Exceptionally strong electronic coupling between [Mo_2] units linked by substituted dianionic quinones†

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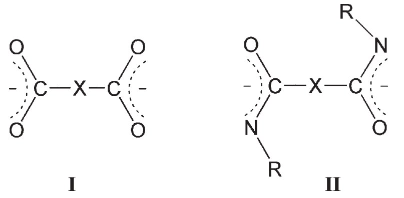
Ligands derived from N–CH_3 substituted benzoquinonemonoimines are exceedingly good facilitators of electronic communication between two quadruply bonded dimolybdenum units and provide record values for comproportionation constants

The study of electronic interactions between redox centers having structurally identical single metal sites mediated by various bridging groups has been a topic of great interest since the synthesis of the Creutz–Taube ion in the 1960s.[1] Conjugated electron carriers, such as polyenes, polypyrroles and polycondensed aromatics have been utilized as linkers to promote long-range electronic coupling.[2] These complexes not only provide an elegant model for the electron transfer processes in biochemistry, but also have potential for use as molecular wires and single-molecule transistors in a new computer generation.[3]

Recently our laboratory and others have been interested in analogues containing two dimetal species, usually Mo_2^{4+} units, linked by a variety of bridging ligands,[4] in which electronic communication between dimetal units can be conveniently evaluated. Because structural and spectroscopic properties of dimetal units are generally well understood such units provide several advantages for probing electronic coupling.[5] Electrochemistry has been extensively used to evaluate how linkers facilitate electronic communication between metal centers by using the well-known relationship that relates comproportionation constants with $\Delta E_{1/2}$ values, $K_C = e^{\Delta E_{1/2}/25.69}$.[6] By selectively changing the linkers, K_C's ranging from the statistical value of 4 to as much as 6.2×10^{13} have been observed.[7]

It should be mentioned that the most frequently used type of ligands, namely dianions of dicarboxylic acids (**I** in Scheme 1), led to low K_C values.[8] However, other work has shown that amidate ligands (**II**) possess attractive properties since such groups are much stronger Lewis bases than the carboxylate groups and substituents on the N atoms can be synthetically adjusted both sterically and electronically.[9] Electronic coupling in these amidate bridged compounds is usually much stronger than in those linked by the corresponding carboxylates. Other ligands that allow strong electronic communication between Mo_2 units are the dioxolene group (the anion of 2,5-dihydroxy-1,4-benzoquinone ($dhbq^{2-}$), **III** in Scheme 2, and its derivatives (**IV**), X = Cl and NO_2.[8b]

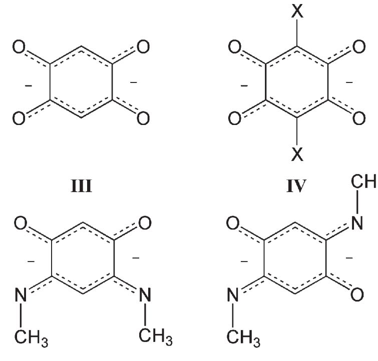


Scheme 1

Here we report that analogues of [Mo_2]dioxolene[Mo_2] ([Mo_2] represents an Mo_2(formamidinate)$_3$ unit) having two O atoms in the dioxolene linker replaced by isoelectronic N–CH_3 groups have been made and one of these compounds give the largest K_C yet known for species containing quadruply bonded Mo_2^{4+} units. These N-substituted benzoquinonemonoimines first made by Braunstein and co-workers[10] have attracted attention because they are antiaromatic having 6π + 6π electrons (Scheme 2). For the linker precursors, two isomers that differ in the position of the N atoms within the ring have been isolated, 1,5-dihydroxy-2,4-di(methylamino)benzene (**V**, *cis*) and 1,4-dihydroxy-2,5-dimethylaminebenzene (**VI**, *trans*).

The respective *pairs of pairs* having Mo_2 units, isomers **1** and **2**, were synthesized as shown in eqn (1) by substitution of the labile acetate ligand in $Mo_2(DAniF)_3(O_2CCH_3)$[11] by the more basic N-substituted benzoquinonemonoimines linkers.§ Here DAniF represents the anion *N*,*N'*-di-*p*-anisylformamidinate.

$$2Mo_2(DAniF)_3(O_2CCH_3) + H_2C_8H_8N_2O_2 \xrightarrow[\text{r.t.}]{\text{2NaOCH}_3\text{/THF}} [Mo_2(DAniF)_3]_2(C_8H_8N_2O_2) \quad (1)$$



