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Tuning the electronic coupling in Mo₂–Mo₂ systems by variation of the coordinating atoms of the bridging ligands[†]

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Three novel [Mo₂]-bridge-[Mo₂] complexes were synthesized by a convergent assembling reaction of the dimetal precursor $Mo_2(DAniF)_3(O_2CCH_3)$ (DAniF = N,N'-di(p-anisyl)formamidinate) with the bridging ligands terephthalamidine, terephthalamide and dithioterephthalamide. The structures of these compounds, $[Mo_2(DAniF)_3]_2[\mu-1,4-\{C(E)NH\}_2-C_6H_4]$ (E = NH (1), O (2) or S (3)), were determined, either by X-ray crystallography or ¹H NMR spectroscopy, to be the analogues of the terephthalate bridged dimolybdenum dimer. These compounds are structurally and electronically closely related by having the same structural skeleton and similar bonding parameters, which allowed us to analyze the differences between N, O and S atoms on the bridging ligand in promoting electronic interaction between the two [Mo₂] units. In the electronic spectra, the metal to ligand charge transfer absorption bands, attributed to the HOMO $(d\delta) \rightarrow LUMO (p\pi^*)$ transition, was red shifted as the variable atoms change from N to O to S. The mixedvalence species $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{3}^+$, generated by one-electron oxidation of the neutral precursors and measured in situ, exhibited characteristic intervalence absorption bands, for which the energy and halfheight bandwidth decreased from $\mathbf{1}^+$ to $\mathbf{3}^+$. Therefore, in comparison to O atoms, S atoms are capable of enhancing the electronic coupling between the two [Mo₂] units, and the incorporation of N atoms to the bridging ligands slightly diminished the metal-metal interaction. The molecular structures and spectroscopic properties of these compounds were simulated by theoretical calculations at DFT level on the simplified models, which gave results consistent with the experimental observations.

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Introduction

To a large extent, our understanding of electronic coupling (EC) and intramolecular electron transfer (ET) are obtained from the studies on simple models that are generally constructed with three units, electron donor (D), bridge (B) and electron acceptor (A), namely, D–B–A assembly. In the theoretical aspect, the classical two-state model based on a D–B–A molecular entity has achieved a great success in interpreting and predicting the optical behaviors,^{1,2} mixed-valence properties,^{3,4} electron transfer kinetics and mechanism of the experimental systems.^{5,6} Starting with the Creutz–Taube complex, $[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{5+,7,8}$ thousands of

model compounds with varying structural and electronic compositions of the D (or A) and B units have been synthesized and investigated. To address their electronic configuration, redox and optically active molecular entities are favorable candidates as electron donor and acceptor for the D-B-A molecules. With this prerequisite, majority of the studied compounds are those with dinuclear d^6/d^5 metal centers, e.g., Ru-Ru, Os-Os, Ru-Os and Fc-Fc systems.9-12 Thereafter, bridged triruthenium clusters, Ru₃-Ru₃, have been studied in terms of electronic coupling and electron transfer.13-16 Because of their redox and charge transfer properties, specially designed organic radicals are also made use of in this research practice since the 1990s.¹⁷⁻¹⁹ Slightly after the aforementioned work, covalently bonded dimetal units were employed as electron donor and acceptor for the study in this field mainly by Cotton²⁰⁻²² and Chisholm.^{23,24} The important and unique feature for the dimetal based D-B-A models is that the electronic configuration of the donor and acceptor are well defined. For example, for quadruply bonded $[M_2]$ -bridge- $[M_2]$ complexes, only the δ electrons are involved in the charge or electron transfer process, which greatly facilitates the optical



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Scheme 1 Three new Mo_2-Mo_2 complexes (1–3) with N-containing bridging ligands and related terephthalate derivatives (I–III) ($[Mo_2] = [Mo_2(DAniF)_3]^+$).

analysis. It is believed that the great variety of redox centers and spacer moieties that may be combined in D–B–A systems will help the ongoing refinement of the ET theories.

During the course of investigation on the Mo₂-Mo₂ systems, it is discovered that replacing the O atoms in the parent terephthalate ligand framework ($[p-O_2C-C_6H_4-CO_2]^{2-}$) with S atoms largely improves the electronic communication between the two Mo_2 units, possibly because of the enhanced $d(\delta)-p(\pi)$ orbital interaction.²⁵⁻²⁸ Obviously, it would be of great interest to further evaluate the electronic effect of introducing other heteroatoms into the carboxylate groups of the bridging ligands. For example, full or partial substitution of the O atoms of the carboxylate ligand with N atoms would afford amidinate or amidate ligands, respectively. Although some diamidate bridged dimolybdenum dimers have been studied, the difference between O and N atoms in affecting electronic coupling is not clarified because of their very close redox and optical behaviors. On the other hand, amidinate and amidate groups are much stronger Lewis bases than the carboxylate; thus, it is anticipated that the resulting Mo₂-Mo₂ complexes with these N-containing bridges would be thermodynamically more stable. Amidinate ligands (especially the sterically bulky ones) have been widely used in the synthesis and isolation of various uncommon inorganic/organometallic structural motifs, including the first and to date only example of Mo-Mo quintuple bonds.^{29,30} However, to date, dimers of dimers synthesized with an amidinate bridging ligand are scarce because of the synthetic obstacles for ligands and complexes of this type,³¹ although the most commonly used ancillary ligands in such M₂-M₂ systems are indeed formamidinate ligands. In contrast, N-aryl amidate ligands have been employed to link [Mo₂] units to form molecular triangles and squares,³² and related *dimers of dimers* have been constructed using either N-aryl33 or N-alkyl34 amidates. Tetrarhenate complex $[NBu_4]_2[{Re_2Cl_6 \cdot C_3H_7NO}_2{1,4-(C(O)NH)_2C_6H_4}]$ is the only example of M₂-M₂ compounds having a terephthalamidate linker,³⁵ which was prepared by hydrolysis of 1,4-dicyanobenzene in the presence of a dirhenium complex.

