/	/	/	/
[SS–SS] ⁺	2.160	1.443	18318	11364	4992	4926	7470	3735/2950

Topologically, the $\delta\pi$ - $\delta\pi$ interaction between the two $[\text{Mo}_2]$ fragments is similar to p - p π -bonding interaction that occurs between two atoms of the second row. Consequently as the orbitals of the $[\text{Mo}_2]$ units interact, in-phase (bonding; HOMO-1) and out-of-phase (anti-bonding; HOMO) combinations arise. The stronger the interaction between the orbitals of the $[\text{Mo}_2]$ fragments, the larger the separation of the in- and out-of-phase combinations, and the larger the energy gap between the HOMO-1 and HOMO. Increasing the sulfur content enhances the metal-metal interactions even in these closed shell systems, evinced by the larger HOMO-HOMO-1 gaps (Figure 8). In contrast, the smaller energy gap between HOMO and HOMO-1 in the oxa-bridged species **[OO-OO]** is consistent with the description of this compound as a more weakly coupled compound, further evinced by the longer C-C single bond (1.519 Å) linking the two $[\text{Mo}_2]$ units (Table 3).

Returning to the semi-classical description, the $\delta\pi$ -orbitals of the $[\text{Mo}_2]$ fragments can be considered as the pseudo “one-particle” diabatic states, ϕ_D and ϕ_A for a non-interacting system (Class I). Interaction of ϕ_D and ϕ_A gives rise to the two adiabatic states,

$$\begin{aligned}\psi_g &= (\phi_D + \phi_A) / \sqrt{2(1 + S_{DA})} \\ \psi_e &= (\phi_D - \phi_A) / \sqrt{2(1 - S_{DA})}\end{aligned}\tag{8}$$

where the diabatic overlap integral $S_{DA} = 0$. For Class III systems, these two states are represented by the HOMO (or SOMO) ($\delta\pi$ - $\delta\pi$) and HOMO-1($\delta\pi^* + \delta\pi^*$), respectively. Assuming Koopmans Theorem holds, the MV state is then well represented by depopulation of the HOMO by one electron. The ground and excited states for the system become $(\delta\pi^* + \delta\pi^*)^2(\delta\pi - \delta\pi)^1$ and $(\delta\pi^* + \delta\pi^*)^1(\delta\pi - \delta\pi)^2$, respectively. The ‘IVCT’ absorption band in these Class III systems can then be described in terms of an optical transition between these states.

The MV complexes **[OO-OO]⁺**, **[OS-OS]⁺** and **[SS-SS]⁺** were also studied using DFT methods and the simplified models. Key structural features of these MV models include elongation of the Mo-Mo bond in the $[\text{Mo}_2]$ fragments, and contraction of C-C bond length associated with the bridges (Table 3). The optimized structures provide some insight regarding the relative intensity of the IVCT bands (Figure 6, Figure 7) from symmetry considerations. The molecular structures and the optimized models of **[OO-OO]** and **[OO-OO]⁺** belong to the point group D_{2h} . For the

crystallographically determined structure of $[\text{SS-SS}]$, the symmetry is lowered to D_2 , because of the torsion angle ($\sim 22^\circ$) between the two $[\text{Mo}_2]$ units, although the optimized structures of $[\text{SS-SS}]$ and $[\text{SS-SS}]^+$ are both D_{2h} . With this symmetry, the HOMO-1 $\rightarrow$ SOMO transitions, $B_{1u}\rightarrow B_{3g}$ for $[\text{OO-OO}]^+$ and $[\text{SS-SS}]^+$ are allowed with polarization in y direction. However, for $[\text{OS-OS}]^+$ with C_{2h} symmetry, the direct product of HOMO-1 (A_u) and SOMO (B_g) is transformed by a B_u irreducible representation, which corresponds to light dipole moments in both the x and y directions. Consistent with this analysis, the molar extinction of the Near-IR band from $[\text{OS-OS}]^+$ (ϵ_{IT} , $2.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) is approximately twice that of $[\text{OO-OO}]^+$ (ϵ_{IT} , $7.7 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) and $[\text{SS-SS}]^+$ (ϵ_{IT} , $9.9 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) (Figure 6).

