

Dimolybdenum-Containing Molecular Triangles and Squares with Diamidate Linkers: Structural Diversity and Complexity

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By employing $cis\text{-Mo}_2(\text{DAniF})_2^{2+}$ ($\text{DAniF} = N,N\text{-di}(p\text{-anisyl})\text{formamidinate}$) as the vertex building block and terephthaloyldiamidate as the linker, four dimolybdenum-containing cyclic oligomers have been synthesized and structurally characterized. In these compounds, described by the general formula $[cis\text{-Mo}_2(\text{DAniF})_2(\text{ArNOC})_2\text{C}_6\text{H}_4]_n$, $n = 3$ and 4, the geometry and composition of the products are affected by the identity of the aromatic groups of the linker. When $\text{Ar} = \text{phenyl}$, $n = 3$ (**1a** and **1b**); however, $n = 4$ for $\text{Ar} = p\text{-trifluoromethylphenyl}$ (**2**) and when $\text{Ar} = m\text{-trifluoromethylphenyl}$ (**3**). All these compounds have a central cavity, shaped by the diamidate linker, that is capable of serving as host to guest molecules in a selective manner. For compounds **2** and **3**, self-assembly that takes place in the crystalline state entails intermolecular $\text{C}\cdots\text{F}\cdots\text{C}$ interactions. Such interactions generate a one-dimensional network with a tunnel cross section of $10 \times 10 \text{ \AA}^2$ in **2**, whereas in **3**, they result in a cage in which two THF molecules are encapsulated. The $\text{F}\cdots\text{H}$ distances vary in a broad range from 2.38 to 2.70 \AA .

Introduction

Countless infinite and discrete inorganic supramolecular arrays have been built up using two basic components: units containing coordinated metal atoms and polydentate organic donors.^{1,2} In many cases, the former are angular and serve to set the geometry, whereas the latter serve as linkers in a process of molecular design that resembles architectural engineering. The requirements for the metallic building block are 2-fold; it must conform geometrically to the shape of the target molecule, and it must be synthetically compatible with the assembling reaction. These requirements are met by taking advantage of various coordination modes of various metal elements and the principles of coordination chemistry. The general strategy has been to use nonlabile ligands to block preselected metal coordination sites not needed for

assembly along with labile ligands which are intended to be replaced by the linkers. The earliest work in this area involved mostly mononuclear coordination units, for example, the corner species $cis\text{-ML}_2$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{L} = \text{bidentate ligand}$)^{1,3} and other units such as $\text{Re}(\text{CO})_2\text{Cl}$ ⁴ for triangles and squares and $([\text{9}]\text{aneS}_3)\text{Ru}^{2+}$ ⁵ and $([\text{tacn}]\text{M}(\text{H}_2\text{O})_3)^{3+}$ ($\text{M} = \text{Cr}, \text{Co}$)⁶ for cuboidal boxes.

Our approach to this type of molecular design has been to make use of covalently bonded dimetal units as the building blocks in the construction of supramolecular arrays. A dimetal unit, as a whole, may in certain aspects, e.g., in terms of coordination modes and geometry, resemble a single metal ion but differ in others. The basic structural motif for dimetal complexes with the paddlewheel framework has four equatorially arranged paddles (Scheme 1), and thus it bears a resemblance to the square planar geometry of certain single metal ions, e. g., Pt^{2+} , Pd^{2+} , or octahedral metal atoms when

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(1) See for example: (a) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371. (b) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (c) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53. (d) Ruben, M.; Rojo, J.; Romero-Salguero, F. J.; Uppadine, L. H.; Lehn, J.-M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3644. (e) Mirkin, C. A.; Holliday, B. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022.
(2) (a) Caulder, D.; Raymond, R. N. *Acc. Chem. Res.* **1999**, *32*, 975. (b) Klausmeyer, K. K.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 2705. (c) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511. (d) Giananeschi, N. C.; Masar, M. S., III; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825.

(3) See for example: (a) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (c) Schalley, C. A.; Lützen, A.; Albrecht, M. *Chem.—Eur. J.* **2004**, *10*, 1072. (c) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483.
(4) Slone, R. V.; Huppy, J. T.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **1996**, *35*, 4096.
(5) Roche, S.; Haslam, C.; Adams, H.; Heath, S. L.; Thomas, J. A. *Chem. Commun.* **1998**, 1681.
(6) Heinrich, J. L.; Berseth, P. A.; Long, J. R. *Chem. Commun.* **1998**, 1231.

Scheme 1

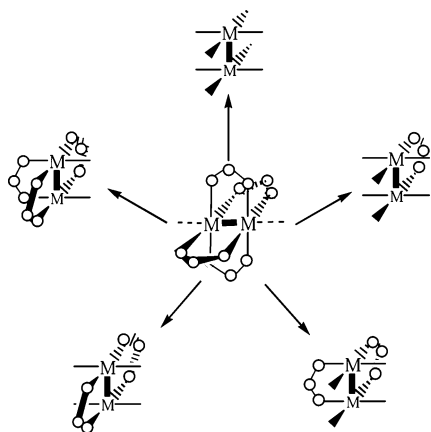
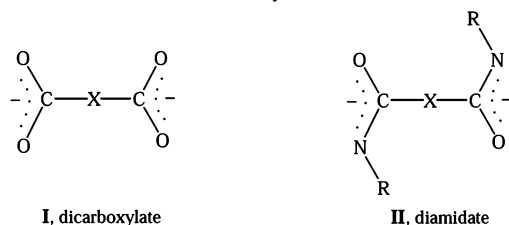