Scheme 2

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† Electronic supplementary information (ESI) available: Tables of crystallography data and selected bond distances and angles. The UV-vis spectra of **1** and **2** and EPR spectrum of **1**$^+$. See DOI: 10.1039/b710804d

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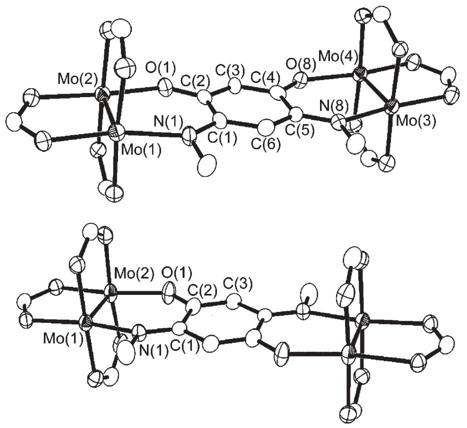

Fig. 1 The cores for compounds **1** and **2**. Thermal ellipsoids are drawn at the 40% probability level, and all *p*-anisyl groups and hydrogen atoms are omitted for clarity.

After routine treatment of the reaction mixtures, crystals of **1** formed by diffusion of ethanol into the solution of **1** dissolved in THF while crystals of **2** were obtained by diffusion of hexanes into solutions of **2** dissolved in CH_2Cl_2–acetone (1 : 1).¶ The core structures are shown in Fig. 1. Compound **1** crystallized in the space group $P2_1/c$ with one molecule in a general position and five disordered THF molecules. The linker and the two dimolybdenum units are essentially planar with the two Mo_2 axes essentially parallel to each other. The Mo–Mo distances are 2.0966(7) and 2.0945(7) Å and the separation between Mo_2 units is 8.816 Å. Compound **2** crystallized in the triclinic space group $P\bar{1}$ with $Z = 1$. There are also four interstitial CH_2Cl_2 molecules per unit cell. The two Mo_2 units are related by an inversion center located at the center of the linker C_6 ring. The two sets of quadruply bonded Mo_2 bonds and the linker are essentially flat, providing what appears to be a well conjugated platform for electron transport between the metal redox sites. This is different from the analogue linked by dioxolene ($dhbq^{2-}$) which has a chair conformation.[8b] The Mo–Mo distance of 2.0902(7) Å is within the typical range for Mo–Mo quadruple bonds.[6] The separation between the two Mo_2 units of 8.832 Å is similar to that in **1** and about 0.3 Å longer than that of the $dhbq^{2-}$ analogue (see Table 1). The C–C bond lengths within the linker C_6 ring show variations of 0.06–0.08 Å for both **1** and **2**, *i.e.*, C(1)–C(2) is long (1.457(5) Å) and C(2)–C(3) is short (1.389(5) Å) for **2**. The corresponding distances in **1** are similar. These large differences in bond distances suggest that the electron conjugation within the ring likely follows a 6π + 6π pattern as shown in Scheme 2.

The cyclic voltammogram (CV) of **1** in CH_2Cl_2 shows two well-separated, reversible waves at 310 and 1160 mV (*vs.* Ag/AgCl) (Fig. 2). These two redox waves correspond to two one-electron oxidation processes that take place at the $[Mo_2]$ centers (*vide infra*). The $\Delta E_{1/2}$ of 850 mV for **1**, represents the largest potential separation in compounds having two $[Mo_2]$ units joined by any of a large variety of linkers. The corresponding comproportionation constant for **1** is 2.34×10^{14}. For **2** the two $E_{1/2}$ values are 345 and 1125 mV. The slightly smaller $\Delta E_{1/2}$ of 780 mV corresponds to a K_C of 1.54×10^{13}. The large electronic communication and large K_C values are in accord with what has been observed for compounds containing these linkers and single metal units, M(acac), where M = Ni or Pd.[12]

The electrochemical data for **1**, **2** and selected $[Mo_2(DAniF)_3](L)[Mo_2(DAniF)_3]$ compounds are shown in Table 1 for comparison purposes. These data clearly shows that the family of compounds having benzoquinones and benzoquinonemonoimines have an exceptionally large ability to delocalize electrons with the *cis*-substituted *N*-methyl benzoquinonemonoimine being the best. It should be noted that the oxalate linker, which represents the best dicarboxylate linker for electron delocalization has a K_C many orders of magnitude smaller than **1**. Because C–C distances in each linker C_6 ring differ significantly (*vide supra*), electron delocalization in both isomers **1** and **2** is expected to extend through a 14-atom ring that includes the linker (Scheme 2) and the two dimolybdenum units, similarly to the $dhbq^{2-}$ analogue.[8b]

It should also be noted that the electronic spectra for **1** and **2** show intense absorption bands at 750 and 779 nm, respectively (see ESI†). Because the existence of low energy metal-to-ligand charge transfer (MLCT) is critical for the electronic coupling between the dimetal units by facilitating an 'electron hopping' pathway,[13] these MLCT transitions account not only for the green color of the compounds but are also consistent with the exceptional strong electronic coupling in these species.

