

Coupling Mo₂ⁿ⁺ units via dicarboxylate bridges

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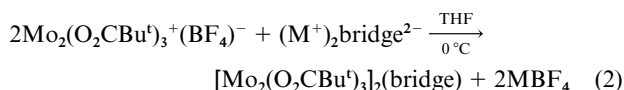
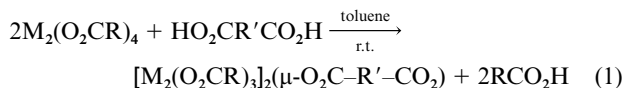
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The compounds Mo₂(DArF)₃(O₂CC₂H₅) **1**, (DArF)₃Mo₂-(O₂CCO₂)Mo₂(DArF)₃ **2** and (DArF)₃Mo₂(O₂CC₆F₄CO₂)-Mo₂(DArF)₃ **3** (DArF = *N,N'*-diarylformamidinate, Ar = *p*-anisyl) have been selectively prepared in good yield from the reactions of Mo₂(DArF)₃Cl₂ and the corresponding carboxylate salts in the presence of NaHBEt₃; their crystal structures, electronic spectra and electrochemistry have been studied.

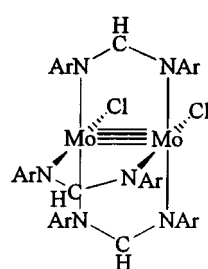
Compounds built upon M₂ⁿ⁺ units display many kinds of interesting properties and chemistry,¹ not the least of which is electrochemistry. Clearly, however, considerably more elaborate and interesting electrochemistry would be expected if two (or more) such centers could be connected so that they are electronically coupled. As a long-range goal it would be interesting to study species of the schematic type **I**. Synthesis and structural characterization of such species is clearly the first task, and it would seem equally clear that the "first of the first" task is to make and characterize the first member (**I**, *n* = 0).

A promising first step in this direction was reported in 1991 by Chisholm *et al.*² who described several species of type **I** (*n* = 0) wherein the metal atoms were Mo, W, the non-connective ligands were pivalate anions (Piv) and the connective ligands were dicarboxylates, specifically, oxalate, 1,4-C₆F₄(CO₂)₂²⁻, 1,8-anthracenedicarboxylate and 9,10-dihydroanthracene-1,8-dicarboxylate. They made some very significant observations concerning these eight compounds, but were unable to obtain crystallographic structural information on any of them. These were made by two types of reactions (1 and 2) using quadruply-bonded Mo₂⁴⁺ species as starting materials:



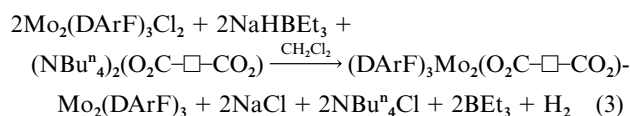
Unfortunately, serious synthetic limitations were found, *i.e.* the reversibility of the substitutions when using M₂(O₂CR)₄ compounds, and the formation of higher oligomers that compete with the targeted tetranuclear species. Reaction 1 is an equilibrium process, and thus the separation of the products is non-trivial.

We have recently employed compounds of the type **II** as starting materials³ in the preparation of compounds in which Mo₂(DArF)₃ (DArF = *N,N'*-diarylformamidinate) units are linked by μ-H, μ-OH and μ-O groups.⁴ A variety of Ar groups may be employed in the formamidinate ligands.⁵ We have now used a molecule of type **II** with Ar = *p*-MeOC₆H₄ and in this way we have cleanly made compounds of type **I** (*n* = 0) that can be characterized structurally. Two of these are described here.



II, Mo₂(DArF)₃Cl₂

The preparations[†] were carried out by the general reaction (3) and the crystallographic studies[‡] led to the structures



shown in Figs. 1 and 2. In **2** where the connective ligand is oxalate the main structural features that are relevant here are: (1) The oxalate connector is in an end-to-end (as opposed to a conceivable side-to-side) posture. (2) The entire Mo₂O₂CCO₂-Mo₂ unit is planar. (3) The Mo-Mo distances show that Mo-Mo quadruple bonds are retained. In **3**, the plane of the central C₆F₄ unit is rotated by 30.4° from the two coplanar Mo₂O₂C units.

