The use of dimetal building blocks in convergent syntheses of large arrays

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Within the broad field called “supramolecular chemistry,” there is a sector that is based on the use of metal atoms or ions as key elements in promoting the assembly and dictating the main structural features of the supramolecular products. Considerable success has been achieved utilizing M2+–ligand bonds, bond energies of up to 50 kcal mol−1 being quite normal and, altruistically speaking, nothing weak or “noncovalent” about metal bonded units. Metal–metal bonded cationic complexes of the [M2(DAniF)(MeCN)b2]4−–n+ type, where M = Mo or Rh and DAniF is an N,N′-di-p-anisyldiamidinate anion, have been used as subunit precursors and then linked by various equatorial and axial bridging groups such as polycarboxylate anions, polyamides, and polynitriles. Characterization of the products by single-crystal x-ray diffraction, cyclic voltammetry, differential pulse voltammetry, NMR, and other spectroscopic techniques has revealed the presence of discrete tetranuclear (pairs or loops), hexanuclear (triangles), octanuclear (squares), and dodecanuclear (cages) species and one-, two-, or three-dimensional molecular nanotubes. These compounds display a rich electrochemical behavior that is affected by the nature of the linkers.

Dimetal units can be used to create neutral rather than highly positive oligomers and networks, which can then be oxidized in a controlled way, with retention of structural integrity. (ii) An enormous range of metals (i.e., V, Nb, Cr, Mo, W, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Cu) are known (1), quite sufficient for the use of metal bonded units. Dimetal units are extremely varied and thus potentially available to form homologous structures. (iii) A very large variety of organic ligands may be used to vary solubility, pore sizes, electrochemical activity, and still other properties. (iv) The spectroscopic and magnetic properties of dimetal units are extremely varied and thus the arrays containing them can be designed with an extremely diversified range of such electronic properties. (v) By suitable choice of both equatorial and axial connecting elements, an enormous range of structures is available, and the nature and degree of interaction between adjacent dimetal units can be finely controlled.

It may be noted that, although there is still much to be learned about all types of compounds with M2+ cores, a great deal is known (1), quite sufficient for the use of these species in making large arrays by designed syntheses.

In constructing large arrays with dimetal units, M2+, as one component, two key choices have to be made: (i) the type of nonlinking ligands (protective ligands, so to speak) that partly surround the M2+ cores; and (ii) the linking ligands, which must offer a range of structural options. The first point is critical, because if the protective ligands are too labile, too sterically bulky (or not bulky enough), etc., designed syntheses will not proceed as planned or, equally bad, products that can be isolated in crystalline form and then structurally characterized will not be obtained. It is also very desirable that the syntheses be convergent so that high yields can be obtained. Before turning to a survey of specific results, these general points will be addressed.

We have found amidinates, as nonlinking ligands, to be very useful. It is helpful if they are substituted to give convenient solubility properties. One that we have relied on heavily is shown in Fig. 1a, and two generalized examples of the starting materials that incorporate this, or similar, ligands are shown in Fig. 1b and c. For equatorial linking, the most obvious and convenient choices are di- and polycarboxylate ions, a few examples of which are shown in Fig. 2a. Of course, there are many other stereoelectronically similar possibilities (e.g., diamidate ions and dianidinate ions), as well as some completely inorganic ones, as will be mentioned later. For axial linkers, there are numerous possibilities, especially di- and polyamines, or dinitriles, four of which are shown in Fig. 2b.

Large arrays of dimetal units may be created in three ways, as shown schemati
cally in Fig. 3. The linking may be entirely by means of equatorial connectors, entirely by means of axial connectors, or by the combined use of both.

**Small- to Medium-Size Arrays**

Our work began with the preparation, structural characterization, and electrochemical study of compounds of the type \[(\text{DAniF})_3\text{Mo}_2\]O_2CO_2\[\text{X}\]OCO_2\[\text{Mo}_2(\text{DAniF})_3\]. In the first example (2), O_2CXCO_2 was oxalate O_2CCO_2 (see Fig. 4a), but this has been followed by many more such compounds, some published (3) and others, as yet unpublished, containing a variety of unsaturated connectors such as CH—CH—(CH—CH)_n (F.A.C., J. P. Donahue, and C.A.M., unpublished work). The major point of interest for these compounds is not so much structural as it is the degree of electronic communication between the two dimetal units, as evidenced by electrochemistry, spectra, and magnetism.