Herein, we report the synthesis and isolation of three dimolybdenum *dimers of dimers* $[Mo_2(DAniF)_3]_2[\mu-1,4-{C(E)NH}_2-C_6H_4]$ (DAniF = *N*,*N*'-di(*p*-anisyl)-formamidinate; E = NH (1), O (2) or S (3)) through direct assembly of Mo₂(DAniF)₃- (O_2CCH_3) with the corresponding tetradentate ligands. The structures of all the three compounds were determined by ¹H NMR spectra and two of them (2 and 3) were characterized by crystallographic methods also. In order to evaluate the influence of various donor atoms with respect to electronic interactions, their electrochemical and spectroscopic behaviors were compared with those analogues, which are structurally and electronically closely related (I, II and III in Scheme 1).^{26–28} On this basis, the correlations of the energy of the metal to ligand charge transfer band (λ_{max}) in the spectrum and the potential separation $(\Delta E_{1/2})$ in the cyclic voltammogram (CV) with the extent of metal-metal interaction are discussed. DFT calculations were performed on the simplified model compounds, which further elucidated the electronic effects of coordinating atoms on the EC interactions. From the magnetic and optical behaviors of the singly oxidized species 1^+ , 2^+ and 3^+ , the mixed-valence properties of the system were preliminarily evaluated.

Results and discussion

Molecular design and synthesis

As mentioned earlier, our current investigation focused mainly on the electronic effect of the substitution of N donor atoms in the bridging ligands of Mo₂-Mo₂ complexes. Thus, we chose three new *dimers of dimers* as our synthetic targets (Scheme 1), which contain amidinate, amidate and thioamidate bridging ligands. It is noteworthy that the three new compounds have similar molecular scaffolds, and the only variation is the type of the donor atoms of the bridging ligand. It was expected that such subtle compositional and structural differences would facilitate the direct comparison of the electron coupling interaction within the complex series, including previously reported terephthalate (I) and thioterephthalate (II and III) derivatives.²⁶⁻²⁸ Bridging ligands terephthalamide³⁶ and dithioterephthalamide³⁷ were prepared in good yields by following the literature procedures. For the preparation of terephthalamidine dihydrochloride modification was made to the published methods.³⁸ These new Mo₂-Mo₂ complexes were

synthesized by mixing two equiv. of dimetal precursor Mo_2 - $(DAniF)_3(O_2CCH_3)$ with one equiv. of bridging ligand in the presence of $NaOC_2H_5$. By following this known synthetic protocol,^{39,40} crystalline products of $[Mo_2(DAniF)_3]_2[\mu-1,4-{C(E)-NH}_2-C_6H_4]$ (E = NH (1), O (2) or S (3)) were obtained in high yields after standard workup and recrystallization procedures. Compound 1 represents the first example of dimolybdenum dimers bridged by an amidinate ligand, thus affording a completely *N*-coordinated analogue.

Molecular structures

The molecular structures of 1-3 were determined by ¹H NMR spectroscopy. In each of the ¹H NMR spectra for 1-3, only a single resonance at 7.74, 8.04 and 7.88 ppm, respectively, was observed for the four protons on the bridging aromatic ring. This is consistent with the highly symmetric structures of amidinate bridged complex 1 in solution, and also suggests that the C-C bond connecting the amidate (2) or thioamidate (3) group and the phenylene ring can rotate freely at the measurement conditions. In addition, singlet resonances for the amidate NH protons in compounds 2 and 3 were detected in the downfield region (9.01 ppm for 2 and 10.29 ppm for 3) and integrated into two protons. In contrast, no such resonance was observed for the previously reported amidate bridged Re2-Re2 compound and its absence was explained by the existence of hydrogen bonding.35 Such comparison indicates that complexes 2 and 3 show discrete structures in the solution and there is no hydrogen bonding interactions, possibly due to the steric bulk of the ancillary DAniF ligands on each Mo2 units. As expected, the ¹H NMR spectrum of 1 displayed a singlet resonance for the four amidinate protons at 8.23 ppm. This signal is shifted toward upfield relative to that of the ligand precursor terephthalamidine dihydrochloride (9.00 ppm).

