

Square and Triangular Arrays Based on Mo_2^{4+} and Rh_2^{4+} Units

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We have recently reported¹ that $\text{Mo}_2(\text{DArF})_3^+$ units (DArF represents an N,N' -diarylformamidinate anion) may be linked by linear or quasilinear dicarboxylate anions, and this is also true of $\text{Rh}_2(\text{DArF})_3^+$ units.² With this in mind, we turned to the possibility of making polygons by using similar linking groups and $\text{M}_2(\text{DArF})_2^{2+}$ corner pieces. The first step was to prepare suitable precursors of these corner pieces, and for this purpose we chose compounds containing the $[\text{Mo}_2(\text{DArF})_2(\text{CH}_3\text{CN})_4]^{2+}$ ions. These were prepared and characterized as their BF_4^- salts with $\text{Ar} = p\text{-MeOC}_6\text{H}_4$.³

With suitable precursors for corner pieces in hand, we proceeded to link them, using for this purpose oxalate, tetrafluorophthalate, and ferrocene-1,1'-dicarboxylate dianions. With the dimolybdenum corner pieces, we obtained squares, of the general type I shown in Scheme 1.⁴ As representative examples, we present the structures of the squares linked by oxalate and ferrocene-1,1'-dicarboxylate dianions.⁵ Drawings of these are shown in Figures 1 and 2. The crystals of **1** contain a large number of CH_2Cl_2 molecules, owing to the large lacunae in the cyclic, though rigid, molecules. Some of these solvent molecules are quite disordered on their sites. Compound **2** has been characterized spectroscopically; its crystal structure has not been carried out yet because the crystals quickly lose solvent. Nevertheless, the structures of **1** and **3** establish that the square tetramers are formed,

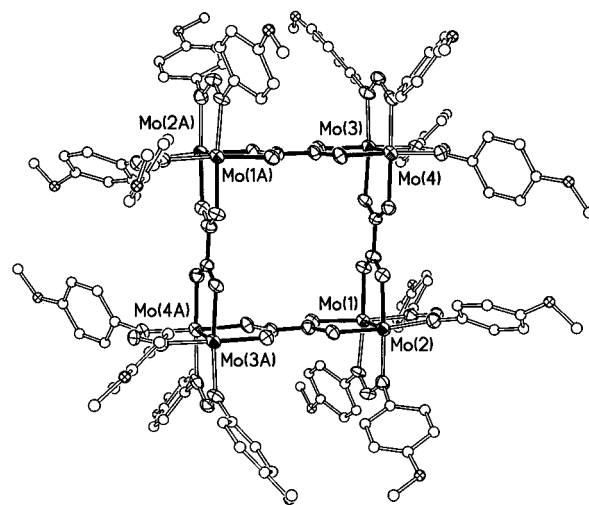
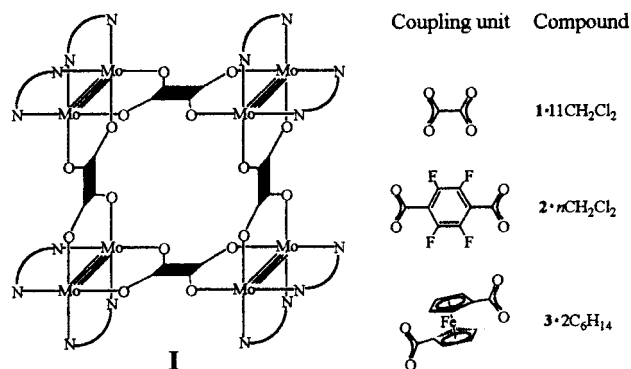


Figure 1. Molecular structure of **1** in $1 \cdot 11\text{CH}_2\text{Cl}_2$. Selected bond distances (Å) are: Mo(1)–Mo(2) 2.0865(8), Mo(3)–Mo(4) 2.0940(8), Mo–N (av) 2.111(3), Mo–O (av) 2.129(4).