Definite confirmation of the delocalized nature of the odd electron in the singly oxidized species 1^+ and 2^+ is provided by the EPR spectra taken on samples of the corresponding precursors that had been oxidized *in situ* by adding slightly less than one equivalent of $FeCp_2PF_6$. The EPR spectrum for 2^+ is given in Fig. 3 and that for 1^+ in the ESI.†

In both cases the *g* values are less than *ca.* 2.0 which are typical for organic radicals. The values of 1.944 for 1^+ and 1.947 for 2^+,

Table 1 Electrochemical data for **1**, **2** and selected $[Mo_2(DAniF)_3](L)[Mo_2(DAniF)_3]$ compounds (L = linker)

L	d^a/Å	$E_{1/2}{}^{1\ b}$	$E_{1/2}{}^{2\ b}$	$\Delta E_{1/2}$	K_C	Ref.
1	8.816	310	1160	850	2.34×10^{14}	This work
2	8.832	345	1125	780	1.54×10^{13}	This work
$dhbq^{2-}$	8.536	−200	563	763	7.92×10^{12}	8*b*
$ca^{2-\ c}$	8.718	−15	780	795	2.75×10^{13}	8*b*
$na^{2-\ c}$	—	45	861	816	6.23×10^{13}	8*b*
oxalate	6.953	294	506	212	3.8×10^{3}	7

[a] The distance *d* between the two $[Mo_2]$ units measured by the centers of two Mo_2 axis. [b] Potentials are in mV referenced to Ag/AgCl and $E_{1/2} = (E_{pa} + E_{pc})/2$ obtained from the CV for isomers **1** and **2**. [c] ca^{2-} = Chloranilate, na^{2-} = nitranilate.

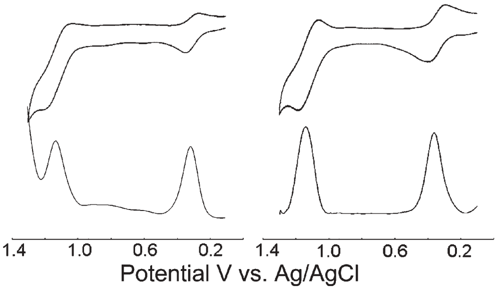

Fig. 2 CVs and the differential pulse voltammograms (DPVs) for **1** (left) and **2** (right) recorded in CH_2Cl_2 solution with potentials referenced to Ag/AgCl.

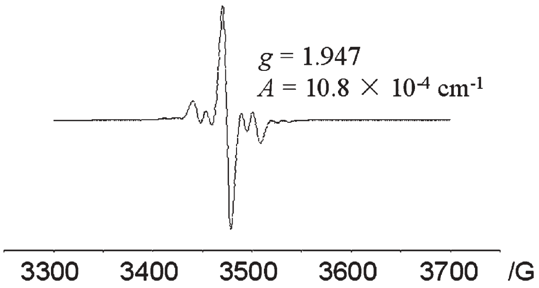

Fig. 3 X-Band EPR spectrum for **2**$^+$ in CH_2Cl_2 solution at room temperature. The simulated spectrum is in very good agreement with the experimental data as shown in the ESI.†

are consistent with a metal-based oxidation. More importantly the small hyperfine values of 11.8×10^{-4} cm^{-1} for **1**$^+$ and 10.8×10^{-4} for **2**$^+$ are characteristic of delocalized systems containing *pairs of pairs* with dimolybdenum units.[8] These *A* values are *ca.* 50% of those in analogous compounds having localized oxidations and that in the parent ion $Mo_2(DAniF)_4{}^+$.[14]

In conclusion, two isomers having $[Mo_2]$ units linked by N–CH_3 substituted benzoquinonemonoimines give *pairs of pairs* with an exceptionally large electronic coupling.