Many efforts have been made to grow single crystals of 1 for X-ray characterization. Diffusion of ethanol into tetrahydrofuran (THF) solution of 1 afforded orange yellow coloured plates. Unfortunately, crystallographic data collection failed because the crystal was very fragile and extremely air sensitive. For 2 and 3, the solid-state structures were further confirmed by X-ray crystallography. Compound 2 crystallizes in the monoclinic space group $P2_1/c$ and 3 in the triclinic group $P\overline{1}$. The crystallographic data and collection parameters are presented in Table 1 and selected bond distances and angles are listed in Table 2. Generally, both complexes show the same structural skeleton (Fig. 1) and have similar bond lengths and angles in comparison to the terephthalamide and dithioterephthalamide analogues.^{27,28} For instance, the Mo₂...Mo₂ separations in the structures are determined to be 11.36 (2) and 11.76 Å (3), respectively. These values fall in the range of 11.24-12.24 Å for the carboxylate and thiocarboxylate derivatives.²⁷ The similar metal-to-metal distances exclude the differences in the electrostatic interaction between them and thus would allow the evaluation of the electronic coupling effect arising from alternation of the donor atoms. As shown in Fig. 1, for both 2 and 3, the same donor atoms on the bridging ligand are located in the trans position and no cis-isomers and structure

Table 1 Crystallographic data and collection parameters for $2\cdot6C_4H_8O$ and $3\cdot5.6C_4H_8O\cdot2C_2H_5OH$

	$2 \cdot 6 C_4 H_8 O$	$\textbf{3.5.6C_4H_8O.2C_2H_5OH}$			
Formula	C ₁₂₂ H ₁₄₄ Mo ₄ N ₁₄ O ₂₀	C _{124.4} H _{152.8} Mo ₄ N ₁₄ O _{19.6} S ₂			
fw	2510.33	2605.76			
Space group	$P2_1/c$	$P\bar{1}$			
a(Å)	19.8102(3)	11.5410(4)			
b (Å)	18.2488(2)	11.7590(4)			
c (Å)	17.1298(3)	24.0969(9)			
α (°)	90	76.162(3)			
$\beta(\circ)$	107.273(2)	86.324(3)			
γ (°)	90	72.438(3)			
$V(Å^3)$	5913.35(15)	3027.18(19)			
Z	2	1			
$T(\mathbf{K})$	149(2)	173(2)			
$d_{\rm calcd}$ (g cm ⁻³)	1.401	1.416			
$\mu (\text{mm}^{-1})$	3.989	4.228			
R_1^a	0.0484	0.0505			
wR ₂ ^b	0.1363	0.1271			
${}^{a}R_{1} = \sum F_{0} - F_{c} / \sum F_{0} . {}^{b}WR_{2} = [\sum W(F_{0}^{2} - F_{c}^{2})^{2}] / \sum W(F_{0}^{2})^{2}]^{1/2}.$					

Table 2 Selected bond distance (Å) for 2 and 3, in comparison with those of I, II and III^a

	2	3	Ι	Π	III
Mo(1)-Mo(2)	2.0892(5)	2.0943(5)	2.090(1)	2.1051(6)	2.103(1)
Mo(1)-N(1)	2.172(4)	2.155(4)	2.155(5)	2.133(4)	2.149(5)
Mo(1) - N(3)	2.152(3)	2.150(4)	2.123(5)	2.143(4)	2.153(5)
Mo(1) - N(5)	2.164(3)	2.160(4)	2.152(5)	2.137(4)	2.146(5)
Mo(2) - N(2)	2.138(4)	2.166(4)	2.137(5)	2.161(4)	2.141(5)
Mo(2) - N(4)	2.139(3)	2.188(4)	2.119(5)	2.174(4)	2.164(5)
Mo(2) - N(6)	2.141(3)	2.150(4)	2.137(5)	2.142(4)	2.148(5)
Mo(1) - O(7)			2.144(4)	2.112(4)	
Mo(2) - O(8)	2.119(3)		2.122(4)		
Mo(1)-S(1)		2.4692(13)			2.442(2)
Mo(2) - S(2)				2.469(1)	2.445(2)
Mo(1) - N(7)	2.148(3)				
$M_0(2) - N(8)$	- (-)	2.144(4)			
$Mo_2 \cdots Mo_2$	11.36	11.76	11.24	11.67	12.24
^a Data cited fro	om ref. 27.				

disorder were detected, even in solution. Moreover, each compound showed typical Mo-Mo quadruple bond lengths, 2.0892(5) Å for 2 and 2.0943(5) Å for 3. The Mo(1)-N(7) (2.148(3) Å) and Mo(2)–O(8) (2.119(3) Å) distances in 2 are comparable to the corresponding values in the analogues containing N,N'-diethylterephthalamidate (2.177(5) and 2.112(4) Å)³⁴ or N,N'-diphenylterephthalamidate (2.170(4) and 2.106(3) Å)³³ bridging ligand. In the solid-state structure of 2, the central *p*-phenylene group is almost coplanar with the Mo-Mo vectors. However, for the diamidate analogues with N-substituents, there is a considerable deviation between the phenylene bridge and the two Mo₂ units. For instance, torsion angles of 34.45° and 36.21° were found for the N,N'-diphenyl and N,N'di(*m*-trifluoromethyl)phenylterephthalamidate derivatives, respectively.33 Even more extreme distortion was reported for the N,N'-diethylterephthalamidate analogue (50.14°).³⁴ Apparently, the steric hindrance of the N-substituents is responsible for the non co-planarity, which weakens the electronic coupling