Chart 1. Structures of the Dicarboxylate and Diamidate Linkers



two axial sites are considered. The key to success with dimetal units is that some coordination sites can be selectively blocked by using one to three nonlabile three-atom bridging ligands such as *N,N'*-di(*p*-anisyl)formamidinate (DAniF), giving building blocks such as $[M_2(\text{DAniF})_n]^{(4-n)+}$, $M = \text{Mo}, \text{Rh}, \text{and Ru}$ (Scheme 1).⁷ With such dimetal subunits and polycarboxylate linkers, a great variety of discrete dimetal-containing oligomers, including pairs, loops, triangles, squares, and polyhedra, as well as extended networks, have been synthesized.⁸

Another type of linker that offers two three-atom bridging groups capable of bringing together two dimetal units and is similar to a dicarboxylate (see **I** in Chart 1) is a diamidate (**II** in Chart 1) anion, which offers some attractive properties that the corresponding dicarboxylate species do not have. Because a diamidate has much stronger Lewis basicity than the parent dicarboxylate, an increased thermodynamic stability for the resulting supramolecular arrays is anticipated. Because the substituents (R) of a diamidate (**II**) are synthetically adjustable in both steric demand and electronic properties, one can modify the molecular structure and tune the electronic effect of the ligand more efficiently than when dicarboxylates are used. In prior work, we have used some diamidates to link two dimolybdenum units, giving compounds with the formula $[\text{Mo}_2(\text{DAniF})_2]_2(\text{diamidate})$.⁹ When using an oxamidate anion as linker, we obtained the unexpected result of two structural isomers being isolated.^{9a}

(7) (a) Chisholm, M. H.; Cotton, F. A.; Daniels, L. M.; Folting, K.; Huffman, J. C.; Iyer, S. S.; Lin, C.; MacIntosh, A. M.; Murillo, C. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1387. (b) Cotton, F. A.; Liu, C. Y.; Murillo, C. A. *Inorg. Chem.* **2004**, *43*, 2267. (c) Angaridis, P.; Berry, J. F.; Cotton, F. A.; Murillo, C. A.; Wang, X. *J. Am. Chem. Soc.* **2003**, *125*, 10327.

(8) See for example: (a) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759. (b) Cotton, F. A.; Lin, C.; Murillo, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4810.

The two isomers differ from each other in coordination modes and geometries. As a result, they also differ in their ability to facilitate electronic communication between the two dimolybdenum units. The α isomers, which structurally resemble oxalate-bridged systems, give rise to singly oxidized species that are electronically localized because of poor communication between $[\text{Mo}_2]$ units, whereas the singly oxidized β isomers are electronically delocalized.^{9b}

In the present work, we report the synthesis and structures of several dimolybdenum-containing cyclic triads and tetrads with terephthaloyldiamidate ligands and explore the effect of substituents in setting the geometry of the products. The compounds included here are two geometrically isomeric *N,N'*-diphenylterephthaloyl diamidate-linked cyclic triads (**1a** and **1b**) and two cyclic tetrads, one linked by *N,N'*-di(*p*-trifluoromethyl)phenylterephthaloyldiamidate (**2**) and the other by *N,N'*-di(*m*-trifluoromethyl)phenylterephthaloyldiamidate (**3**). It should be noted that these compounds differ from each other in geometry and/or conformation even though they are derived from the same dimetal building block $[\text{cis-Mo}_2(\text{DAniF})_2]^{2+}$ and contain linkers that are not greatly dissimilar. Interestingly, compounds **2** and **3** form complex, highly ordered structural architectures in the crystalline state. Large numbers of weak intermolecular $\text{C-H}\cdots\text{F}-\text{C}$ interactions¹⁰ generate infinite one-dimensional tubes for **2** and cage-shaped dimers for **3**, in which two THF molecules are encapsulated. Thus, greater structural diversity and complexity arise by changing the linker from dicarboxylate to diamidate.

Experimental Section

Materials and Methods. All reactions and manipulations were performed under a nitrogen atmosphere, using either a nitrogen drybox or standard Schlenk line techniques. Solvents were purified under argon using a Glass Contour solvent purification system or distilled over appropriate drying agents under nitrogen. Diamide compounds were conveniently prepared by reacting terephthaloyl chloride with the corresponding aromatic amine. *cis*- $[\text{Mo}_2(\text{DAniF})_2(\text{NCCCH}_3)_4](\text{BF}_4)_2$ ^{7a} and *cis*- $\text{Mo}_2(\text{DAniF})_2(\text{O}_2\text{CCH}_3)_2$ ^{7b} were prepared by following reported procedures; commercially available chemicals were used as received.

X-ray Structure Determinations. Single crystals of **1a**·3CH₂Cl₂, **1b**·1.5CH₂Cl₂, **2**, and **3**·THF were mounted and centered on the goniometer of a Bruker SMART 1000 CCD area detector diffractometer and cooled to -60 °C. Cell parameters were determined using the program SMART.¹¹ Data reduction and integration were performed with the software package SAINT,¹²

(9) (a) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Villagrán, D.; Wang, X. *J. Am. Chem. Soc.* **2003**, *125*, 13564. (b) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Villagrán, D.; Wang, X. *J. Am. Chem. Soc.* **2004**, *126*, 14822.