Scheme 1



as expected. We are now seeking to fill these holes with single molecules of appropriate size so as to have just one guest molecule in each, hopefully in an ordered way. In the case of the oxalate-linked tetramer, where a high degree of redox coupling between the several $\text{Mo}_2^{4+} \rightarrow \text{Mo}_2^{5+}$ oxidations was expected, the electrochemistry has been examined in detail. Some of these results, given in Figure 3, show three consecutive one-electron oxidation processes. The values of $E_{1/2}$ (vs Ag/AgCl and based on $E_{1/2} = E_p + E_{\text{pu}}/2$, $E_{\text{pu}} = 25$ mV) are 407, 567, and 661 mV, for steps I, II, and III, respectively. The difference of 160 mV between the potentials $E_{1/2}(\text{II})$ and $E_{1/2}(\text{I})$, and 254 mV between $E_{1/2}(\text{III})$ and $E_{1/2}(\text{I})$ clearly indicate there is electronic coupling between these processes. The expected values for three consecutive one-electron oxidations occurring at three initially identical noninteracting sites would be 35.6 and 56.5 mV, respectively, based on the equation $E_k - E_j = (2RT/F) \ln k$ at 25 °C.⁶

It seemed reasonable to expect that with $\text{Rh}_2(\text{DArF})_2^{2+}$ corner pieces square tetramers similar to those just described for molybdenum would be easily formed, and indeed a molecule analogous to **1**, namely, $[\text{Rh}_2(\text{DArF})_2(\mu_4\text{-C}_2\text{O}_4)]_4$ (**4**), has been made⁷ and structurally characterized.⁸ However, as an example par excellence that nothing (or at least very little) can be taken completely for granted in chemistry, our first attempt to make a rhodium compound of type I linked by oxalate groups gave instead the triangular molecule $[\text{Rh}_2(\text{DArF})_2(\mu_4\text{-C}_2\text{O}_4)]_3$ (**5**), the structure

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(4) The general experimental conditions were described in ref 1. Elemental analyses were satisfactory for all compounds. The following procedure describes the preparation of **1**·11 CH_2Cl_2 . A similar method was used for **2**· $n\text{CH}_2\text{Cl}_2$ and **3**·2 C_6H_{14} . To a stirred solution of $[\text{Mo}_2(\text{DArF})_2(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (312 mg, 0.30 mmol) in 30 mL of CH_3CN was added $[\text{Bu}_4\text{N}]_2[\text{C}_2\text{O}_4]$ (180 mg, 0.31 mmol) in 20 mL of CH_3CN . An immediate reaction took place with the formation of a bright red precipitate, which was collected, washed several times with CH_3CN , and dried. The crude product was extracted with CH_2Cl_2 (3 × 5 mL). Hexanes were then carefully layered on the top to afford a bright red crystalline material after 7 days diffusion. Yield, 205 mg, 86% (after elimination of the interstitial molecules). ¹H NMR δ (ppm, in CD_2Cl_2) 8.57 (s, 8H, -NCHN-), 6.65 (dd, 64H, aromatic), 3.70 (s, 48H, -OCH₃). Dark red compound **2**: yield, 85%. ¹H NMR δ (ppm, in CD_2Cl_2) 8.57 (s, 8H, -NCHN-), 6.71 (m, 64H, aromatic), 3.71 (s, 48H, -OCH₃). Yellow compound **3**: yield, 80%. ¹H NMR δ (ppm, in CD_2Cl_2) 8.68 (s, 8H, -NCHN-), 6.69 (m, 64H, aromatic), 5.05 (d, 16H, Cp ring), 4.16 (t, 16H, Cp ring), 3.69 (s, 48H, -OCH₃).

(5) Crystal data for **1**·11 CH_2Cl_2 : $\text{C}_{139}\text{H}_{142}\text{Cl}_{22}\text{Mo}_8\text{N}_{16}\text{O}_{32}$, $M = 4096.11$, monoclinic, space group $P2_1/n$, $a = 19.089(1)$ Å, $b = 18.708(1)$ Å, $c = 23.708(1)$ Å, $\beta = 90.70(1)^\circ$, $V = 8465.9(7)$ Å³, $Z = 2$, $\mu(\text{Mo K}\alpha) = 0.991$ mm⁻¹. Data were collected at 213(2) K. The structure, refined on F^2 , converged for 10993 unique reflections and 960 parameters to give $R1 = 0.075$ and $wR2 = 0.172$ and a goodness-of fit = 1.090. Crystal data for **3**·2 C_6H_{14} : $\text{C}_{180}\text{H}_{180}\text{Fe}_4\text{Mo}_8\text{N}_{16}\text{O}_{32}$, $M = 4070.32$, triclinic, space group $P1$, $a = 16.951(3)$ Å, $b = 17.07(1)$ Å, $c = 20.935(8)$ Å, $\alpha = 103.84(2)^\circ$, $\beta = 104.85(4)^\circ$, $\gamma = 105.92(3)^\circ$, $V = 5309(4)$ Å³, $Z = 1$, $\mu(\text{Mo-K}\alpha) = 0.782$ mm⁻¹. Data were collected at 273(2) K. The structure, refined on F^2 , converged for 13143 unique reflections and 1026 parameters to give $R1 = 0.085$ and $wR2 = 0.206$ and a goodness-of fit = 1.077.