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Fig. 1 X-ray crystal structures for 2 (top) and 3 (bottom). In the compound formula, $[Mo_2]$ represents the dimetal building block, $[Mo_2(DAniF)_3]^+$. The hydrogen atoms have been omitted, except for those on the bridging ligands.

between the two $[Mo_2]$ units. For the thioamidate compound (3), the steric repulsion between the sulfur atoms and the neighboring phenyl protons also causes a N(8)–C(1)–C(2)–C(3) torsion angle of 25.62°.

Electrochemical studies

For complexes 1–3, the electrochemical process in CH₂Cl₂ were recorded by cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs), as shown in Fig. 2, which involves two redox events corresponding to the stepwise removal of one $\boldsymbol{\delta}$ electron from each of the two bridged $[Mo_2]^{4+}$ units. The potential separation ($\Delta E_{1/2}$) between the two redox couples was employed to probe the relative strength of the electronic communication between the two redox sites. However, for these compounds, the two redox cycles were not resolved in the CVs because of the weak EC interaction. The small $\Delta E_{1/2}$ values for 1-3 were determined from their DPVs by Richardson and Taube's methods,41 and the electrochemical data are summarized in Table 3. For easier comparison, $\Delta E_{1/2}$ values for the terephthalate (I),²¹ dithioterephthalate (II)²⁷ and tetrathioterephthalate (III)²⁶ analogues from literatures are also included. As it can be seen, compound **1** has the smallest $\Delta E_{1/2}$ value,



Fig. 2 Differential pulse voltammograms (DPVs) (top) and cyclic voltammograms (CVs) (bottom) for complexes 1-3.

 Table 3
 Electrochemical measurements and the parameters for the comproportionation equilibrium

Compound	$E_{1/2}(1)$ (mV)	$E_{1/2}(2)$ (mV)	$\Delta E_{1/2}$ (mV)	Kc	$\Delta G_{\rm c}$ (cm ⁻¹)
1	178	272	80	23	-645
2	327	411	96	42	-774
3	398	508	115	88	-928
\mathbf{I}^{a}	225	325	100	49	-807
\mathbf{H}^{b}	468	584	116	91	-935
III ^c	500	700	200	2405	-1613

^a Data cited from ref. 21. ^b Data cited from ref. 27. ^c Data cited from ref. 26.

ca. 80 mV, indicating that compared to O and S atoms, nitrogen donor atoms on the bridging ligand has an effect of diminishing the EC interaction. The thiolated analogue (3), on the other hand, has the largest potential separation, *i.e.*, $\Delta E_{1/2} = 115$ mV, which is consistent with the previous studies.^{27,28} Compound 2, which has O/N mixed donors, gave a $\Delta E_{1/2}$ value (96 mV) in the middle. A possible explanation on the coordinating atom effect is that the softness of the atoms E increases the covalent character of the M–E bonds, consequently, enhancing the coupling interaction between the [Mo₂] units in the order of N < O < S.

The difference between O and N atoms in mediating electronic interaction is further manifested by comparing the $\Delta E_{1/2}$ values for the three closely related compounds **I**, **2** and **1**, which can be viewed to be the derivatives of stepwise replacement of the O donor atoms of the terephthalate analogue by N atoms. As indicated in Table 3, as a result of increasing the N donors, the potential separation $\Delta E_{1/2}$ is lowered in order, *i.e.*, from 100 mV (for **I**) to 96 mV (for 2) to 80 mV (for **1**). These results demonstrate that among the three types of donor

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atoms we have investigated to date, the electronic effects for enhancing the electronic communication in the Mo₂-Mo₂ systems are in the sequence of S > O > N. It should be noted that the $\Delta E_{1/2}$ value (96 mV) for 2 is compatible to those (100 mV) for the N,N'-diarylterephthalamidate complexes,³³ but larger than that (85 mV) for the N.N'-diethylterephthalamidate analogue.³⁴ For the N/O complexes, the N-substituted diamidate analogues are expected to have a larger $\Delta E_{1/2}$ because of the electron donating property of the substituent groups. This explains that the N,N'-diarylterephthalamidate complexes (100 mV) has the $\Delta E_{1/2}$ value slightly larger than that for 2. In comparison, the diethyl substituted analogue has an exceptionally small potential separation. This is likely due to the large deviation (50.14°) between the two planes defined by the bridging phenyl ring and the associated dimetal chelating ring, which diminishes the π conjugation through the bridge. Therefore, for these structurally and electronically similar complexes, comparison of the $\Delta E_{1/2}$ values indeed shows the relative strength of the metal-metal electronic interaction, even though the difference caused by O/N atomic alternation is small.