(10) For examples of $\text{F}\cdots\text{H}$ interactions, see: (a) Reger, D. L.; Semeniuc, R. F.; Rassolov, V.; Smith, M. D. *Inorg. Chem.* **2004**, *43*, 537. (b) Alonso, J. L.; Antolínez, S.; Blanco, S.; Lesarri, A.; López, J. C.; Caminati, W. *J. Am. Chem. Soc.* **2004**, *126*, 3244. (c) Thalladi, V. R.; Weiss, H.-C.; Bläser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 8702. (d) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441.

(11) *SMART Software for the CCD Detector System*, version 5.05; Bruker Analytical X-ray System, Inc.: Madison, WI, 1998.

(12) *SAINT Data Reduction Software*, version 6.36A; Bruker Analytical X-ray System, Inc.: Madison, WI, 2002.

Table 1. X-ray Crystallographic Data for **1a**·3CH₂Cl₂, **2**, and **3**·THF

	1a ·3CH ₂ Cl ₂	2	3 ·THF
empirical formula	C ₁₅₃ H ₁₃₈ Cl ₆ Mo ₆ N ₁₈ O ₁₈	C ₂₀₈ H ₁₆₈ F ₂₄ Mo ₈ N ₂₄ O ₂₄	C ₂₁₂ H ₁₇₅ F ₂₄ Mo ₈ N ₂₄ O ₂₅
fw	3305.15	4611.18	4682.8
space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	19.213(2)	50.70(2)	21.521(9)
<i>b</i> (Å)	19.612(2)	14.477(6)	24.215(10)
<i>c</i> (Å)	21.815(2)	43.93(2)	26.002(11)
α (deg)	107.808(2)	90	98.158(9)
β (deg)	99.706(2)	120.07(2)	105.366(7)
γ (deg)	98.856(2)	90	107.629(8)
<i>V</i> (Å ³)	7527.2(1)	27905	12083(9)
<i>Z</i>	2	4	2
<i>T</i> (K)	213	213	213
λ (Å)	0.71073	0.71073	0.71073
<i>d</i> _{calcd} (g/cm ³)	1.458	1.098	1.2875
μ (mm ⁻¹)	0.660	0.415	0.481
R1, ^a wR2 ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0701, 0.1513	0.0664, 0.1628	0.0760, 0.1489

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b wR2 = $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1a**·3CH₂Cl₂, **2**, and **3**·THF

	1a ·3CH ₂ Cl ₂	2	3 ·THF	1a ·3CH ₂ Cl ₂	2	3 ·THF
Mo(1)–Mo(2)	2.086(1)	2.095(1)	2.073(2)	Mo(4)–N(2)	2.183(9)	
Mo(1)–N(1)	2.146(9)	2.163(5)	2.17(1)	Mo(4)–N(3)		2.16(1)
Mo(1)–O(4)		2.120(4)		Mo(4)–N(3A)		2.165(5)
Mo(1)–O(6)	2.113(7)			Mo(4)–O(2)		2.125(4)
Mo(1)–O(8)			2.13(1)	Mo(4)–O(3)	2.095(7)	
Mo(2)–N(4)		2.180(5)		Mo(5)–Mo(6)	2.088(1)	2.072(2)
Mo(2)–N(6)	2.157(8)			Mo(5)–N(5)	2.187(9)	2.16(1)
Mo(2)–N(8)			2.18(1)	Mo(5)–O(4)	2.008(7)	2.12(1)
Mo(2)–O(1)	2.105(7)	2.119(4)	2.09(1)	Mo(6)–N(4)	2.177(8)	2.18(1)
Mo(3)–Mo(4)	2.091(2)	2.091(1)	2.080(2)	Mo(6)–O(5)	2.099(7)	2.123(9)
Mo(3)–N(2)		2.160(5)	2.17(1)	Mo(7)–Mo(8)		2.071(2)
Mo(3)–N(3)	2.150(8)			Mo(7)–N(6)		2.18(1)
Mo(3)–O(2)	2.124(7)			Mo(7)–O(7)		2.11(1)
Mo(3)–O(3)			2.12(1)	Mo(8)–N(7)		2.16(1)
Mo(3)–O(3A)		2.121(4)		Mo(8)–O(6)		2.10(1)
O(4)–Mo(1)–N(1)		87.9(2)		O(3A)–Mo(3)–N(2)		90.5(2)
O(6)–Mo(1)–N(1)	84.9(3)			O(3)–Mo(4)–N(2)	83.6(3)	
O(8)–Mo(1)–N(1)			88.6(4)	O(2)–Mo(4)–N(3A)		90.9(2)
O(1)–Mo(2)–N(4)		88.0(2)		O(2)–Mo(4)–N(3)		86.2(4)
O(1)–Mo(2)–N(6)	83.8(2)			O(4)–Mo(5)–N(5)	86.0(3)	87.4(4)
O(1)–Mo(2)–N(8)			85.9(4)	O(5)–Mo(6)–N(4)	84.9(3)	85.5(4)
O(2)–Mo(3)–N(3)	85.4(3)			O(7)–Mo(7)–N(6)		87.5(4)
O(3)–Mo(3)–N(2)			86.8(4)	O(6)–Mo(8)–N(7)		85.5(4)

whereas absorption corrections were applied using the program SADABS.¹³ In all structures, the positions of the heavy atoms were found via direct methods using the program SHELXTL.¹⁴ Subsequent cycles of least-squares refinement alternated with difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were added in idealized positions. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Compound **2** crystallized with highly disordered interstitial solvent molecules. The diffuse electron density created by the interstitial molecules in **2** was analyzed using the program SQUEEZE in the PLATON software package.¹⁵ There are two symmetry-related solvent accessible voids, each of about 4665 Å³, in the unit cell. A total of 2210 electrons were found in the two cavities, corresponding to about 52.6 dichloromethane molecules per unit cell. The SQUEEZE program was then applied to subtract the contribution of the disordered solvent molecules from the diffraction data.