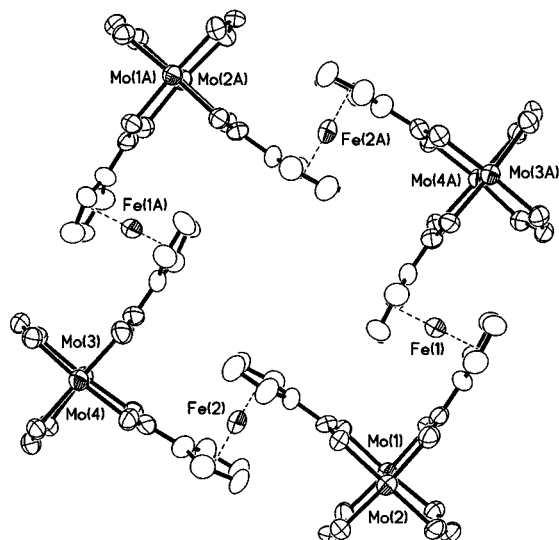


Figure 2. Thermal ellipsoid drawing of the core of **3** in $3 \cdot 2\text{C}_6\text{H}_{14}$. Selected bond distances (Å) are: Mo(1)–Mo(2) 2.084(2), Mo(3)–Mo(4) 2.075(2), Mo–N (av) 2.121(7), Mo–O (av) 2.132(3). Aryl groups on the ligands are omitted.

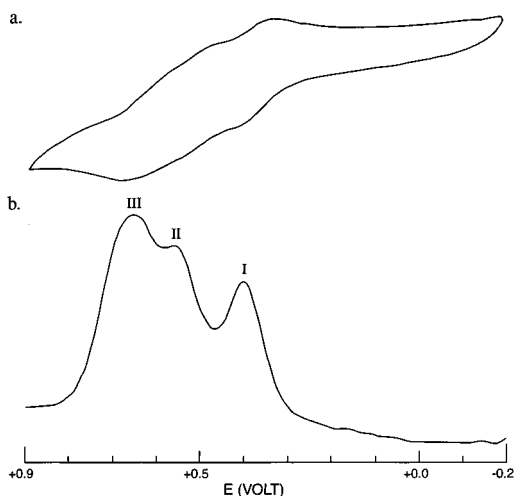


Figure 3. Cyclic voltammogram (a) and differential pulse voltammogram (b) for compound **1**, details of experimental conditions have been described in ref 1.

of which is shown in Figure 4.⁹ The preparative reaction¹⁰ proceeded quantitatively to afford well-formed red crystals leaving a colorless supernatant liquid. The ^1H NMR spectra of these two compounds are identical within experimental error. Thus, it is impossible to tell whether there is only one species in solution or the NMR spectra are coincidentally the same. However, the electrochemical behavior is distinctly different. There are three measurable $E_{1/2}$ for each complex. For the square **4**, they are at 445, 845, and 1109 mV; those for the triangular **5** are at 509,

(7) Compound **4** was synthesized by stirring a CH_3CN solution of $[\text{Rh}_2(\text{DArF})_2(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ and $[\text{Bu}_4\text{N}]_2[\text{C}_2\text{O}_4]$ in a 1:10 ratio for 24 h. The crude product was obtained by filtration, and then extracted in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (v/v, 10/1). Ether was then carefully layered on the top of the extract to afford crystalline material after one week. ^1H NMR δ (ppm, in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$) 7.28 (b, 8H, $-\text{NCHN}-$), 6.89 (d, 32H, aromatic), 6.63 (d, 32H, aromatic), 3.69 (s, 48H, $-\text{OCH}_3$).