For this dimetal system, the equilibrium constant (K_c) for the comproportionation of the neutral [Mo₂–Mo₂] and the doubly oxidized [Mo₂–Mo₂]²⁺ to the mixed-valent species [Mo₂–Mo₂]⁺ can be derived from the redox potential separation $\Delta E_{1/2}$ by the expression $K_c = \exp(\Delta E_{1/2}/25.69)$.⁴¹ Accordingly, the free energy change (ΔG_c) for the comproportionation reaction can be determined electrochemically (Table 3). For the same reason mentioned above, in this system, ΔG_c can be used to evaluate the extent of electronic delocalization. The similar K_c and ΔG_c values for 2 and I are indicative of comparable metal–metal interactions in these N- or O-donor compounds.

Electronic structures and spectroscopic properties

To further investigate the electronic structures of compounds 1–3, DFT calculations were performed on the simplified model compounds $[Mo_2(NHCHNH)_3]_2[\mu-1,4-\{C(E)NH\}_2-C_6H_4]$ (E = NH (1'), O (2') or S (3')), where the *p*-anisyl groups in the DAniF ligands of 1–3 were replaced with hydrogen atoms. The calculated bond distances are in good agreement with those found by X-ray crystallography (Table 4). The calculated frontier molecular orbitals for model complexes 1'–3' are presented in Fig. 3. As can be seen, the LUMO is mainly based on the conjugated π orbitals of the bridging ligand, while the HOMO and

Table 4 Calculated bond distances and HOMO–LUMO energy gap for 1'-3'

Model	Bond dis	HOMO-				
	Мо-Мо	Mo ₂ …Mo ₂	Мо-О	Mo-S	Mo-N	LUMO energy gap (eV)
1' 2' 3'	2.131 2.129 2.133	11.50 11.47 11.90	2.130	2.524	2.149 2.164 2.150	2.868 2.791 2.682

HOMO–1 are metal based orbitals. More specifically, the HOMO mainly consists of the out-of-phase combination of Mo δ orbitals ($\delta - \delta$), and the HOMO–1 mainly consists the corresponding in-phase combination ($\delta + \delta$). Our previous study demonstrated that in Mo₂–Mo₂ systems, HOMO–LUMO energy gap determines the electron transfer rate between the two dimetal sites.^{27,28} A system with smaller HOMO–LUMO energy gap would show a higher electron transfer rate between the donor and acceptor sites. Hence, the calculated HOMO–LUMO energy gap for complexes 1'–3' (Table 4) suggests that the enhancement of the electronic interaction by the coordinating atoms follows the sequence of S > O > N, supporting our electrochemical results.

The three compounds show distinct colors, *i.e.* orange yellow (1), red (2) and purple (3), despite the subtle difference on the bridging ligands. Consistent with the different colors for these compounds, in the spectra, each of them exhibits a characteristic absorption band with similar intensity at 465 (1), 490 (2) and 560 nm (3) (Fig. 4). This absorbance should be assigned to the metal to ligand charge transfer (MLCT). Simulations from the DFT calculations generated spectra having similar variation tendency for the band energies (Fig. 4), confirming that the absorption corresponds to the HOMO \rightarrow LUMO transition. The transition energy for 2 is comparable to that found for the related N,N'-diarylterephthalamidate complexes (aryl = Ph (462 nm) and m-CF₃C₆H₄ (473 nm)).³³ However, the N,N'-diethylterephthalamidate analogue showed a considerably less intense absorption at shorter wavelength (442 nm; ε = 3200 M⁻¹ cm⁻¹). This result is consistent with the electrochemical measurement, which shows small potential separation ($\Delta E_{1/2}$ = 84 mV).³⁴ The absorption bands of 1–3, as well as I, II and III, are summarized in Table 5. In consistence with our previous finding,^{27,28} stepwise introduction of S atoms to the bridging amidinate ligand shifts the MLCT band to 560 nm for 3 from 465 nm for 1, and then further to 715 nm for III. In contrast, it appears that substitution of O atoms with N atoms only slightly shifts the band in the opposite direction, from 492 nm (I) to 490 nm (2) and 465 nm (1). Therefore, it is evident that introducing N donor to the bridging ligand increases the MLCT energy, while S donor atoms on the bridging ligand lower the MLCT energy. These observed trends are well stated by theoretical prediction.

Through our studies on the *dimers of dimers* with conjugated bridging ligands, we found that the MLCT energy is correlated with the extent of electron delocalization and for the mixed-valence species, the HOMO–LUMO gap determines the rate of electron transfer from one site to the other.²⁸ These results are reflection of superexchange mechanism, by which electron hopping from one dimetal center to the other *via* the bridge. Note that sulfur atoms as the coordination donors are capable of enhancing the electronic delocalization and increasing the electron transfer rate. It is confirmed that nitrogenchelating groups would weaken the Mo₂–Mo₂ interaction and lower the electron transfer rate. As is well known, oxygen (O),⁴² nitrogen (N)⁴³ and sulfur (S)^{44,45} are the major donor atoms in naturally occurring metal enzyme systems, which may function



Fig. 3 Illustrations of the 0.04 contour surface of the TD-DFT calculated frontier molecular orbitals for model compounds 1'-3' (O (red), S (yellow) and N (blue)).