The electrochemical results (Table 1) obtained on **2** and **3** are very similar to those obtained by Chisholm *et al.* on the pivalate analogues.²

Acknowledgements

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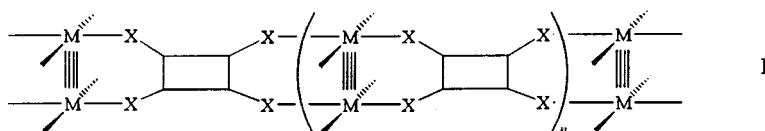


Table 1 Electrochemical data for compounds **1**, **2** and **3**

Compound ^a	$E_2(+/0)/\text{mV}^b$	$\Delta E_p/\text{mV}^c$	$E_2(2+/+)/\text{mV}$	$\Delta E_p/\text{mV}$	$\Delta E_2/\text{mV}^d$
Mo ₂ (DArF) ₄	119	90	—	—	—
1	218	74	—	—	—
Mo ₂ (Piv) ₄	850	78	—	—	—
2	260	64	472	68	212
Piv analogue	860	79	1140	110	280
3	332 ^e	133 ^e	—	—	41 ^f
Piv analogue	990	92	—	—	65

^a The cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer on 0.1 M (Buⁿ)₄NPF₆ solution (CH₂Cl₂) with Pt working and auxiliary electrodes and a Ag/AgCl reference electrode, and scan rate of 100 mV s⁻¹. All the potential values are referred to Ag/AgCl, and under the present experimental conditions, the $E_2(\text{Fc}^+/\text{Fc})$ was consistently measured at 440 mV. The values for pivalate analogues were taken from ref. 2, and have been converted to be referred to Ag/AgCl. ^b $E_2 = (E_{pa} + E_{pc})/2$. ^c $\Delta E_p = E_{pa} - E_{pc}$. ^d $\Delta E_2 = E_2(2+/+) - E_2(+/0)$. ^e E_2 and ΔE_p values for **3** are average values for both redox couples, i.e., 2+/0. ^f ΔE_2 for **3** was obtained from differential pulse voltammetry (rate = 2 mV s⁻¹, pulse amplitude = 10 mV).

