The designed ‘self-assembly’ of a three-dimensional molecule containing six quadruply-bonded Mo_2^{4+} units

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Reaction of 1,3,5-tricarboxylatobenzene (trimesic acid) with $[Mo_2(DAniF)_2(MeCN)_4][BF_4]_2$ (DAniF = *N*,*N′*-di-*p*-anisylformamidinate) leads to the quantitative formation of a large tetrahedral molecule containing four triply-bridging $C_6H_3(CO_2)_3$ (trimesic acid trianion) groups and six $Mo_2(DAniF)_2$ units; the structure has been determined by X-ray crystallography.

Since the early 1990s there has been a lot of research activity directed toward the synthesis of nanosize polynuclear coordination compounds having two or more metal atoms assembled by suitable ligands into dinuclear (linear), trinuclear (triangular), and tetranuclear (square) molecules. Until very recently all of the reported work was done with building blocks consisting of single metal atoms associated with a few ligands (*e.g.* $[Pd(en)]^{2+}$, $[Pt(Ph_2PCH_2CH_2CH_2PPh_2)]^{2+}$, *etc.*) and these were linked by linear bidentate ligands such as 4,4′-dipyridine.[1]

Recently, in keeping with Chisholm’s assertion[2] (‘Anything one can do, two can do, too—and it’s more interesting’), we have been developing this kind of chemistry with dimetal units, M_2^{n+}, where M = Mo, Rh, W, Ir, and others.[3] The metal-containing building blocks that we use are entities such as $[Mo_2(DAniF)_3]^+$ and $[Rh_2(DAniF)_2]^{2+}$, in which the remaining coordination sites are occupied by the easily displaced ligand, acetonitrile. In this way we have created molecules of the types shown in Scheme 1, where the dinuclear metal units are symbolized by the nicked circles and the linkers are dicarboxylate dianions, symbolized by the heavy double arrows. These linkers can be enormously varied; a few examples are shown in Scheme 2. In this way we have achieved results topologically equivalent to many of those obtained by using single metal centers. All these results, however, have been in the realm of one- or two-dimensional arrays. What about three-dimensional assemblages?

In the realm of single-metal compounds, although imaginative projections of what might be doable in three dimensions have not been lacking,[1a,b] relatively few actual syntheses have been reported,[4–9] and only a few three-dimensional assemblages have been confirmed by X-ray crystallography. Two[4] contain a tetrahedral array of four iron atoms, two others a set of six copper or silver atoms.[5] Fujita *et al.* have characterized an assembly of six metal atoms (Pd) connected by four trifunctional linkers[6] and another Pd compound has also been characterized crystallographically.

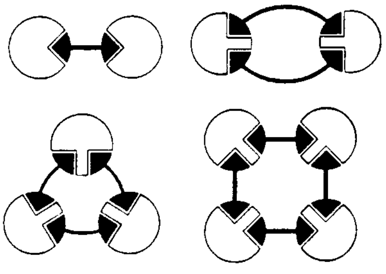
The molecule reported here was obtained in the so-called ‘self-assembly’ manner, but by design.† The key to this synthesis was, as in other cases,[6–9] the use of a trifunctional linker that imparts threefold symmetry to the assemblage.

The molecular structure is shown in Fig. 1.‡ The centroids of the four six-membered rings define a tetrahedron and the centroids of the six Mo_2^{4+} units define an octahedron. The overall idealized symmetry is T_d, but crystallographically there is only a single twofold axis that bisects the bonds between the atoms Mo(4), Mo(4A) and Mo(3), Mo(3A). The ^1H NMR spectrum is consistent with this high symmetry; it shows only one resonance for all of the 12 aromatic protons on the $C_6H_3(CO_2)_3^{3-}$ linkers and the signals for the twelve *N*,*N′*-di-*p*-anisylformamidinate ligands show them to be equivalent. Refinement of the structure presented some challenge, due to disorder in many of the peripheral anisyl groups and some disorder of the dimetal units spanning the two-fold axis. Disorder was also present at several of the 20 different sites containing interstitial acetonitrile and dichloromethane. The most prominent instance of CH_2Cl_2 is a disordered ‘ball’ of the solvent located directly in the center of the metal-complex cage. Careful modeling and judicious use of restraints allowed successful refinement of the whole model.

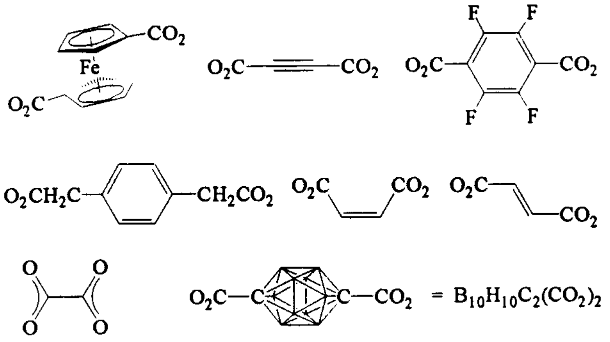
Cyclic and differential pulse voltammetries show three distinct reversible oxidation steps at $E_{1/2}$ of 268, 330 and 370 mV *vs.* the Ag/AgCl couple.§ Based on DPV, the ratio of the number of electrons involved in these steps is 1 : 1 : 1, respectively. Using $Mo_2[(m\text{-}CF_3C_6H_4N)_2CH]_4$ as a standard, these have been assigned as one-electron oxidation steps.

In closing, we make two observations. In the preparation of several of the previously reported three-dimensional assemblages, the use of a template or guest was said to be essential[8] or at least preferred. In the present case this is not so. We are not unmindful, however that the cavity in our molecule is well suited to being occupied by a variety of medium size entities, *inter alia*, N_2 and the noble gases.