Fig. 4 Electronic absorption spectra of 1–3 (top) and the simulated electronic absorption spectra from the time-dependent DFT (TD-DFT)

 $0 \quad 1000$ spectra (Fig. 5). The main EPR signal in the spectra unambiguously confirmed the existence of an unpaired electron in each of the oxidized complexes. The corresponding *g* values fell in the range of 1.940–1.948, suggesting that the unpaired electron

biochemical systems.

the range of 1.940–1.948, suggesting that the unpaired electron resides mainly on a Mo-based orbital. These *g* values are very close to those obtained for complexes I^+ – III^{+27} and the biphenylene bridged analogues (1.942 to 1.947).⁴⁶ Such a narrow range of *g* values in both series of mixed-valence compounds indicates that all the molecular orbitals containing the unpaired electron have very similar electronic structures. The hyperfine structure in the EPR spectra is due to the coupling of the unpaired electron with ⁹⁵Mo or ⁹⁷Mo (*I* = 5/2) nuclei.

as electron transporter or involve electron transfer processes.

Hence, the understanding obtained from this study has the

significance of elucidating the electronic properties of some

Magnetic and optical properties of the mixed-valence species Single-electron oxidation of compounds 1–3 with ferrocenium hexafluorophosphate (FcPF₆) afforded the expected mixedvalence complexes 1^+-3^+ as evidenced by the measured EPR

 Table 5
 Experimentally observed and theoretically predicted absorption bands for 1–3 in comparison with those for I–III^a

MLCT (nm)	1	2	3	Ι	II	III
Exp.	465	490	560	492	618	715
Cal.	517	520	555	548	652	685

^{*a*} Data cited from ref. 27.

calculations on the models 1'-3' (bottom).



Fig. 5 X-band EPR spectra of the radical cations generated by single oxidation of the neutral compounds. Samples were measured in CH_2Cl_2 solution at 173 K.

In the spectra from visible to near-infrared region, the *in situ* generated samples of 1^+-3^+ display characteristic intervalence (IV) transition absorption bands, in addition to the MLCT absorptions similar to those observed for the neutral complexes (Fig. 6). For the series, the band energy decreases but the intensity increases in order from 1^+ to 3^+ . As shown in Table 6, the IV transition for the amidinate bridged complex 1^+ has the highest energy (4980 cm⁻¹). This band is slightly red shifted to 4651 cm⁻¹ for the amidate analogue (2^+), and further down to 3182 cm⁻¹ for the thioamidate derivative (3^+). In comparison with I^+-III^+ , which have similar Mo₂···Mo₂ distance, complexes 1^+-3^+ present the IV bands with considerably



Fig. 6 Visible and near-infrared spectra for the MV complexes 1^+-3^+ , along with the spectra of the neutral compounds 1-3. The intervalence absorption bands are simulated with Gaussian-shaped curves as shown by the dashed line profiles.

Table 6 Spectroscopic data for the mixed-valence $1^+\!-\!3^+\!,$ along with those for $l^+\!-\!III^+$ for comparisonª

Complex	$E_{\rm IV}$ (cm ⁻¹)	${e_{\rm IV} \over ({ m M}^{-1}~{ m cm}^{-1})}$	Exp. $\Delta \nu_{1/2}$ (cm ⁻¹)	$\begin{array}{c} \text{Cald} \Delta \nu_{1/2} \\ (\text{cm}^{-1}) \end{array}$	Г
1 ⁺	4980	520	8840	3392	-1.45
2^+	4651	1171	5242	3278	-0.60
3 ⁺	3182	3589	3688	2711	-0.36
\mathbf{I}^+	4240	1470	4410	3190	-0.17
\mathbf{II}^+	3440	3690	3290	2820	-0.14
\mathbf{III}^+	2640	12 660	1770	2470	0.30

^a Data cited from ref. 27.

lower intensities, and the bandwidth becomes narrower as the donor atoms vary from N to O to S (Table 6). The measured half-height bandwidths $(\Delta \nu_{1/2})$ are much larger than the calculated values $(2310\nu_{max})^{1/2}$. According to $\Gamma = 1 - (\Delta \nu_{1/2})/(2310\nu_{max})^{1/2}$, 47 a Γ value of -1.45, -0.60 and -0.36 cm⁻¹ is found for 1⁺, 2⁺ and 3⁺, respectively, indicating that the mixed-valence series belongs to the weakly coupled Class II in Robin–Day's scheme. The variation trends of the IV band energy and intensity as well as width are consistent with our observation for the related series of \mathbf{I}^+ - \mathbf{III}^+ and the biphenylene bridged analogues.^{27,45} These mixed-valence behaviors of $\mathbf{1}^+$ - $\mathbf{3}^+$

conform well to the electrochemical and spectroscopic properties for 1–3 described above. Thus, it is confirmed that variation of the coordinating atoms from N to O and further to S would induce the enhancement of the electronic coupling in the [Mo₂]-bridge–[Mo₂] systems.