For compound **3**·THF, the THF molecule at the center of the molecular square was found disordered in three positions and refined with distance constraints. Other interstitial cavities containing highly disordered molecules have also been found in the structure. The void volume (2200 Å³), residual peak distribution, and residual electron-density count (308 electrons) as calculated by SQUEEZE are consistent with the presence of about 7.6 THF molecules per unit cell. Except for that of the THF molecule at the center of the molecular square, the contribution to the diffraction intensities from the remaining solvent molecules was subtracted from the diffraction data, and these modified diffraction data were used subsequently in the final refinement of the structure. Crystallographic data for **1a**·3CH₂Cl₂, **2**, and **3**·THF are listed in Table 1, and selected bond distances are in Table 2.

Preparation of [cis-Mo₂(DAniF)₂]₃(N,N'-diphenylterephthaloyldiamide)₃, **1a (and **1b**).** To a yellow suspension of *cis*-Mo₂(DAniF)₂(O₂CCH₃)₂ (0.245 g, 0.300 mmol) and *N,N'*-diphenylterephthaloyldiamide (0.095 g, 0.300 mmol) in 40 mL of THF was added slowly, and with stirring, 1.5 mL of a 0.5 M NaOCH₃ solution in CH₃OH. The color of the mixture changed immediately from yellow to dark red. The reaction mixture was stirred at room temperature for 8 h, during which the color changed to red. The solvent was removed under reduced pressure, and the residue was

(13) SADABS Bruker/Siemens Area Detector Absorption and Other Corrections, version 2.03; Bruker Analytical X-ray System, Inc.: Madison, WI, 2002.

(14) Sheldrick, G. M., SHELXTL, version 6.12; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.

(15) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

extracted with 10 mL of CH_2Cl_2 and filtered through a Celite-packed frit. To the filtrate, with stirring, was added 40 mL of ethanol, producing an orange-red solid that was washed with 10 mL of hexanes and then redissolved in 15 mL of CH_2Cl_2 . This solution was layered with 40 mL of isomeric hexanes. Diffusion over a period of two weeks gave two types of crystals, **1a** and **1b**. The major product was **1a**, which formed as very small, orange-red crystals. Crystals of **1b** were slightly larger and red. Combined yield: 0.132 g (40% on the basis of $\mathbf{1a} \cdot 3\text{CH}_2\text{Cl}_2$). $^1\text{H NMR}$ for **1a** (δ , in CD_2Cl_2): 8.68 (s, 6H, $-\text{NCHN}-$), 7.46 (s, 12H, $-\text{C}_6\text{H}_4-$), 6.92 (m, 18H, phenyl C-H), 6.78–6.62 (m, 24H, anisyl C-H), 6.60 (d, $2 \times 6\text{H}$, phenyl C-H), 6.42 (d, 12H, anisyl C-H), 6.12 (d, 12H, anisyl C-H), 3.74 (s, 18H, $-\text{OCH}_3$), 3.66 (s, 18H, $-\text{OCH}_3$). Anal. Calcd for $\text{C}_{153}\text{H}_{138}\text{Cl}_6\text{Mo}_6\text{N}_{18}\text{O}_{18}$ ($\mathbf{1a} \cdot 3\text{CH}_2\text{Cl}_2$): C, 55.60; H, 4.21; N, 7.63. Found: C, 55.40; H, 4.36; N, 7.51.

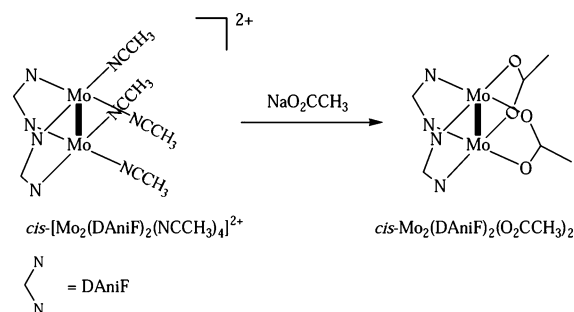
Preparation of $[\text{cis-Mo}_2(\text{DAniF})_2]_4[\text{N,N}'\text{-di}(p\text{-trifluoromethyl})\text{-terephthaloyldiamidate}]_4$, **2.** To a yellow solution prepared by mixing $\text{cis-Mo}_2(\text{DAniF})_2(\text{O}_2\text{CCH}_3)_2$ (0.245 g, 0.300 mmol) and $\text{N,N}'\text{-di}(m\text{-trifluoromethyl})\text{terephthaloyldiamide}$ (0.135 g, 0.300 mmol) in 20 mL of THF was added slowly, with stirring, 1.5 mL of a 0.5 M NaOCH_3 solution in CH_3OH . The color of the solution changed immediately from yellow to dark red. The reaction mixture was stirred at room temperature for 5 h, at which time a less intense red color appeared. After removal of the solvent under reduced pressure, the residue was extracted with ca. 15 mL of CH_2Cl_2 and filtered through a Celite-packed frit. The addition of 30 mL of hexanes to the filtrate precipitated a red solid. Slow diffusion of hexanes into a dichloromethane solution gave red crystalline material. Yield of $\mathbf{2} \cdot 2\text{CH}_2\text{Cl}_2$: 0.195 g (54%). $^1\text{H NMR}$ (δ , in CD_2Cl_2): 8.61 (s, 8H, $-\text{NCHN}-$), 7.26 (s, 16H, $-\text{C}_6\text{H}_4-$), 7.16 (d, 8H, aromatic C-H), 7.09 (t, 8H, aromatic C-H), 6.71 (m, 32H, anisyl C-H), 6.61 (t, 8H, aromatic C-H), 6.58 (s, 8H, aromatic C-H), 6.55 (d, 16H, anisyl C-H), 6.26 (d, 16H, anisyl C-H), 3.70 (s, 24H, $-\text{OCH}_3$), 3.69 (s, 24H, $-\text{OCH}_3$). Anal. Calcd for $\text{C}_{210}\text{F}_{24}\text{H}_{172}\text{Cl}_4\text{Mo}_8\text{N}_{24}\text{O}_{24}$ ($\mathbf{2} \cdot 2\text{CH}_2\text{Cl}_2$): C, 52.76; H, 3.63; N, 7.03. Found: C, 52.67; H, 3.51; N, 6.99.

