Coupling Mo_2^{n+} units *via* dicarboxylate bridges

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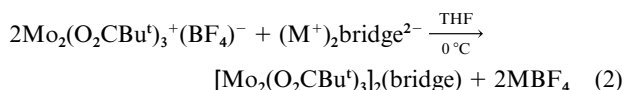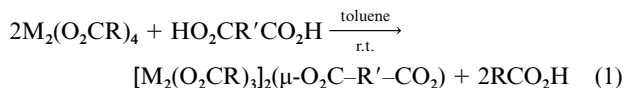 *E-mail: cotton@tamu; edumurillo@tamu.edu*
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The compounds $Mo_2(DArF)_3(O_2CC_2H_5)$ **1**, $(DArF)_3Mo_2$-$(O_2CCO_2)Mo_2(DArF)_3$ **2** and $(DArF)_3Mo_2(O_2CC_6F_4CO_2)$-$Mo_2(DArF)_3$ **3** (DArF = *N*,*N*′-diarylformamidinate, Ar = *p*-anisyl) have been selectively prepared in good yield from the reactions of $Mo_2(DArF)_3Cl_2$ and the corresponding carboxylate salts in the presence of $NaHBEt_3$; their crystal structures, electronic spectra and electrochemistry have been studied.

Compounds built upon M_2^{n+} 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, $1,4-C_6F_4(CO_2)_2^{2-}$, 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 Mo_2^{4+} species as starting materials:
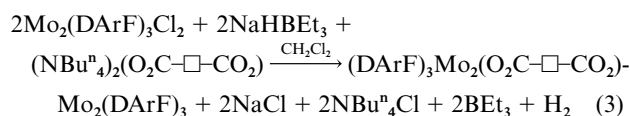
$$2M_2(O_2CR)_4 + HO_2CR'CO_2H \xrightarrow[\text{r.t.}]{\text{toluene}}$$
$$[M_2(O_2CR)_3]_2(\mu\text{-}O_2C\text{-}R'\text{-}CO_2) + 2RCO_2H \quad (1)$$

$$2Mo_2(O_2CBu^t)_3^+(BF_4)^- + (M^+)_2\text{bridge}^{2-} \xrightarrow[\text{0 °C}]{\text{THF}}$$
$$[Mo_2(O_2CBu^t)_3]_2(\text{bridge}) + 2MBF_4 \quad (2)$$

Unfortunately, serious synthetic limitations were found, *i.e.* the reversibility of the substitutions when using $M_2(O_2CR)_4$ 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 materials[3] in the preparation of compounds in which $Mo_2(DArF)_3$ (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-$MeOC_6H_4$ 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.
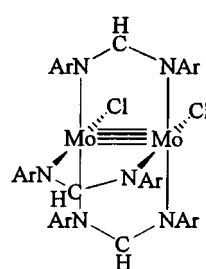
II, $Mo_2(DArF)_3Cl_2$

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

$$2Mo_2(DArF)_3Cl_2 + 2NaHBEt_3 +$$
$$(NBu^n_4)_2(O_2C\text{-}\square\text{-}CO_2) \xrightarrow{CH_2Cl_2} (DArF)_3Mo_2(O_2C\text{-}\square\text{-}CO_2)\text{-}$$
$$Mo_2(DArF)_3 + 2NaCl + 2NBu^n_4Cl + 2BEt_3 + H_2 \quad (3)$$

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 $Mo_2O_2CCO_2$-Mo_2 unit is planar. (3) The Mo–Mo distances show that Mo–Mo quadruple bonds are retained. In **3**, the plane of the central C_6F_4 unit is rotated by 30.4° from the two coplanar Mo_2O_2C 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

I
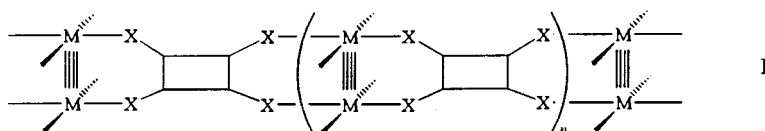
Compound[a]	$E_{\frac{1}{2}}(+/0)$/mV[b]	ΔE_p/mV[c]	$E_{\frac{1}{2}}(2+/+)$/mV	ΔE_p/mV	$\Delta E_{\frac{1}{2}}$/mV[d]
Mo$_2$(DArF)$_4$	119	90	—	—	—
1	218	74	—	—	—
Mo$_2$(Piv)$_4$	850	78	—	—	—
2	260	64	472	68	212
Piv analogue	860	79	1140	110	280
3	332[e]	133[e]	—	—	41[f]
Piv analogue	990	92	—	—	65