We also note that while this type of chemistry has often been characterized[7] as using ‘metal atoms to control self-assembly of



Scheme 1



Scheme 2

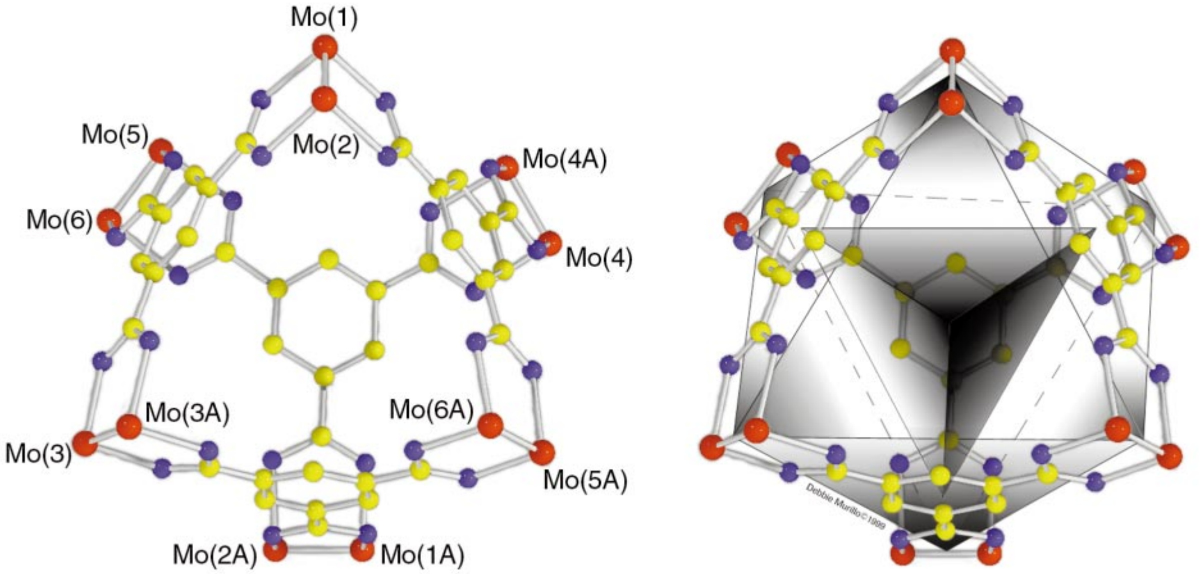


Fig. 1 The core of the molecular structure of [Mo$_2$(DAniF)$_2$]$_6$[μ$_3$-C$_6$H$_3$(CO$_2$)$_3$]$_4$. The two DAniF anions attached to each quadruply bonded Mo$_2^{4+}$ units and the interstitial solvent molecules have been omitted for clarity. The left view shows the atom labelling scheme. Selected bond distances (Å) are Mo(1)–Mo(2) 2.099(2), Mo(3)–Mo(3A) 2.098(2), Mo(4)–Mo(4A) 2.104(5), Mo(5)–Mo(6) 2.098[4]; Mo–N (av) 2.10[1]; Mo–O (av) 2.20[2]. The right drawing emphasizes the pseudo-octahedral distribution of the Mo$_2^{4+}$ units. A cut of the octahedron shows the tetrahedral cavity; the apices are located at the center of the rings of the trimesate anions. © 1999. All rights reserved. This figure may not be reproduced in any manner without written permission from the artist.

multicomponent supramolecular structures' this seems to us a one-sided view of the matter. The synthesis reported here, as well as several by Fujita and others, seem better characterized as using a suitably chosen linker to control the 'self-assembly'.

We thank the National Science Foundation for financial support and Debbie Murillo for the artwork in Fig. 1.

Notes and references

Note added in proof: The use of trimesic acid to form a similar structure was very recently reported by others: S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.

† To a stirred solution of [Mo$_2$(DAniF)$_2$(MeCN)$_4$][BF$_4$]$_2$ (312 mg, 0.30 mmol) in 30 mL of MeCN was added [NBu$_4$]$_3$[1,3,5-C$_6$H$_3$(CO$_2$)$_3$] (187 mg, 0.20 mmol) in 20 mL of MeCN. An immediate reaction took place with the formation of a bright red precipitate, which was collected, washed several times with MeCN, and dried. The crude product was extracted with CH$_2$Cl$_2$ (3×5 mL). Acetonitrile was then carefully layered on top. Bright red crystals were collected after about two weeks. The yield was essentially quantitative. ^{1}H NMR δ (ppm, in CD$_2$Cl$_2$) 9.39 (s, 12H, aromatic of trimesate), 8.52 (s, 12H, –NC*H*N–), 6.62 (dd, 96H, aromatic of formamidinate), 3.67 (s, 72H, –OC*H*$_3$).

‡ *Crystal data* for [Mo$_2$(DAniF)$_2$]$_6$[C$_6$H$_3$(CO$_2$)$_3$]$_4$·22.1MeCN·2.3CH$_2$Cl$_2$: C$_{262.5}$H$_{262.9}$Cl$_{4.6}$Mo$_{12}$N$_{46.1}$O$_{48}$, M = 6145.84, monoclinic, space group $C2/c$, a = 29.825(3), b = 27.377(2), c = 38.248(3), β = 112.71(1)°, V = 28809(4) Å^3, Z = 4, μ(Mo-Kα) = 0.622 mm^{-1}. Data were collected at 173(2) K. The structure, refined on F^2, converged for 13285 unique reflections and 1190 parameters to give $R1(F)$ = 0.098 and $wR2(F^2)$ = 0.217 with a goodness-of-fit of 1.073. CCDC 182/1205. See http://www.rsc.org/suppdata/cc/1999/841/ for crystallographic files in .cif format.

§ For detailed experimental conditions, see ref 3.

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