Preparation of $[\text{cis-Mo}_2(\text{DAniF})_2]_4[\text{N,N}'\text{-di}(m\text{-trifluoromethyl})\text{-terephthaloyldiamidate}]_4$, **3.** This compound was prepared by using an analogous reaction scale and following a procedure similar to that for the synthesis of **2**. Yield of $\mathbf{3} \cdot 2\text{CH}_2\text{Cl}_2$: 0.233 g (65%). $^1\text{H NMR}$ (δ , in CD_2Cl_2): 8.64 (s, 8H, $-\text{NCHN}-$), 7.49 (s, 16H, $-\text{C}_6\text{H}_4-$), 7.04 (d, 16H, aromatic C-H), 6.08–6.75 (m, 32H, anisyl C-H), 6.71 (d, 16H, aromatic C-H), 6.32 (d, 16H anisyl C-H), 5.87 (d, 16H, anisyl C-H), 3.78 (s, 24H, $-\text{OCH}_3$), 3.61 (s, 24H, $-\text{OCH}_3$). Anal. Calcd. for $\text{C}_{210}\text{F}_{24}\text{H}_{172}\text{Cl}_4\text{Mo}_8\text{N}_{24}\text{O}_{24}$ ($\mathbf{3} \cdot 2\text{CH}_2\text{Cl}_2$): C, 52.76; H, 3.63; N, 7.03. Found: C, 52.54; H, 3.54; N, 7.01.

Results and Discussion

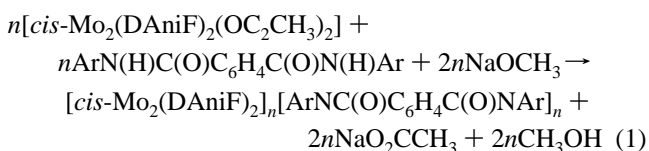
Syntheses. All dicarboxylate-linked dimolybdenum-containing molecular triangles and squares previously reported have been synthesized by assembling the dimetal building block $\text{cis-[Mo}_2(\text{DAniF})_2(\text{NCCH}_3)_4]^{2+}$ with a tetrabutylammonium salt of a dicarboxylate anion,¹⁶ a procedure that also works well for the preparation of the dirhodium analogues.¹⁷ However, during our work on diamidate-linked dimolybdenum pairs, it was recognized that the cation $[\text{Mo}_2(\text{DAniF})_3(\text{NCCH}_3)_2]^+$ was not suitable for these reactions¹⁸ because the acetonitrile molecules, activated by coordination

Scheme 2



to the Mo_2^{4+} unit, are subject to nucleophilic attack by the diamidate ligands. The problem was eliminated by replacing $[\text{Mo}_2(\text{DAniF})_3(\text{NCCH}_3)_2]^+$ with $\text{Mo}_2(\text{DAniF})_3(\text{O}_2\text{CCH}_3)$ and modifying the reaction conditions accordingly.⁹

Clearly, the same problem would arise in the synthesis of triangles or squares with bridging amidates from $[\text{cis-Mo}_2(\text{DAniF})_2(\text{CH}_3\text{CN})_4]^{2+}$. Again, however, the problem was solved by turning to the neutral compound $\text{cis-Mo}_2(\text{DAniF})_2(\text{O}_2\text{CCH}_3)_2$, which can be conveniently prepared^{7b} by adding sodium acetate to an acetonitrile solution containing $\text{cis-[Mo}_2(\text{DAniF})_2(\text{NCCH}_3)_2]^{2+}$, as shown in Scheme 2. Because the acetate ligand is significantly more labile than the formamidate (DAniF) ligand, the use of $\text{cis-Mo}_2(\text{DAniF})_2(\text{O}_2\text{CCH}_3)_2$ guarantees convergent syntheses that lead to cyclic dimolybdenum oligomers (eq 1). An additional advantage of using the $\text{DAniF}/\text{O}_2\text{CCH}_3$ mixed-ligand compound as the starting material is that there is no need to prepare a diamidate salt prior to the assembly reaction. The reaction may be carried out directly by mixing the neutral precursor of the corner species with the diamide, and then adding the strong base NaOCH_3 .