Accurate calculations of transition energies in large, open-shell transition metal complexes carry significant computational expense,⁶⁴ necessitating compromises and approximation in the methodologies employed.⁶⁵ Since the key absorption bands in cation radicals involve electronic transitions between doubly occupied orbitals and the SOMO, the transition energies can be approximated as the difference in the relevant ionization potentials (i.e. Koopmans' Theorem orbital energies). Since Koopmans' Theorem refers to the relationship between ionization energies and orbital energies from closed-shell HF theory, the 'neutral in cation geometry' (NCG) method,⁶⁶ in which a single point at the geometry of the radical cation is calculated with a neutral charge, has been proposed. The absorptions arising from the HOMO-1–HOMO transitions are referred to as K bands and the NCG approach has been successfully used in organic radical MV systems.^{19,67} Although the appropriateness of Koopmans' Theorem to DFT-based orbital energies (Kohn-Sham orbitals) has been debated,^{68,69} it is interesting to note that for the two very strongly coupled complexes, $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$, HOMO-1 $\rightarrow$ SOMO transition energy ($\Delta E_{\text{H-1.S}}$) is close to the observed IVCT band energies (Table 3). However, for $[\text{OO-OO}]^+$, as shown in Table 3, there is better consistency between the experimental and theoretical data for the MLCT absorption, whereas a relatively large difference is found between E_{IT} and $\Delta E_{\text{H-1.S}}$. For systems at the Class II-III borderline, adiabatic ET and vertical transition between electronic states may occur simultaneously, thus, showing the character of both Class II and III.^{11,21,31} The adiabatic ET behavior of this complex is shown by the co-presence of MLCT (480 nm) and LMCT (620 nm) absorptions in the spectra. Presumably, for $[\text{OO-OO}]^+$, the deviations of the calculated results from the

observations is reflective of its character as a Class II-III borderline species. Nevertheless, with the defined donor (acceptor) orbitals, the electron transition HOMO-1→SOMO can be expressed as the difference in energy eigenvalue between ground and excited states,⁷⁰

$$\begin{aligned}\langle\phi_b|h|\phi_a\rangle &= \frac{1}{2}\{\langle\psi_g|H_{el}|\psi_g\rangle - \langle\psi_e|H_{el}|\psi_e\rangle\} \\ &= (H_{gg} - H_{ee})/2 \\ &= \Delta E/2 = H_{ab}\end{aligned}\quad (9)$$

with assumptions

$$\langle\psi_g|H_{el}|\psi_e\rangle = H_{ge} = H_{eg} = \langle\psi_e|H_{el}|\psi_g\rangle = 0$$

This quantum mechanical treatment to the [Mo₂]-[Mo₂] system establishes clearly the relationship between E_{IT} and coupling H_{ab} , which is verified by the good agreements between the energetic parameters E_{IT} , ΔE_{H-1-S} and $2H_{ab}$, as shown in Table 3. Therefore, in this study, the semi-classical theories and quantum mechanical description on MV systems are remarkably unified.

Figure 9. Energy diagram of the key orbitals derived from TD-DFT calculations on the corresponding complex models of [OO-OO]⁺, [OS-OS]⁺ and [SS-SS]⁺. The orbital energies shown in the same color code are referred to the same MOs for the neutral precursor, turquoise for LUMO, green for HOMO, orange for HOMO-1. β -LUMO is omitted for each of the systems.

In seeking to provide further confirmation of the results and interpretations drawn for the Koopmans' based approach, attention was next turned to TD-DFT methods. In spin unrestricted TD-DFT calculations, the spin up (α) and spin down (β) electrons are