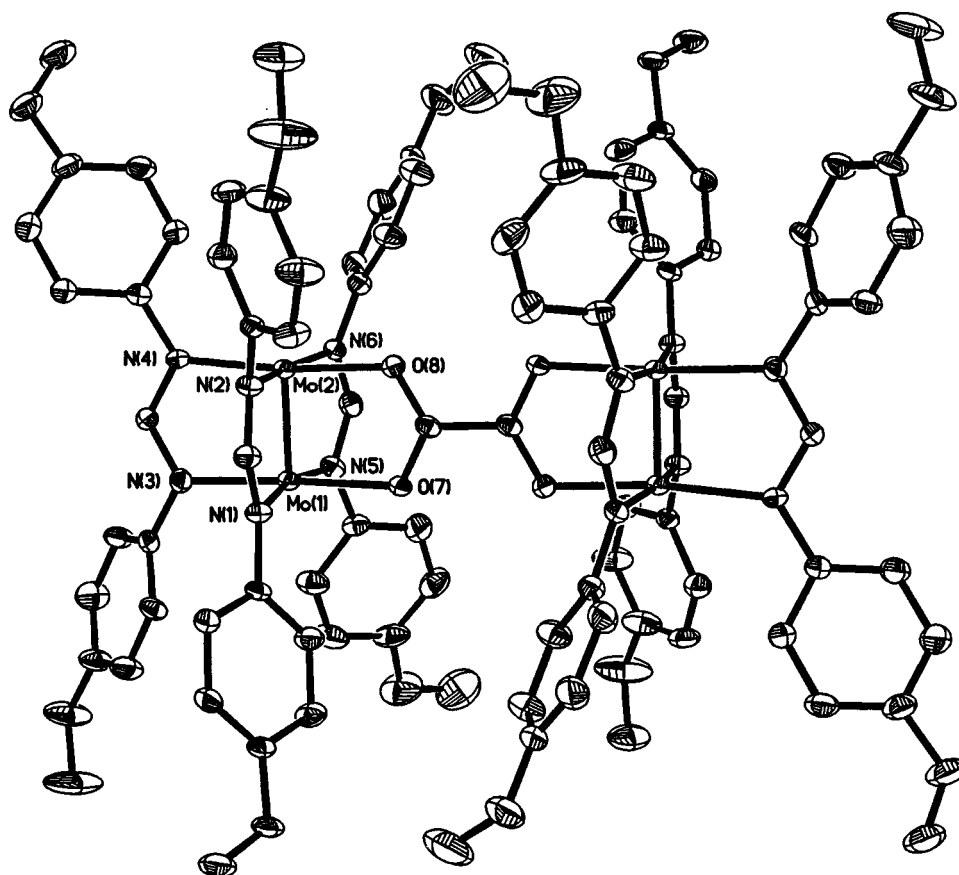


Fig. 1 The molecular structure of **2** in 2·2CH₂Cl₂. Selected bond distances (Å) and angles (°): Mo(1)–Mo(2) 2.0900(7), Mo(1)–O(7) 2.145(3), Mo(2)–O(8) 2.115(3), Mo–N (av) 2.141[7]; Mo(2)–Mo(1)–O(7) 90.9(1), Mo(1)–Mo(2)–O(8) 93.1(1), *cis*-N–Mo–O (av) 85.5[3], N(3)–Mo(1)–O(7) 176.8(2), N(4)–Mo(2)–O(8) 173.2(2), Mo–Mo–N (av) 92.7[6], *trans*-N–Mo–N (av) 169[1], *cis*-N–Mo–N (av) 94.4[4].

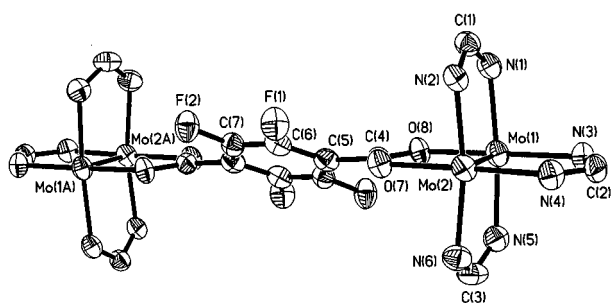


Fig. 2 A thermal ellipsoid drawing of the core of **3** in 3·2CH₂Cl₂·C₆H₁₄. Selected bond distances (Å) and angles (°): Mo(1)–Mo(2) 2.0902(9), Mo(1)–O(8) 2.124(5), Mo(2)–O(7) 2.162(5), Mo–N (av) 2.133[7]; Mo(1)–Mo(2)–O(7) 90.4(1), Mo(2)–Mo(1)–O(8) 93.1(1), *cis*-N–Mo–O (av) 86.2[7], N(3)–Mo(1)–O(8) 173.3(2), N(4)–Mo(2)–O(7) 177.4(2), Mo–Mo–N (av) 92.6[4], *trans*-N–Mo–N (av) 171[2], *cis*-N–Mo–N (av) 93.6[4].

Notes and references

† The following procedure describes the preparation of **2** [(DArF)₃Mo₂(O₂CCO₂)Mo₂(DArF)₃]. A similar method was used for **1** [Mo₂(DArF)₃(OCC₂H₅)] and **3** [(DArF)₃Mo₂(O₂CC₆F₄CO₂)Mo₂(DArF)₃]. To a mixture of Mo₂(DArF)₃Cl₂ (154 mg, 0.15 mmol) and (Buⁿ)₄N₂(C₂O₄) (43.0 mg, 0.075 mmol) in 60 mL of CH₂Cl₂ was added NaHBET₃ (1.0 mmol). The reaction mixture was stirred for 24 h at room temperature, then the volatile materials were removed under vacuum, and the resulting residue was washed with Et₂O (10 mL), EtOH (2 × 20 mL), H₂O (2 × 10 mL) and EtOH (10 mL). Finally it was extracted with CH₂Cl₂ (3 × 7 mL). The combined extracts were concentrated to 4 mL. Hexanes (25 mL) were then carefully added without stirring, and the solution was kept for 12 h at room temperature. The bright red block-shaped crystals that formed were collected by filtration and dried *in vacuo*. Yield: 80.5 mg, 53.6%. Single crystals suitable for X-ray analysis were grown by diffusion of hexanes into a CH₂Cl₂ solution. ¹H NMR δ (ppm, in CD₂Cl₂): 8.52 (s, 2H, NCHN), 8.47 (s, 4H, NCHN), 6.56 (m, 32H, aromatic), 6.45 (d, 8H, aromatic, ³J = 9.0), 6.23 (d, 8H, aromatic, ³J = 8.9 Hz), 3.67 (s, 24H, OCH₃), 3.64 (s, 12H, OCH₃). IR (KBr, cm⁻¹): 1700w, 1646w, 1609m, 1548s, 1504s, 1464m, 1441m, 1296s, 1246s, 1217s,