where $\text{Ar} = \text{C}_6\text{H}_5$, $n = 3$ or $\text{Ar} = (p\text{-CF}_3)\text{C}_6\text{H}_4$ or $(m\text{-CF}_3)\text{-C}_6\text{H}_4$, $n = 4$. Depending on the linker, the dimetal unit $[\text{cis-M}_2(\text{DAniF})_2]^{2+}$ ($\text{M} = \text{Mo}, \text{Rh}$) can form the vertexes of either molecular triangles or squares,⁸ and sometimes, control of the crystallization conditions allows selective generation of both species, even for the same linker.¹⁹ The reactions described here using diamidate linkers give only one product in each case, but that product may be either triads or tetrads depending on small variations in the substituents of the linkers. When $\text{N,N}'\text{-diphenylterephthaloyldiamidate}$ is used, the only product is a cyclic triad. However, such a triad can be isolated as two different geometric isomers, **1a** and **1b** (vide infra). In contrast, only molecular squares, **2** and **3**, have been obtained when the ligand is modified by introducing a trifluoromethyl substituent onto the phenyl groups. No

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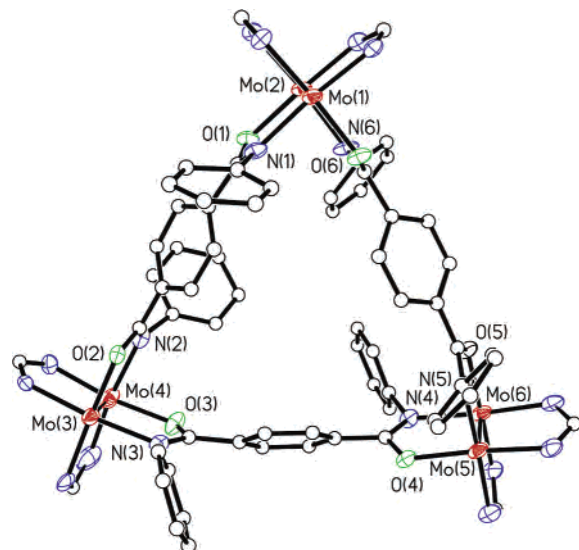


Figure 1. Core structure of **1a** in **1a**·3CH₂Cl₂ with displacement ellipsoids drawn at the 30% probability level. Note that the two phenyl groups on each edge are pointing in opposite directions, with one lying above and the other below the plane of the triangle.

Scheme 3



evidence was found for interchange between the triangle and square under our experimental conditions.

Structural Characterization. Compound **1a** crystallized in the triclinic space group $P\bar{1}$ with the molecule residing on a general position. As shown in Figure 1, the triangular molecule consists of three [Mo₂] vertexes and three *N,N'*-diphenylterephthaloyldiamidate edges. The triangular molecule can be described as a cyclic oligomer of general formula [*cis*-Mo₂(DAniF)₂((ArNOC)₂C₆H₄)_n], where *n* = 3 and Ar = phenyl. Each dimetal unit has two supporting ligands (DAniF) and two amidate groups (ArNOC), each linked to two different [Mo₂] units through a phenylene spacer (–C₆H₄–). In **1a**, the two phenyl groups on each edge of the triangle are pointing in opposite directions; that is, one lies above and the other below the plane of the triangle. Furthermore, the two phenyl groups adjacent to each [Mo₂] unit (but belonging to different linkers) are also on opposite sides of the molecular plane. This conformation confers on the molecule an idealized *D*₃ symmetry. The distribution of the pendant phenyl rings is shown schematically in Scheme 3. For the three crystallographically independent dimolybdenum units, the Mo–Mo bond distances are 2.086(1), 2.091(1), and 2.088(1) Å, which are within the expected range for quadruply bonded Mo₂⁴⁺ units in analogous coordination environments.^{18,20} The average N_{linker}–Mo–O_{linker} angle of 84.7(4)° is much larger than 60° for an equilateral triangle but smaller than the angle of about 90° normally formed by two *cis* ligands in paddlewheel com-

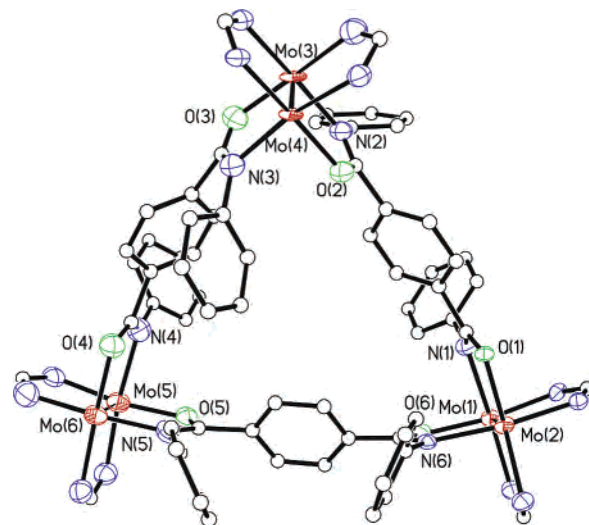


Figure 2. Core structure of **1b** in **1b**·1.5CH₂Cl₂ with displacement ellipsoids drawn at the 30% probability level. Note that similar to **1a**, the molecule has three phenyl groups on each side of the triangular plane, but here the two phenyl rings on the right and bottom edges point in the one direction and these alternate on the left edge.

pounds such as *cis*-Mo₂(DAniF)₂(O₂CCH₃)₂. Thus, it is clear that some strain is induced in each linker by the formation of a triangular molecule, and this results in a bowing of the entire linker. This bowing results in the distance between the [Mo₂] units in **1a** (11.24 Å) being 0.16 Å shorter than the separation found in a dimolybdenum pair with the same linker and two Mo₂(DAniF)₃ units (11.40 Å).¹⁸ It may be noted that each molecule is chiral and there are two of each enantiomer in the unit cell.