Conclusions

In summary, the synthesis and isolation of three Mo₂-Mo₂ complexes with amidinate, amidate and thioamidate bridges are described. Many reported dimolybdenum dimers are bridged by dicarboxylate and several by thiodicarboxylate, and still others have mixed-donor (O, N and S) bridges; however, compound 1 is the first complete nitrogen-coordinated analogue. Structural characterization in both solid-state and solution indicates that all three complexes share the same molecular structural skeleton. Electrochemical and spectroscopic studies of 1-3 suggest that while S donor atoms induce the largest enhancement of the electronic communication, N atoms on the bridge promote, relative to O atoms, slightly weaker metalmetal interaction. This trend is consistent with the variation of the coordinating atoms E in softness. More covalent character for the Mo–S bonds enhances the $d(\delta)$ – $p(\pi)$ conjugation and promotes stronger metal-metal interaction, while harder N atoms take effect oppositely. The mixed-valence species 1^+-3^+ , generated by single oxidations of the corresponding neutral compounds and measured in situ, displayed an isotropic EPR signal with a g value of 1.942-1.947 and a broad metal to metal intervalence transition band in near-IR region. The energy and half-height width of the IV bands decrease in order from $\mathbf{1}^+$ to $\mathbf{3}^+$. This demonstrates that simply by varying the functional groups of the bridging ligand, the electronic coupling between the two Mo₂ units could be modulated in a relatively wide range. Subtly tuning the electron coupling in mixed-valence compounds of this type may be achieved by alternation of O/N donors, which provides valuable guidance for the development of experimental models for the refinement of electron-transfer theories. Furthermore, the molecular structures of 1-3 and the electronic spectra could be reproduced by DFT calculation using simplified model compounds. The trend of MLCT energy variation predicted by TD-DFT calculation was consistent with the experimental results, on the basis of which modulation of electron coupling by varying the coordinating atoms (S > O > N) is confirmed.

Experimental

Materials and methods

All manipulations were performed in a nitrogen-filled glove box or by using standard Schlenk-line techniques. All solvents were freshly distilled and dried over appropriate drying agents under N₂. Terephthalamide,³⁶ dithioterephthalamide,³⁷ HDAniF,⁴⁸ and Mo₂(DAniF)₃(O₂CCH₃),³⁹ were prepared according to published methods. Terephthalamidine dihydrochloride was synthesized by modification of a reported procedure.³⁸

Physical measurements

Elemental analyses were performed by an Elementar Vario EL elemental analyzer. UV-vis spectra were obtained on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer in CH_2Cl_2 solution. ¹H NMR spectra were recorded on a Bruker-400 spectrometer. Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) were obtained using a CH Instruments model-CHI660D electrochemical analyzer in 0.10 M CH_2Cl_2 solution of ^{*n*}Bu₄NPF₆, with Pt working and auxiliary electrodes, an Ag/AgCl reference electrode, and a scan rate of 100 mV s⁻¹.

X-ray structure determinations

Single-crystal data for 2.6C4H8O were collected on an Agilent Gemini S Ultra diffractometer with Cu-Ka radiation (λ = 1.54178 Å) at 149(2) K and single-crystal data for 3.5.6C4H8O.2CH3CH2OH were collected on an Agilent Xcalibur Nova diffractometer with Cu-K α radiation (λ = 1.54178 Å) at 173(2) K. For both, the empirical absorption corrections were applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.49 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-97 and SHELXL-97 programs, respectively.⁵⁰ 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 an isotropic displacement parameters.

Computational details

All DFT (density functional theory) calculations were performed with the hybrid B3LYP^{51,52} functional implemented in the Gaussian 09 package (Revision A0.2).⁵³ The model complexes were fully optimized. The standard 6-31G* basis set were used for H, C and N atoms, and aug-CC-pvDZ basis set for S and O atoms of the bridging ligands. The SDD basis set together with SDD pseudo-potential were used for the heavy metal Mo atoms. Time-dependent DFT (TD-DFT) calculations were carried out to obtain 60 excitations for all the model compounds. By replacing the *p*-anisyl groups on $[Mo_2(DAniF)_3]^+$ with hydrogen atoms, the employed calculation models have $[Mo_2(NHCHNH)_3]^+$ units as the building blocks.

Preparation of terephthalamidine dihydrochloride

To a solution of benzene-1,4-dicarbonitrile (1.24 g, 9.7 mmol) in 20 mL of THF, 40 mL of 1 M LiN(SiMe₃)₂ solution was added dropwise in 30 min at 0 °C. The mixture was stirred at room temperature for 3 h and then cooled to 0 °C in an ice bath. The reaction was quenched by careful addition of 6 M HCl–EtOH (35 mL) and the mixture was set aside for several hours. The precipitate was then filtered, washed with Et₂O,

and then the powder was recrystallized from H₂O–EtOH mixture. Yield: (1.74 g, 96%). ¹H NMR δ (ppm in DMSO-d₆): 9.00 (s, 8H, NH), 8.06 (s, 4H, aromatic *H*).