1178m, 1107w, 1034s, 938w, 829s, 771m, 590w, 536w. UV/VIS, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 296 (54300), 450 (6210). Compound **1**: Yield, 45.3%. ^1H NMR δ (ppm, in CD_2Cl_2): 8.46 (s, 2H, NCHN), 8.42 (s, 1H, NCHN), 6.65 (d, 8H, aromatic, $^3J = 8.9$), 6.51 (d, 8H, aromatic, $^3J = 9.0$), 6.43 (d, 4H, aromatic, $^3J = 9.0$), 6.22 (d, 4H, aromatic, $^3J = 8.9$), 3.70 (s, 12H, OCH_3), 3.63 (s, 6H, OCH_3), 2.85 (q, 2H, $\text{O}_2\text{CCH}_2\text{CH}_3$, $^3J = 7.6$), 1.34 (t, 3H, $\text{O}_2\text{CCH}_2\text{CH}_3$, $^3J = 7.6$ Hz). IR (KBr, cm^{-1}): 1609w, 1540s, 1503s, 1463m, 1292m, 1245s, 1217s, 1176m, 1108w, 1034s, 937w, 829m, 764w, 722w, 650w, 618w, 590w, 536w. UV/VIS, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 290 (sh), 303 (47900), 385 (sh), 430 (sh). Compound **3**: Yield, 46.5%. Single crystals suitable for X-ray analysis were grown by diffusion of hexanes into a CH_2Cl_2 solution. ^1H NMR δ (ppm, in CD_2Cl_2): 8.52 (s, 2H, NCHN), 8.51 (s, 4H, NCHN), 6.66 (d, 16H, aromatic, $^3J = 9.2$), 6.57 (d, 16H, aromatic, $^3J = 9.2$), 6.46 (d, 8H, aromatic, $^3J = 9.0$), 6.25 (d, 8H, aromatic, $^3J = 8.9$ Hz), 3.70 (s, 24H, OCH_3), 3.64 (s, 12H, OCH_3). IR (KBr, cm^{-1}): 1541s, 1501s, 1466m, 1459m, 1438w, 1388w, 1289m, 1245s, 1217s, 1178m, 1107m, 1035s, 993w, 938w, 828m, 765w, 742m, 644w, 589w, 468w. UV/VIS, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 297 (94370), 477 (8230). Elemental analyses were satisfactory for all compounds.

‡ Crystal data for $2 \cdot 2\text{CH}_2\text{Cl}_2$: $\text{C}_{94}\text{H}_{94}\text{Cl}_4\text{Mo}_4\text{N}_{12}\text{O}_{16}$, $M = 2173.37$, monoclinic, space group $P2_1/c$, $a = 13.998(2)$, $b = 17.441(3)$, $c = 20.229(1)$ Å, $\beta = 97.40(1)^\circ$, $U = 4898(1)$ Å³, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.678$ mm⁻¹. Data were collected at 213(2) K. The structure, refined on F^2 , converged for 6356 unique reflections and 596 parameters to give

$R1 = 0.052$ and $wR2 = 0.121$ and a goodness-of fit = 1.096. Crystal data for $3 \cdot 2\text{CH}_2\text{Cl}_2 \cdot \text{C}_6\text{H}_{14}$: $\text{C}_{106}\text{H}_{108}\text{Cl}_4\text{F}_4\text{Mo}_4\text{N}_{12}\text{O}_{16}$, $M = 2407.60$, triclinic, space group $P\bar{1}$, $a = 9.791(1)$, $b = 15.756(2)$, $c = 18.090(3)$ Å, $\alpha = 76.65(1)^\circ$, $\beta = 79.61(1)^\circ$, $\gamma = 87.63(1)^\circ$, $U = 2670.8(6)$ Å³, $Z = 1$, $\mu(\text{Mo-K}\alpha) = 0.635$ mm⁻¹. Data were collected at 213(2) K. The structure, refined on F^2 , converged for 6664 unique reflections and 647 parameters to give $R1 = 0.068$ and $wR2 = 0.166$ and a goodness-of-fit = 1.036. CCDC reference number 186/1126. See <http://www.rsc.org/suppdata/dat/1998/3151/> for crystallographic files in .cif format.

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