treated separately (Figure 9). In the present case, the β -LUMO and α -HOMO of the one-electron oxidized compounds $[\text{EE-EE}]^+$ are topologically similar to the HOMO of the corresponding neutral precursors $[\text{EE-EE}]$. Similarly, the α -HOMO-1 and β -HOMO of $[\text{EE-EE}]^+$ have similar character to the HOMO-1 of $[\text{EE-EE}]$ (Figure S11). In the computational models of $[\text{OO-OO}]^+$ and $[\text{OS-OS}]^+$ the β -HOMO-1s lie above the α -HOMOs, whilst this order is reversed in the $[\text{SS-SS}]^+$ model. The β -HOMO- β -LUMO transition energies from the TD-DFT calculations are generally larger than the experimental IVCT band energies (E_{IT}) (Table 3). The $[\text{OO-OO}]^+$ model has the smallest excitation energy E_{ex} (6038 cm^{-1}) and $[\text{SS-SS}]^+$ model has the largest value (7470 cm^{-1}), and follow the same trends in increasing energy with increasing sulfur composition as E_{IT} . Therefore, our results on the strongly coupled $\text{Mo}_2\text{-Mo}_2$ systems show that single-point calculation gives more accurate estimation on the IV transition energy than the TD-DFT methods, which agrees with the reported results by Nelsen.¹⁹ The TD-DFT calculated coupling elements, $H_{\text{DA}}(\text{cal}) (= E_{\text{ex}}/2)$, as listed in Table 3, are about 25% larger than the H_{ab} values derived from the two-state model. The general agreement between H_{ab} and $H_{\text{DA}}(\text{cal})$ validates the use of the two-state model in estimating the coupling energy. The deviation could be due to the systematic errors caused by simplified computational models and experimental measurements. More importantly, in this study, the system is regulated with specified donor and acceptor orbitals, symmetry and energy-adapted D-A interactions as well as well-defined “IV” transition, which satisfy the preset conditions of the contemporary theories. Thus, the $\text{Mo}_2\text{-Mo}_2$ system provides a valuable example of “one-particle” D-B-A experimental model that unravels the quantum mechanical insights of electronic delocalization.

Comparison of the IVCT Band Profile with the Predicated from the Two-state Model. In the two-state model, a Gaussian-shaped IVCT band is expected for Class II compounds and the bandwidth at half-height ($\Delta\nu_{1/2}$) can be calculated by eq 10,

$$\Delta\nu_{1/2} = 2[4\ln(2)\lambda RT]^{1/2} \quad (10)$$

One of the pronounced optical properties for the Class II-III and Class III limit systems is that the low energy side of the IVCT band is truncated at $2H_{\text{ab}}$.^{20,71} The “cut-off” phenomenon is well interpreted by the two-state model weighted by a Boltzmann distribution.^{13,32} As a consequence of the cut-off of the absorption band,

when systems in which the observed bandwidth ($\Delta\nu_{1/2}(\text{exp})$) is significantly smaller than $\Delta\nu_{1/2}^\circ$, are considered to lie at or within the delocalized regime, e.g., Class II-III or Class III. To have a quantitative criterion for classification of MV compounds, a parameter Γ has been defined in terms of the experimental $\Delta\nu_{1/2}(\text{exp})$ and calculated $\Delta\nu_{1/2}^\circ$ half-height band-widths,²⁰

$$\Gamma = 1 - \theta \quad (11)$$

$$\theta = (\Delta\nu_{1/2}(\text{exp}))/\Delta\nu_{1/2}^\circ$$

When $\Delta\nu_{1/2}(\text{exp})$ is less than a half of $\Delta\nu_{1/2}^\circ$ ($\theta < 0.5$), or $\Gamma > 0.5$, the system is considered to be in Class III. The half-height bandwidth can also be calculated using Eq 12,²⁰

$$\Delta\nu_{hi} = \left[\left(2H_{ab} - \lambda \right)^2 + 4 \ln(2) \lambda RT \right]^{1/2} - (2H_{ab} - \lambda) \quad (12)$$

where $\Delta\nu_{hi}$ is the half-height width of the high energy side, that is, $\Delta\nu_{hi} = \Delta\nu_{1/2}^\circ/2$. In the strongly coupled case, $\Delta\nu_{1/2}(\text{exp})$ should be compatible with $\Delta\nu_{hi}$ because the low energy “half” ($\Delta\nu_{lo}$) is cut. For all the three complexes, $\Gamma > 0.5$ and the Γ parameter increases with increasing the coupling, as expected (Table 4). Surprisingly, very similar IVCT bandwidths ($\sim 1200 \text{ cm}^{-1}$) are observed for the three complexes, although the extent of electronic coupling varies significantly. Only for $[\text{OO-OO}]^+$ the measured bandwidth, $\Delta\nu_{1/2}(\text{exp}) = 1210 \text{ cm}^{-1}$, is comparable to the calculated $\Delta\nu_{hi}$ value (1535 cm^{-1}), derived from the calculated $\Delta\nu_{1/2}^\circ (= 3069 \text{ cm}^{-1})$. In comparison with the Gaussian-shape simulated band profile (Figure 10), the “cut-off” of the bandwidth at half-height is 38%. This measured value is less than 50% because in the real situation, solvent broadening leads to a rounded band envelope. For example, a cut-off of $\sim 22\%$ was found for the radical cation of *N,N,N',N'*-tetra-4-methoxy phenyl-*p*-phenylenediamine at the Class II-III borderline.¹³ Similar optical behavior was also observed for $[\text{N(H)O-N(H)O}]^+$ and $[\text{SS-ph-SS}]^+$.^{35,53} The IVCT band features for $[\text{OO-OO}]^+$ agree with the assignment to the Class II-III borderline, offering a pronounced asymmetry and low-energy cut-off. However, although the strength of electronic coupling increases from $[\text{OO-OO}]^+$ to $[\text{SS-SS}]^+$ (Table 1), the IVCT band envelope becomes increasingly *less* asymmetric as shown in Figure 10. These results are in sharp contrast to those predicated by the two-state model for Class III systems, where increasing coupling should lead to a progressively narrower and increasingly asymmetric IVCT band.^{20,71} The smallest cut-off, ca. 16%, is found for