[a] The cyclic votammograms were recorded on a BAS 100 electrochemical analyzer on 0.1 M (Bu^n)$_4$NPF$_6$ solution (CH$_2$Cl$_2$) 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 $E_{\frac{1}{2}}$(Fc$^+$/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] $E_{\frac{1}{2}} = (E_{pa} + E_{pc})/2$. [c] $\Delta E_p = E_{pa} - E_{pc}$. [d] $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}(2+/+) - E_{\frac{1}{2}}(+/0)$. [e] $E_{\frac{1}{2}}$ and ΔE_p values for **3** are average values for both redox couples, i.e., 2+/0. [f] $\Delta E_{\frac{1}{2}}$ for **3** was obtained from differential pulse votammetry (rate = 2 mV s^{-1}, pulse amplitude = 10 mV).
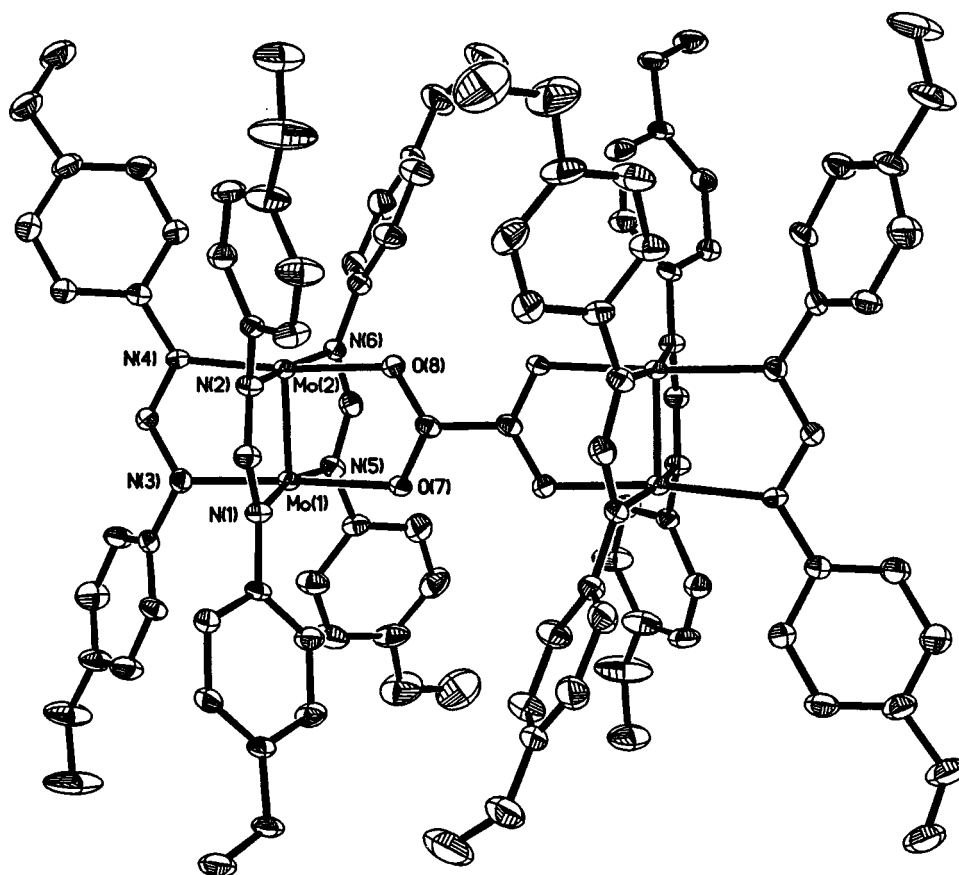

Fig. 1 The molecular structure of **2** in **2**·2CH$_2$Cl$_2$. Selected bond distances (Å) and angles (°): Mo(1)–Mo(2) 2.0900(7), Mo(1)–O(7) 2.145(3), Mo(2)–O(8) 2.115(3), Mo–N (av) 2.141[7]; Mo(2)–Mo(1)–O(7) 90.9(1), Mo(1)–Mo(2)–O(8) 93.1(1), *cis*-N–Mo–O (av) 85.5[3], N(3)–Mo(1)–O(7) 176.8(2), N(4)–Mo(2)–O(8) 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].
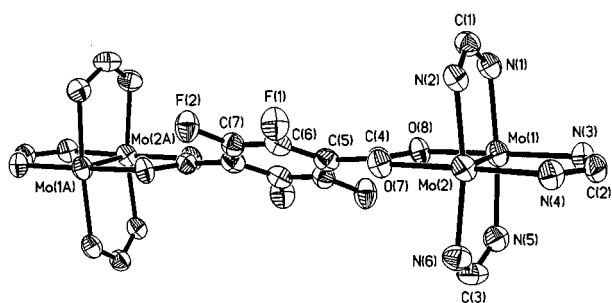