Before leaving the simple “dimer of dimers” structures, an interesting variation should be mentioned. In general, in compounds of the \[\text{[M}_2\text{]O}_2\text{C—X—CO}_2\text{[M}_2\text{]}\] type, where \[\text{[M}_2\text{]}\] is a general symbol for a dimetal unit carrying some protective ligands, the two \[\text{M}_2\] units are coplanar or nearly so. One notable exception is when X = C=C=C (F.A.C., J. P. Donahue, and C.A.M., unpublished work). It is also possible to have the two \[\text{[M}_2\text{]}\] units closely coupled but held perpendicular to each other by using a tetrahedral linker, as shown in Fig. 4b, where the linker is the sulfate ion. Similar molecules with MoO_4^2− and WO_4^2− have also been made (4) as well as one with ZnCl_4^2− (F.A.C., C.-Y. Liu, C.A.M., unpublished work). Quite strong electronic coupling across these tetrahedral bridges is observed.

For products of greater structural range, we turn to compounds made from the type of dimetal unit in Fig. 1c. Because of the (idealized) right angle between the planes defined by the metal atoms and the 1,2 pairs of replaceable equatorial ligands, it is reasonable to expect that when these dimetal units react with equatorial linkers, the formation of square products would be the most likely outcome—and it is, as shown in Fig. 4c, where again the linker is oxalate (5). This was the first reported square of dimolybdenum units, but we have since made many others (6). At this same time (5), we also reported the first square with dirhodium units. A few other dirhodium squares have subsequently been reported from other laboratories (7–9).

However, at a very early stage, it became clear that this “most likely outcome” was not the only possible outcome. Indeed, when the first Rh_2 square compound was studied (5), it was found that by a suitable choice of reaction conditions a triangular product, Fig. 5a, could also be obtained (5). In solution, there is an equilibrium ratio between the two that does not differ much from 1:1. Later, we obtained both another \[\text{[Mo}_2\text{]}\], Fig. 5b, and a \[\text{[Re}_2\text{]}\] compound as triangles (10, 11) but have not yet found a way to make the corresponding squares.

The actual isolation of square or triangular products, of course, is subject to

Fig. 2. (a) A few of the polycarboxylato polyanions used as equatorial linkers. (b) A selection of neutral nitrogen-containing molecules used as axial linkers.

Fig. 3. Schemes of three basic modes of assembly of dinuclear units.

Fig. 4. (a) The molecular structure of the \[\text{[Mo}_3(\text{DAniF})_3\text{]}\text{O}_2\text{C—CO}_2\text{[Mo}_2(\text{DAniF})_3\text{]}\] molecule having two essentially parallel quadruply bonded Mo_2 units linked by an oxalate anion. (b) Molecular core structure of \[\text{[Mo}_3(\text{DAniF})_3\text{]}\text{SO}_4\] showing two essentially perpendicular Mo_2 units joined by a SO_4^2− anion. (c) Structure of a molecular square with four Mo_2 units linked by four oxalate anions.
kinetic as well as thermodynamic control. However, the presence of one oligomer or the other, or both, in solution is a thermodynamic question. In some cases, there may be little strain in the triangular as compared with the square oligomer, as in the molecule shown in Fig. 5b. One would then expect the entropic factor to favor the triangle decisively (by at least 10 kcal/mol) and therefore, unless some uncommon packing energies were to come into play, only triangles would crystallize. In a case such as the oxalate-bridged [Rh2] oligomers, where strain enthalpy is expected to be serious in the triangle as compared with the square, the outcome of the competition between the two becomes more difficult to predict, and kinetic and crystal packing considerations will enter strongly into the question of what can be isolated in the crystalline state. With compounds containing Mo2(DAniF)2 corners, which resist twisting because of their δ bonds, squares have always been obtained, except for the case cited above, where the bridging dicarboxylate is very flexible.

Still another more or less deliberate way to not get the “most likely outcome” is to make loops by using bridging dicarboxylate ligands that cannot conform themselves so as to have oppositely directed carboxyl groups. One example of these loops (12), with malonic acid, is shown in Fig. 5c.

The cyclic molecules, that is, triangles, squares and loops, have a strong tendency to stack in their crystals so that infinite channels are formed. It is surprising that the stacking pattern, as illustrated in Fig. 5a and c, is most often prismatic, i.e., with the molecules in register, although in a few instances, as with the molecule in Fig. 5b and for the square with [Mo2] corners and 4,4′-diphenyldicarboxylate linkers, shown in Fig. 6, the stacking is antiprismatic. The underlying causes of these stacking patterns are still under study.