$[\text{SS-SS}]^+$ (Table 4). These results are parallel with the observations for the series of oxalate bridged M_2 ($\text{M} = \text{Mo}, \text{W}$) dimers derived by variation of the dimetal centers from Mo_2 to MoW to W_2 , where $[\text{Mo}_2(\text{tBuCO}_2)_3]_2(\mu\text{-O}_2\text{CCO}_2)$ exhibits the most asymmetrical IVCT band and more symmetrical IVCT bands are found for the strongly coupled $[\text{MoW}(\text{tBuCO}_2)_3]_2(\mu\text{-O}_2\text{CCO}_2)$ and $[\text{W}_2(\text{tBuCO}_2)_3]_2(\mu\text{-O}_2\text{CCO}_2)$ complexes.⁴⁷ Furthermore, for $[\text{OS-OS}]^+$ to $[\text{SS-SS}]^+$, calculations of $\Delta\nu_{\text{hi}}$ from Eq 12 give estimates of the band shape that are in poor agreement with experiment (Table 4).

Figure 10. Intervalence absorption bands (solid line) and the Gaussian band fits (dashed lines) for $[\text{OO-OO}]^+$, $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$ in CH_2Cl_2 solutions. For each of them, the cutting-off percentage given in Table 3 is determined from the bandwidth at half height with respect to that of the simulated band profile.

Table 4. Measured and calculated IVCT bandwidths and Γ parameters for the MV complexes.

	$\Delta\nu_{1/2}(\text{exp})$ (cm^{-1})	$\Delta\nu_{1/2}^{\circ}(\text{HTL})^a$ (cm^{-1})	θ	Γ	$\Delta\nu_{\text{hi}}^b$ (cm^{-1})	Cut-off ^c (% exp.)
$[\text{OO-OO}]^+$	1210	3069	0.39	0.61	1535	38
$[\text{OS-OS}]^+$	1210	3096	0.39	0.61	89	23
$[\text{SS-SS}]^+$	1093	3373	0.32	0.68	34	16

^a Data calculated from eq 10 at high temperature limit (HTL) using $\lambda = E_{\text{IT}}$ for the hypothetical Class II systems. ^b Data calculated from Eq 12 using $H_{\text{DA}} (= E_{\text{IT}}/2)$. ^c Reduced bandwidth at half-height relative to the Gaussian simulated band profile.

In seeking to explain the unusual shape of the IVCT band in these most strongly coupled (highly delocalized) complexes, the potential energy surfaces (PES) for the three MV systems were calculated using the H_{ab} and λ parameters (Figure 11 and SI). While $[\text{OO}-\text{OO}]^+$ presents the typical single-well minima adiabatic surfaces for a strongly coupled system, the calculated PESs for $[\text{OS}-\text{OS}]^+$ and $[\text{SS}-\text{SS}]^+$ are almost flat, showing an absence of vibronic features along the reaction coordinate, against the Frank-Condon principle. Obviously, these “flat” PES arising from the application of values of H_{ab} and λ parameters from $[\text{OS}-\text{OS}]^+$ and $[\text{SS}-\text{SS}]^+$ to the two-state model do not account for the narrow but more symmetrical IVCT bands observed for the two thiolated analogues. These two examples show that the two-state model, whilst catering for systems at or near the Class III boundary, does not accurately predict the band shape for very strongly coupled systems that lie well into the delocalized regime.