Compound **1b**, a geometric isomer of **1a**, crystallized as a minor product from the same solution. In the crystalline state, the molecule of **1b** occupies a general position in the monoclinic space group $P2_1/n$ and it has *C*₂ symmetry. Although the crystal structure could be refined only isotropically because of a low diffraction quality of the crystal,²¹ the core structure of **1b** is well-defined, as depicted in Figure 2. Analogous to **1a**, the molecule has three phenyl groups on each side of the triangular plane, which is presumably necessary to minimize repulsive phenyl⋯phenyl contacts, but the pattern of the phenyl groups relative to the plane of the triangle is different from that in **1a**. However, the two patterns have a common feature: at each vertex, the adjacent *N*-phenyl groups lie on opposite sides of the mean plane of the triangle. If it is necessary that this be true (and it probably is for steric reasons), then the arrangements in **1a** and **1b** are the only ones possible. It is interesting to note that both isomers of **1** form cavities. In these molecules, three phenyl groups on one side of the molecule create the opening of the cavity and the other three phenyl groups that are pointing toward each other shape the bottom. In each of the isomers, a guest dichloromethane molecule is clasped inside the cavity.

Compound **2** crystallized in monoclinic space group $C2/c$, with each molecule residing on a special position with

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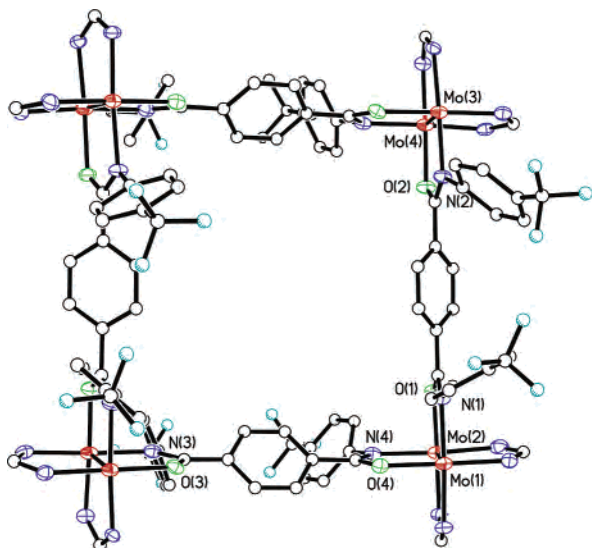


Figure 3. Core structure of **2** with displacement ellipsoids drawn at the 30% probability level. Note that the two p -CF₃C₆H₄ groups on each edge of the square are on the same side of the molecular plane but they alternate from edge to edge by being either above or below the plane.

crystallographic 2-fold symmetry. As shown in Figure 3, this molecule is a square rather than a triangle. For the triangles (**1a** and **1b**) as well as the square (**2**), an aromatic terephthaloyldiamidate anion is used to link the [Mo₂] building block, but for **2**, a modification was made to the linker by introducing a trifluoromethyl group (–CF₃) in the para position of the phenyl groups.

For the diamidate-linked dimolybdenum square, **2**, there are both similarities and differences when it is compared structurally to its dicarboxylate analogues. It resembles the previously reported tetrafluoroterephthalate-linked dimolybdenum²² and terephthalate-linked diruthenium^{7c} molecular squares in shape and size. All the bond distances and angles of the dimetal units (Table 2) are similar to those of the dicarboxylate analogues. The central square area, about $10 \times 10 \text{ \AA}^2$, is fenced by eight p -trifluoromethylphenyl groups, four above and four below the molecular plane, that create an open cavity.

In **2**, the two p -CF₃C₆H₄ groups on each edge of the square are on the same side of the molecular plane but they alternate from edge to edge by being either above or below the plane. This gives rise to an idealized S_4 axis that confers on the molecule an idealized D_{2d} symmetry, as shown on the top left drawing in Scheme 4. It should be noted that as in isomers **1a** and **1b**, there is one aryl group pointing up and one pointing down at each corner. The four phenylene spacers are tilted in and out of the center of the molecule in an alternating fashion as required by the D_{2d} symmetry and have absolute torsion angles of 35–40°. It is interesting to note that the existence of other stereoisomers cannot be ruled out. On the assumption that at each corner the two aryl groups must point in opposite directions to minimize steric crowding hold, as was apparently the case for the triangles, there are four possible geometric isomers, as shown in Scheme 4. Of these geometric isomers, those with idealized

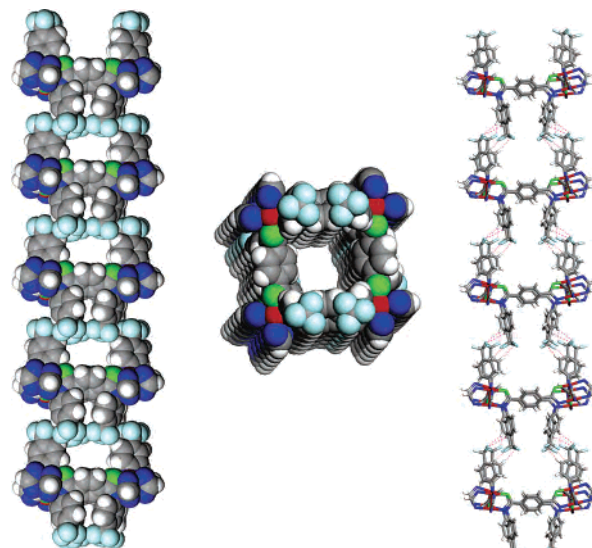
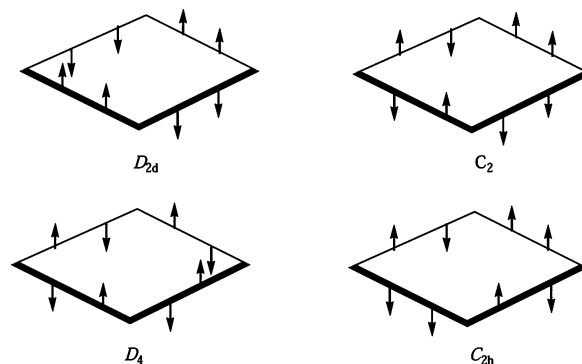