The dimensionality of this chemistry was advanced from polygonal to polyhedral by using the tricarboxylate linker shown in Fig. 2a. The reactions of this linker with dimetal units of the type shown in Fig. 1c, where M = Mo or Rh gave very beautiful polyhedral molecules of $Td$ symmetry (13). A drawing of the core of the rhodium compound is presented in Fig. 7. The centers of the $M_2$ units define the vertices of an octahedron, and the centers of the trimesate anions define the apices of a tetrahedron. Well ordered dichloromethane molecules may be seen inside the rhodium compound. Curiously, in the molybdenum analog they are disordered.

**Extended Structures**

By using both equatorial and axial linking, structures that extend in one, two, and three dimensions have been created. These are made by designed syntheses, in the sense that the general nature, if not all details, of the structure obtained is planned. The structures are porous, with the scale of porosity under control, and the syntheses are convergent, so that yields are high. Moreover, in every case, we have determined the structures crystallographically; no assumptions or “computer modeling of presumed structures” has ever been involved in our work.

To make extended structures, the key has been to use $[M_2]$ building blocks, for which strong axial linking as well as strong equatorial linking can be used. For this purpose, [Mo2] components are unsuitable, but [Rh2] units are ideal. To proceed in a rational way (that is, to obtain a desired type of structure rather than take “pot luck”), it was necessary to recognize that the [Rh2(DAniF)2(O2CCH2CO2)]2 loop unit makes a strong steric demand in the directions parallel to the metal-metal interaction.

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Fig. 5. (a) A view of the stacking pattern for the Rh2 molecular triangle with oxalate linkers. There are CH3CN molecules in the central tunnel and others axially coordinated to the Rh atoms that have been omitted for clarity. The nonplanarity of the bridging oxalate ions is evident. (b) The core of a molecular triangle showing three Mo2 units linked by three 1,4-cyclohexanedicarboxylate anions. (c) Simplified diagram of a malonate loop, showing the channel created by stacking the cores of the molecules in the crystal.

Fig. 6. Packing of the Mo2-biphenyldicarboxylate square, showing the rotation of 45° between consecutive squares in the direction of the stacking.

Fig. 7. The core of the molecular structure of the Mo2 and Rh2 truncated, pseudooctahedral cages, emphasizing the pseudoctohedral distribution of the $M_2$ units, with a CH3Cl2 encapsulated.
bond. Fig. 4a makes this clear in a very general way. Only if the axial linkers are long enough, e.g., (1) or (2) in Fig. 2b, can infinite columns be obtained (14, 15) as shown in Fig. 8.

When the axial linker is too short, e.g., (3) in Fig. 2b, a two-dimensional sheet is obtained (14, 15), which allows all of the \( \text{C}_6\text{H}_4\text{OMe} \) groups of the \([\text{Rh}_2]\) units to steer clear of each other. This is shown in Fig. 9, where there is also a schematic representation of the structure showing that it belongs to the two-dimensional group \( \text{Cmm} \).

By using the axial linker (4) in Fig. 2b, very elaborate three-dimensional linking of the \([\text{Rh}_2]\) units has recently been achieved (16). This work began with the reaction of the \([\text{Rh}_2]\) loop unit with the potentially tridentate axial linker in a 1:2 molar ratio. When reaction of the tetrafunctional axial linker (2) of Fig. 2b, shows the \([\text{Rh}_2]\) loop unit with the potentially tridentate axial linker of Fig. 2b, show-

This does not allow use of all three arms of the linker and leads to the kinked or zig-zag two-dimensional structure shown in Fig. 10a, where unused pyridyl atoms project out. When reaction of the tetrafunctional \([\text{Rh}_2]\) loop with the trifunctional axial linker is carried out in a 3:4 molar ratio, dark red crystals of a compound having the same 3:4 stoichiometry and a very complex three-dimensional structure are obtained. Space does not allow to present a full description of this structure here. The reader is referred to two previous articles (16, 17). Sufficient to say that one way to interpret the structure is as a collection of double helices (Fig. 10b), each with a pitch of about 45 Å and each surrounded by six other double helices.

The very cursory review given here should suffice to show the range of structures that may be intentionally synthesized by using suitably protected dimetal units and appropriate linkers. The simpler structures are relatively easy to understand but offer opportunities to study intramolecular electronic communication via electrochemistry, magnetism, and spectroscopy, although the severe limitation on space here has not permitted discussion of these topics. At the other extreme, structures of enormous complexity can also be obtained, including those with tunable porosity that can serve for sequestration and separation of small guest molecules.

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