Figure 11. Potential energy surfaces for $[\text{OO}-\text{OO}]^+$ (black line), $[\text{OS}-\text{OS}]^+$ (blue line) and $[\text{SS}-\text{SS}]^+$ (red line) drawn based on the coupling parameters (H_{ab}) and reorganization energies (λ) (Table 2). Frank-Condon electronic transition (red dashed line) between ground and excited states is proposed for $[\text{SS}-\text{SS}]^+$ with the assumption of constant nuclear coordinates during the transition.

In the cases of $[\text{OS}-\text{OS}]^+$ and $[\text{SS}-\text{SS}]^+$, we propose that the increased symmetry and narrowed width of the IV bands are due to the equal shape of the ground and excited state potential wells. Therefore, a Frank-Condon energy diagram, with the assumption of constant nuclear coordinates during the transition, is exploited to describe the electronic transition that yields the “IVCT” absorption in such strongly coupled (delocalized) systems (Figure 11). The vibronic features of IVCT bands for

Class II-III or Class III limit, as interpreted by the two-state model, are different in nature from those that arise from such electronic transitions. In the two-state diagram for delocalized systems, the upper curve has a small parabolic curvature, relative to the lower curve. However, for a vertical electronic transition, the potential wells for ground and excited states are similar and narrow. In this context, the more symmetric “IVCT” bands observed for very strongly coupled systems may now be well understood. Our study shows that the IVCT band shape changes from symmetric to asymmetric to symmetrical as the systems vary from weakly to strongly to very strongly coupled. Systems on the Class II-III borderline and Class III limit exhibit the most asymmetric IVCT absorption band.

In the two-state model, all the systems crossing over the Class II-III borderline are treated as Class III. However, the proceeding analyses show that there is a turning point in electronic property from $[\text{OO-OO}]^+$ to $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$, as indicated by the optical characters and computational data. In our systematic study from weakly to strongly coupled systems on $\{[\text{Mo}_2]\text{-bridge-}[\text{Mo}_2]\}^+$ models, the semi-classical theories succeed remarkably in interpreting the extent of electronic delocalization^{35,36,37} and elucidating the electron transfer dynamics and kinetics.^{51,52} However, in the spectra of $[\text{OS-OS}]^+$ and $[\text{SS-SS}]^+$, the IVCT band profiles are significantly different from the predicted from the two-state model, implying that these systems have gone beyond the classical description of a Class III system based on the two-state model. We believe that the differences in optical behavior between strong and very strong coupling systems are due to the system transformation from vibronic to electronic. If this turning point is taken as a borderline separating Class III from another regime, this regime may be termed as the very strongly coupled Class IV. A mixed-valence compound in this category behaves more like a molecular radical, whose electronic properties should be elucidated on the basis of the molecular entity.

Conclusion

Assembling two quadruply bonded Mo_2 complex units with oxalate and its thiolated derivatives have produced three symmetrical *dimers of dimers*, denoted as $[\text{OO-OO}]$, $[\text{OS-OS}]$ and $[\text{SS-SS}]$, which share a common molecular scaffold with subtle structural differences due to the ligating atoms of the bridging ligands. Given an electronic configuration of $\sigma^2\pi^4\delta^2$ for the Mo_2 center, the δ orbital is non-degenerate