$[Mo_{2}(DAniF)_{3}]_{2}[\mu-1,4-\{C(NH)NH\}_{2}-C_{6}H_{4}](1)$

To a mixture of Mo₂(DAniF)₃(O₂CCH₃) (0.406 g, 0.40 mmol) and terephthalamidine dihydrochloride (0.0472 g, 0.20 mmol), 30 mL of THF was added. 4.0 mL of 0.1 M NaOC₂H₅ solution in ethanol was added slowly with stirring, and the reaction mixture was stirred at room temperature for 4 h to produce a red solution. The solvent was removed under reduced pressure, and the residue was washed with ethanol $(3 \times 20 \text{ mL})$ and then dried under vacuum. Diffusion of ethanol into a dichloromethane solution of the compound yielded orange yellow coloured rhombus crystals. Yield: 0.32 g (77%). ¹H NMR δ (ppm in CDCl₃): 8.45 (s, 2H, -NCHN-), 8.26 (s, 4H, -NCHN-), 8.23 (s, 4H, C(NH)NH), 7.74 (s, 4H, aromatic H), 6.62 (d, 16H, aromatic H), 6.47 (d, 8H, aromatic H), 6.38 (d, 16H, aromatic H), 6.25 (d, 8H, aromatic H), 3.71 (s, 24H, OCH₃), 3.68 (s, 12H, OCH₃). UV-vis, λ_{max} nm (ϵ , M⁻¹ cm⁻¹): 465 (2.35 × 10⁴). Anal. Calcd (%) for C₉₈H₉₈Mo₄N₁₆O₁₂: C, 56.71; H, 4.76; N, 10.79. Found: C, 56.39; H, 4.66; N, 10.97.

$[Mo_{2}(DAniF)_{3}]_{2}[\mu-1,4-\{C(O)NH\}_{2}-C_{6}H_{4}](2)$

To a mixture of Mo₂(DAniF)₃(O₂CCH₃) (0.406 g, 0.40 mmol) and terephthalamide (0.0272 g, 0.20 mmol), 30 mL of THF was added. 4.0 mL of 0.1 M NaOC₂H₅ solution in ethanol was added slowly with stirring, and the reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the red residue was washed with ethanol (3 \times 20 mL) and then dried under vacuum. The solid was dissolved in 15 mL of tetrahydrofuran, and the solution was layered with hexane. Red crystals formed in 5 days. Yield: 0.309 g (75%). ¹H NMR δ (ppm in CDCl₃): 9.01 (s, 2H, C(O)-NH), 8.47 (s, 2H, -NCHN-), 8.32 (s, 4H, -NCHN-), 8.04 (s, 4H, aromatic H), 6.62 (d, 24H, aromatic H), 6.50 (d, 4H, aromatic H), 6.43 (d, 4H, aromatic H), 6.38 (d, 8H, aromatic H), 6.30 (d, 4H, aromatic H), 6.22 (d, 4H, aromatic H), 3.71 (s, 24H, OCH₃), 3.68 (s, 6H, OCH₃), 3.66 (s, 6H, OCH₃). UV-vis, λ_{max} nm (ϵ , M⁻¹ cm⁻¹): 490 (2.3 × 10⁴). Anal. Calcd (%) for $C_{98}H_{96}Mo_4N_{14}O_{14}$: C, 56.66; H, 4.66; N, 9.44. Found: C, 56.39; H, 4.60; N, 9.57.

$[Mo_{2}(DAniF)_{3}]_{2}[\mu-1,4-\{C(S)NH\}_{2}-C_{6}H_{4}](3)$

To a mixture of Mo₂(DAniF)₃(O₂CCH₃) (0.406 g, 0.40 mmol) and dithioterephthalamide (0.039 g, 0.20 mmol), 30 mL of THF was added. 4.0 mL of 0.1 M NaOC₂H₅ solution in ethanol was added slowly with stirring, and the reaction mixture was stirred at room temperature for 4 h to produce a purple solution. The solvent was removed under reduced pressure. The residue was washed with ethanol (3 × 20 mL) and then dried under vacuum. Diffusion of ethanol into a tetrahydrofuran solution of the compound yielded purple crystals. Yield: 0.333 g (80%). ¹H NMR δ (ppm in CDCl₃): 10.29 (s, 2H, C(S)-NH), 8.43 (s, 2H, –NCHN–), 8.31 (s, 4H, –NCHN–), 7.88 (s, 4H, aromatic *H*), 6.63 (d, 16H, aromatic *H*), 6.54 (d, 16H, aromatic *H*), 6.37 (d, 8H, aromatic *H*), 6.29 (d, 4H, aromatic *H*), 6.09 (d, 4H, aromatic *H*), 3.72 (s, 24H, OCH₃), 3.70 (s, 6H, OCH₃), 3.63 (s, 6H, OCH₃). UV-vis, λ_{max} nm (ε , M⁻¹ cm⁻¹): 560 (2.6 × 10⁴). Anal. Calcd (%) for C₉₈H₉₆Mo₄N₁₄O₁₂S₂: C, 55.80; H, 4.59; N, 9.29. Found: C, 55.52; H, 4.58; N, 9.41.

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