Fig. 2 A thermal ellipsoid drawing of the core of **3** in **3**·2CH$_2$Cl$_2$· C$_6$H$_{14}$. Selected bond distances (Å) and angles (°): Mo(1)–Mo(2) 2.0902(9), Mo(1)–O(8) 2.124(5), Mo(2)–O(7) 2.162(5), Mo–N (av) 2.133[7]; Mo(1)–Mo(2)–O(7) 90.4(1), Mo(2)–Mo(1)–O(8) 93.1(1), *cis*-N–Mo–O (av) 86.2[7], 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)$_3$-Mo$_2$(O$_2$CCO$_2$)Mo$_2$(DArF)$_3$]. A similar method was used for **1** [Mo$_2$-(DArF)$_3$(OCC$_2$H$_5$)] and **3** [(DArF)$_3$Mo$_2$(O$_2$CC$_6$F$_4$CO$_2$)Mo$_2$(DArF)$_3$]. To a mixture of Mo$_2$(DArF)$_3$Cl$_2$ (154 mg, 0.15 mmol) and (Bu$^n_4$N)$_2$-(C$_2$O$_4$) (43.0 mg, 0.075 mmol) in 60 mL of CH$_2$Cl$_2$ was added NaHBEt$_3$ (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 Et$_2$O (10 mL), EtOH (2 × 20 mL), H$_2$O (2 × 10 mL) and EtOH (10 mL). Finally it was extracted with CH$_2$Cl$_2$ (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 CH$_2$Cl$_2$ solution. ^{1}H NMR δ (ppm, in CD$_2$Cl$_2$): 8.52 (s, 2H, NC*H*N), 8.47 (s, 4H, NC*H*N), 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, OC*H*$_3$), 3.64 (s, 12H, OC*H*$_3$). IR (KBr, cm^{-1}): 1700w, 1646w, 1609m, 1548s, 1504s, 1464m, 1441m, 1296s, 1246s, 1217s,

1178m, 1107w, 1034s, 938w, 829s, 771m, 590w, 536w. UV/VIS, λ_{max}/nm (ε/M^{-1} cm^{-1}): 296 (54300), 450 (6210). Compound **1**: Yield, 45.3%. ^{1}H NMR δ (ppm, in CD$_2$Cl$_2$): 8.46 (s, 2H, NC*H*N), 8.42 (s, 1H, NC*H*N), 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, OC*H*$_3$), 3.63 (s, 6H, OC*H*$_3$), 2.85 (q, 2H, O$_2$CC*H*$_2$CH$_3$, $^3J = 7.6$), 1.34 (t, 3H, O$_2$CCH$_2$C*H*$_3$, $^3J = 7.6$ 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, λ_{max}/nm (ε/M^{-1} 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$_2$Cl$_2$ solution. ^{1}H NMR δ (ppm, in CD$_2$Cl$_2$): 8.52 (s, 2H, NC*H*N), 8.51 (s, 4H, NC*H*N), 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, OC*H*$_3$), 3.64 (s, 12H, OC*H*$_3$). 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, λ_{max}/nm (ε/M^{-1} cm^{-1}): 297 (94370), 477 (8230). Elemental analyses were satisfactory for all compounds.

‡ Crystal data for **2**·2CH$_2$Cl$_2$: C$_{94}$H$_{94}$Cl$_4$Mo$_4$N$_{12}$O$_{16}$, $M = 2173.37$, monoclinic, space group $P2_1/c$, $a = 13.998(2)$, $b = 17.441(3)$, $c = 20.229(1)$ Å, $\beta = 97.40(1)°$, $U = 4898(1)$ Å^3, $Z = 2$, μ(Mo-Kα) = 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**·2CH$_2$Cl$_2$·C$_6$H$_{14}$: C$_{106}$H$_{108}$Cl$_4$F$_4$Mo$_4$N$_{12}$O$_{16}$, $M = 2407.60$, triclinic, space group $P\bar{1}$, $a = 9.791(1)$, $b = 15.756(2)$, $c = 18.090(3)$ Å, $\alpha = 76.65(1)°$, $\beta = 79.61(1)°$, $\gamma = 87.63(1)°$, $U = 2670.8(6)$ Å^3, $Z = 1$, μ(Mo-Kα) = 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.

1 F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, Oxford University Press, Oxford, 2nd edn., 1993.
2 R. H. Cayton, M. H. Chisholm, J. C. Huffman and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1991, **113**, 8709.
3 F. A. Cotton, G. T. Jordan IV, C. A. Murillo and J. Su, *Polyhedron*, 1997, **16**, 1831.
4 F. A. Cotton, L. M. Daniels, G. T. Jordan IV, C. Lin and C. A. Murillo, *Inorg. Chem. Commun.*, 1998, **1** 109; F. A. Cotton, L. M. Daniels, G. T. Jordan IV, C. Lin and C. A. Murillo, *J. Am. Chem. Soc.*, 1998, **120**, 3398.
5 C. Lin, J. D. Protasiewicz, E. T. Smith and T. Ren, *Inorg. Chem.*, 1996, **35**, 6422.

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