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Notes and references

§ *Experimental details*: All reactions and manipulations were performed under a nitrogen atmosphere, using either a drybox or standard Schlenk line techniques. Solvents were purified under argon using a Glass Contour solvent purification system or distilled over the corresponding drying agent under nitrogen. The starting materials, $Mo_2(DAniF)_3(O_2CCH_3)$[11] and the linker precursors for **IV** (1,5-dihydroxy-2,4-di(methylamino)benzene) and **V** (1,4-dihydroxy-2,5-di(methylamino)benzene)[10] were prepared according to reported procedures.

For the preparation of $[Mo_2(DAniF)_3]_2\{cis\text{-}C_6H_2(ONCH_3)_2\}$, **1**, 0.80 mL of a 0.50 M sodium methoxide solution in methanol was added slowly, with stirring, to a suspension of $Mo_2(DAniF)_3(O_2CCH_3)_2$ (406 mg, 0.400 mmol) and 1,5-dihydroxy-2,4-di(methylamino)benzene (33 mg, 0.20 mmol) in 30 mL of THF. The reaction mixture was stirred overnight and during this time the colour changed from yellow-brown to dark green. The solvent was removed under reduced pressure, and dichloromethane (20 mL) was added to the residue. The resulting mixture was filtered. The volume of the filtrate was reduced to a volume of about 5 mL under vacuum and 40 mL hexanes were added to precipitate a green solid. The solvent was then decanted and the solid was washed with ethanol (2 × 15 mL) and hexanes (2 × 15 mL), and dried under vacuum. The solid was dissolved in 15 mL of THF and the solution was then layered with ethanol. Dark green crystals formed within 2 days. Yield: 250 mg (60%). UV-vis, λ_{max}/nm (ε/M^{-1} cm^{-1}): 390 (8.0×10^2), 500 (4.0×10^2), 750 (6.6×10^3). Anal. Calc. for $C_{98}H_{98}Mo_4N_{14}O_{14}$ (**1**): C, 49.36 H, 4.23 N, 8.06. Found: C, 49.59; H, 4.10; N, 8.24%.

For the preparation of $[Mo_2(DAniF)_3]_2\{trans\text{-}C_6H_2(ONCH_3)_2\}$, **2**, a similar procedure as that for **1** was used starting from 1,4-dihydroxy-2,5-di(methylamino)benzene (33 mg, 0.20 mmol) and $Mo_2(DAniF)_3(O_2CCH_3)_2$ (406 mg, 0.400 mmol). Green crystals were obtained by diffusion of ethanol into a solution of the product in a mixture of CH_2Cl_2 and acetone (1 : 1). Yield: 210 mg (50%). UV-vis, λ_{max}/nm (ε/M^{-1} cm^{-1}): 383 (2.2×10^3), 511 (5.8×10^2), 779 (1.4×10^4). Anal. Calc. for $C_{98}H_{98}Mo_4N_{14}O_{14}$ (**2**): C, 56.37, H, 4.73 N, 9.39. Found: C, 56.35; H, 4.70; N, 9.35%.

¶ *Crystal data* for $[Mo_2(DAniF)_3]_2\{cis\text{-}C_6H_2(ONCH_3)_2\}\cdot5THF$, **1**·5THF, monoclinic, space group $P2_1/c$, a = 16.5233(18), b = 24.371(3), c = 29.569(3) Å, β = 106.110(2)°, V = 11440(2) Å^3, T = 213(2) K, Z = 4, $\mu(\lambda$ = 0.71073 Å) = 0.501 mm^{-1}, D_c = 1.417 Mg m^{-3}, 85184 reflections measured, 20356 unique, and 14709 ($I > 2\sigma(I)$) used in the calculations; $R1$ = 0.1030, $wR2$ = 0.1835. Interstitial solvent: C_4H_4O.

Crystal data for $[Mo_2(DAniF)_3]_2\{trans\text{-}C_6H_2(ONCH_3)_2\}\cdot4CH_2Cl_2$, **2**·$4CH_2Cl_2$, triclinic, space group $P\bar{1}$, a = 11.345(4), b = 16.008(6), c = 16.851(6) Å, α = 70.111(7), β = 73.723(6), γ = 70.823(6)°, V = 2668.7(17) Å^3, T = 213(2) K, Z = 1, $\mu(\lambda$ = 0.71073 Å) = 0.727 mm^{-1}, D_c = 1.505 Mg m^{-3}, 13608 reflections measured, 8836 unique, and 6169 ($I > 2\sigma(I)$) used in the calculations; $R1$ = 0.0907, $wR2$ = 0.1809. Interstitial solvent: CH_2Cl_2.

CCDC 652613 and 652614 for **1** and **2**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710804d

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