with respect of the σ and π orbitals, and the δ electrons, conjugated with the oxalate-like π -system are solely responsible for the electronic events; thus, the $\text{Mo}_2\text{--Mo}_2$ system features uniquely the diabatic one-electron donor and acceptor states (ϕ_{D} and ϕ_{A}) derived from the $\delta\pi^*$ orbitals in regard of the $[\text{Mo}_2]$ complex units. The MV complexes generated by one equivalent of $[\text{Cp}_2\text{Fe}]\text{PF}_6$ have the charge distributed over the four Mo atoms, but the extent of delocalization increases largely with increasing the sulfur content. $[\text{OO--OO}]^+$ shows typical Class II-III borderline characters, such as an asymmetrically-shaped and solvent dependent IVCT band, while $[\text{OS--OS}]^+$ and $[\text{SS--SS}]^+$ are well-defined very strongly coupled Class III MV (delocalized) complexes. The optical behavior of the three complexes with increasing electronic coupling has been analyzed within the approximations of the vibronic two-state framework. The coupling parameters (H_{ab}) calculated from the modified Mulliken-Hush equation for Class III fall in the range of 2400 to 3000 cm^{-1} , in excellent agreement with the estimates (2040–2500 cm^{-1}) from the observed intervalence transition energies. However, a more symmetrically-shaped IVCT band is observed for the more strongly coupled system. This is in sharp contrast to the predication from the vibronic two-state model, that is, that the IVCT band is cut in half at $2H_{\text{ab}}$ for Class III systems. DFT calculations on the computational models show that δ orbital interactions between the two Mo_2 units, with minor involvement of the bridge π orbital, generate the HOMO ($\delta\pi\text{--}\delta\pi$) and HOMO-1 ($\delta\pi^*+\delta\pi^*$). Single-point and TD-DFT calculations give consistent results, indicating that the HOMO and HOMO-1 correspond to the excited and ground states for the intervalence transition, respectively, with better accuracy for estimate ($H_{\text{DA}}(\text{cal}) = \Delta E_{\text{H-1-S}}/2$) of the coupling elements provided by the former. It is remarkable that the transition energy of HOMO-1 $\rightarrow$ SOMO equals nearly the intervalence absorption energy for very strongly coupled system. Therefore, the very strongly coupled $[\text{OS--OS}]^+$ and $[\text{SS--SS}]^+$ behave more like a molecular radical, whose electronic properties should be elucidated on the basis of the molecular entity. These results, including the diminished “cut-off” effect, illustrate that system transition from Class II to III is accompanied by the transformation from vibronic to electronic states, in accordance with the quantum mechanical basis of the two-state model. On this basis, the extreme of mixed-valency may be termed as Class IV.

Experimental Sections

Materials and Methods. All manipulations were performed in a nitrogen-filled glovebox or by using standard Schlenk-line techniques. All solvents are freshly distilled over appropriate drying agents under nitrogen. Starting materials, HDAniF⁷² and Mo₂(DAniF)₃(O₂CCH₃)⁷³ and dipotassium 1,2-dithiooxalate⁷⁴ and tetraethylammonium tetrathiooxalate (Et₄N)₂tto⁷⁵ were synthesized according to published methods.

Physical Measurements. Electronic spectra were measured on a Shimadzu UV-3600 UV-Vis-Near-IR spectrophotometer in CH₂Cl₂ solution. ¹H NMR spectra were recorded on a Bruker Avance 500 spectrometer. Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) were obtained using a CH Instruments model CHI660D electrochemical analyzer in 0.10 M CH₂Cl₂ solution of ⁿBu₄NPF₆, with Pt working and auxiliary electrodes, and a Ag/AgCl reference electrode, and a scan rate of 100 mV s⁻¹. EPR spectra were measured using a Bruker A300-10-12 electron paramagnetic resonance spectrometer. Measurements for the mixed-valence complexes were carried out *in situ* after single electron oxidation of the corresponding neutral compounds by FcPF₆.

X-Ray Crystal Structure Determinations. Single-crystal data for [O₂-O₂] $\cdot$ 4CH₂Cl₂ and [S₂-S₂] $\cdot$ 3CH₂Cl₂ were collected on an Agilent Gemini S Ultra Xcalibur Nova diffractometer with Cu-K α radiation (λ = 1.54178 Å) at 173(2) K. The empirical absorption corrections were applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.⁷⁶ All the structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions in the final structure refinement. Structure determination and refinement were carried out using SHELXS-2014 and SHELXL-2014 programs, respectively.⁷⁷ For the two measured crystal structures, the solvent molecules were disordered in multiple orientations, which were refined isotropically. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Computational Details. Before computations were started, simplifications of molecules were taken by using H atoms to replace the anisyl groups (-C₆H₄OCH₃) in auxiliary ligands. Density functional theory (DFT) calculations were performed with

the hybrid Becke three-parameter exchange functional and the Lee-Yang-Parr nonlocal correlation functional (B3LYP) in the Gaussian 09 program (version A.01)⁷⁸. Basis set SDD was used on Mo atoms, while 6-31G was used on C, N, O, S and H atoms. Time-dependent density functional (TD-DFT) calculations (nstate=60) were used to assign the bands on electronic spectra of these molecules.

Preparation of dipotassium-1,2-dithiooxalate (K₂dto). This compound was prepared by modifying a published procedure. To a 500 mL three-neck flask with 150 mL anhydrous ethanol potassium metal (2.2 g, 0.05 mol) was added, slowly and with stirring. When the metallic pieces had dissolved, H₂S was bubbled into the solution until saturated (ca. 2 h). Diphenyl oxalate (3.4 g, 0.0125 mol) was added into the mixture, causing the solution to undertake a faint yellow colour immediately. After 30 h, the reaction mixture was filtered in air and the collected solid was washed with ether (2 × 5 mL). The grey white solid was placed in a desiccator in vacuum and dried for 24h to give the product (2.6 g, 94%).