(8) Crystal data for **4**: triclinic, space group $P\bar{1}$, $a = 14.631(2)$ Å, $b = 17.977(2)$ Å, $c = 18.578(2)$ Å, $\alpha = 104.80(1)^\circ$, $\beta = 96.69(1)^\circ$, $\gamma = 96.78(1)^\circ$, $V = 4636(1)$ Å³, $Z = 1$. The other structural details will be given elsewhere.

(9) Crystal data for **5**: triclinic, space group $P\bar{1}$, $a = 23.035(7)$ Å, $b = 23.483(6)$ Å, $c = 25.154(5)$ Å, $\alpha = 81.37(4)^\circ$, $\beta = 78.63(3)^\circ$, $\gamma = 81.68(3)^\circ$, $V = 13095(6)$ Å³, $Z = 2$. The other structural details will be given elsewhere.

(10) Compound **5** was synthesized similarly to **4**, except that the ratio of $[\text{Rh}_2(\text{DArF})_2(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ to $[\text{Bu}_4\text{N}]_2[\text{C}_2\text{O}_4]$ was 1:1.

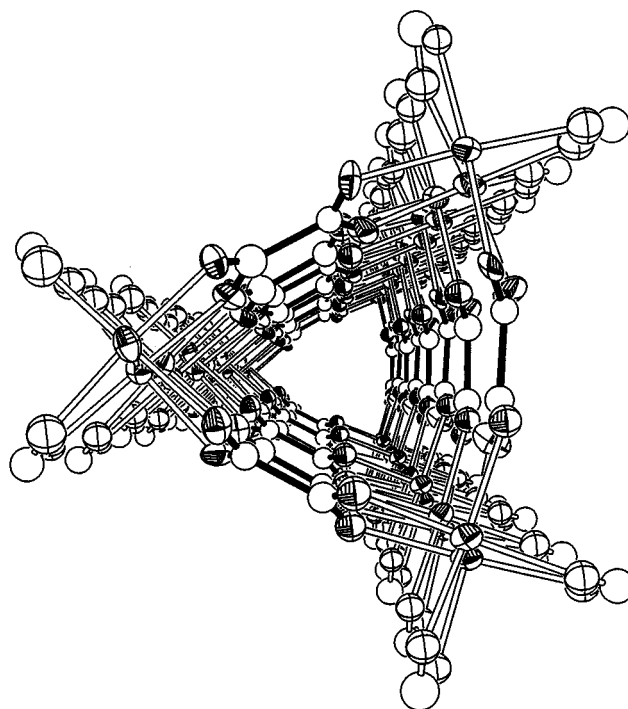


Figure 4. View of the stacking pattern in **5**. CH_3CN molecules in the central tunnel and elsewhere are omitted for clarity. The nonplanarity of the bridging oxalate ions is evident. A few important bond distances (Å) are: Rh–Rh (av) 2.457(2), Rh–N (av) 2.024(5), Rh–O (av) 2.078(3).

1125, and 1441 mV vs the Ag/AgCl couple. A comprehensive study of the solution behavior of these two compounds is underway.

The most important thing about the isolation and structural characterization of the triangular species **5** is that, while triangular species have been postulated in several systems based on Pd^{2+} or Pt^{2+} corner pieces,¹¹ their existence has not heretofore been proven.

We abjure any conventional, wishy-washy locutions (e.g., “we do not fully understand” or “it is not quite clear”) and say forthrightly that for the present we simply do not know why this strained triangular structure, cf. the bowed oxalate bridges, is ever adopted rather than the expected square one. There is at least one precedent of a system that produces somewhat related triangular and square species, namely a triangular hexacobalt complex of cyclo[18]carbon and a square octacobalt complex of cyclo[24]carbon, respectively.¹² A report of possible formation of squares containing dinuclear units has also appeared for a series of molybdenum dicarboxylates,¹³ but for these noncrystalline compounds, rigorous structural characterization has not been accomplished.

Obviously, what we are reporting here is but the tip of the iceberg. Other results are already in hand, and the investigation is being extended widely.

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Supporting Information Available: Tables of crystallographic data including diffractometer and refinement data, final coordinates, bond lengths, bond angles, and anisotropic displacement parameters for molecules **1** and **3** (PDF) and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. JA9901563

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