Preparation of (Mo₂(DAniF)₃)₂(μ-SOCCOS). To a solution of Mo₂(DAniF)₃(O₂CCH₃) (0.50 g, 0.50 mmol) and K₂dto (0.05 g, 0.25 mmol) in THF (30 mL), was added, slowly and with stirring, sodium methoxide (0.5 M, 3.0 mL) in methanol. A blue solid formed in about 30 min. After 5 h, the solvent was evaporated under reduced pressure. The solid residue was extracted using CH₂Cl₂ (ca. 15 mL). The mixture was filtered using a Celite-packed frit, and the volume of the filtrate was reduced under a vacuum to ca. 5 mL. Then, 30 mL of ethanol was added, producing a blue precipitate, which was washed with ethanol (2×20 mL) and hexanes (5 mL). The solid was collected by filtration and dried under a vacuum. Yield: 280 mg (55%). Single crystals for X-ray analysis were obtained by diffusing ethanol into a dichloromethane solution of the blue product. ¹HNMR δ (ppm in CDCl₃): 8.51 (s, 2H, -NCHN-), 8.34 (s, 4H, -NCHN-), 6.76(d, 8H, aromatic C-H), 6.60 (d, 8H, aromatic C-H), 6.54 (m, 16H, aromatic C-H), 6.39 (m, 8H, aromatic -H), 6.10 (m, 8H, aromatic -H), 3.70 (s, 12H, -OCH₃), 3.65 (m, 24H, -OCH₃) (Figure S1). UV-Vis, λ_{max} nm (ε, M⁻¹cm⁻¹): 462 nm (2.7×10³), 682 nm (2.6×10⁴), 733 nm (2.8×10⁴). Anal. Calcd. for C₉₂H₉₀Mo₄N₁₂O₁₄S₂: C, 54.56; H, 4.50; N, 8.32. Found: C, 54.28; H, 4.46; N, 8.26.

Synthesis of [Mo₂(DAniF)₃]₂(μ-S₂CCS₂). A solution of sodium methoxide (0.041 g,

0.75 mmol) in 5 mL of methanol was added dropwise to a solution of $\text{Mo}_2(\text{DAniF})_3(\text{O}_2\text{CCH}_3)$ (0.512 g, 0.50 mmol) in 15 mL of THF. After stirring at room temperature for 2 h, the solvent were removed under vacuum. The residue was dissolved using 20 mL of CH_2Cl_2 and filtered off through a Celite-packed funnel. The filtrate was mixed with tetraethylammonium terephthalate (0.1135 g, 0.275 mmol) in 20 mL of acetonitrile. The mixture was stirring for 3 h, producing a green solid. The product was collected by filtration and washed with ethanol (3×20 mL). Yield: 0.66 g, 63%. Diffusion of ethanol into a dichloromethane solution of the compound affords green flake-shaped crystals. ^1H NMR δ (ppm in CDCl_3): 8.44 (s, 4H, $-\text{NCHN}-$), 8.43 (s, 2H, $-\text{NCHN}-$), 6.60 (m, 32H, aromatic C-H), 6.33 (d, 8H, aromatic C-H), 5.96 (d, 8H, aromatic C-H), 3.69 (s, 24H, $-\text{OCH}_3$), 3.62 (s, 12H, $-\text{OCH}_3$) (see Figure S1). UV-Vis, λ_{max} nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 885 (3.8×10^4). Anal. Calcd. for $\text{C}_{92}\text{H}_{90}\text{Mo}_4\text{N}_{12}\text{O}_{12}\text{S}_4$: C, 53.44; H, 4.39; N, 8.13. Found: C, 54.44; H, 4.51; N, 8.17.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data, orbitals, ^1H NMR, EPR, UV-Vis-Near-IR and Mid-IR spectra.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Optical analyses of three $\text{Mo}_2\text{-Mo}_2$ mixed-valence (MV) complexes illustrate a systematic transition from strongly coupled MV systems on the Class II-III border, to Class III and to those in which the underlying ground state is better described in terms of simple delocalized electronic states rather evolving from strongly coupled diabatic states which define Class III.