Figure 4. One-dimensional network of **2** formed by intermolecular F \cdots H interactions in the solid state. All p -aryl groups and hydrogen atoms have been omitted for clarity.

Scheme 4



C_2 and D_4 symmetries have enantiomers. Clearly, a switch in linker from dicarboxylate to diamidate increases the potential structural diversity and complexity of the products.

In the solid state, the squares in **2** are stacked along the [010] direction to form a one-dimensional (1D) channel structure, in a pattern that resembles the packing in some of the dicarboxylate analogues.^{8a,23} In **2**, the self-assembly of the 1D network appears to be influenced by intermolecular F \cdots H interactions, as shown in Figure 4. For each adjacent pair of molecules, there are four pairs of –CF₃ groups that interact with each other through F \cdots H contacts. Even though each individual C–F \cdots H–C interaction²⁴ is relatively weak (about 2.2 kJ/mol),²⁵ the cumulative binding force is expected to be significantly stronger than those in carboxylate analogues. Short F \cdots H distances (e. g., 2.41 Å) in the network are expected to be the major contributors to such intermolecular interactions.^{10c} It should be noted that the location of the –CF₃ groups on para positions ensures that

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(24) It should be pointed out that by C–F \cdots H–C interactions, we do not mean C–F \cdots H–C hydrogen bonds in the sense used in: Dunitz, J. D.; Taylor, R. *Chem.–Eur. J.* **1997**, *3*, 89. Instead, we use the term C–F \cdots H–C interactions in a manner similar to that used in describing aryl \cdots aryl stacking. See for example: Rebek, J.; Nemeth, D. *J. Am. Chem. Soc.* **1986**, *108*, 5637.

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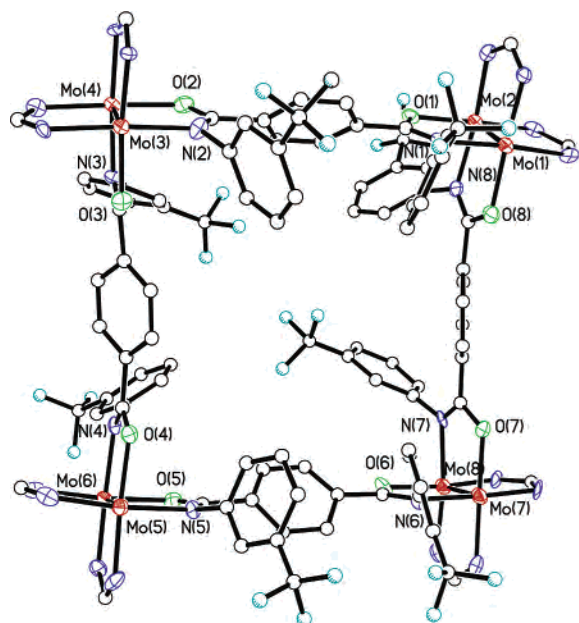


Figure 5. Core structure of the square molecule **3** with displacement ellipsoids drawn at the 30% probability level. Note that above and below the molecular plane, two of the *m*-CF₃ groups are oriented toward the center of the square and two point away from the center of the square, creating a cavity.

the F \cdots H attractions are along the direction in which the superstructure is extended and that the *D*_{2d} symmetry allows the molecules to adapt to one another, forming the highly ordered structure shown in Figure 4.

To better understand the influence of the aryl CF₃ groups, a compound with trifluoromethyl substituents in the meta position, **3**, was synthesized. As Figure 5 shows, this is another cyclic dimolybdenum tetrad and it has the same relative orientations as those of the aryl groups in relation to the molecular plane. However, the meta position of the CF₃ moieties introduces an additional geometric variable. On each side of the molecular plane, two of the *m*-CF₃ groups are oriented toward the center of the square and two point away from the center of the square. This conformation lowers the idealized symmetry of the molecule relative to that in **2**. By leaving one side open and closing the other, this conformation also creates a cavity.

Self-assembly generates pairs of molecules (Figure 6) that again have weak intermolecular F \cdots H interactions (2.38–2.56 Å), but such F \cdots H contacts do not extend beyond these pairs. This precludes the formation of an extended structure similar to that in **2**. In the pairing of molecules of **3**, the two molecules are not bound directly face to face, but are offset.

Space-filling models of **3** (Figure 7) show that four of the aryl groups on the bottom of the square close in, whereas the four on the top of each molecule open out thus creating a bowl. Close approach of two of these bowls creates a cavity that encapsulates two THF molecules. The formation of the cagelike structure in **3** and its ability to trap guest molecules arise from a chemical principle it has in common with other self-assembled molecular encapsulation systems, such as, Rebek's "tennis ball",²⁶ calix[4]arene and its derivatives,²⁷ and resorcin[4]arene,²⁸ where dimerization takes place through regularly defined hydrogen bonding. However, it

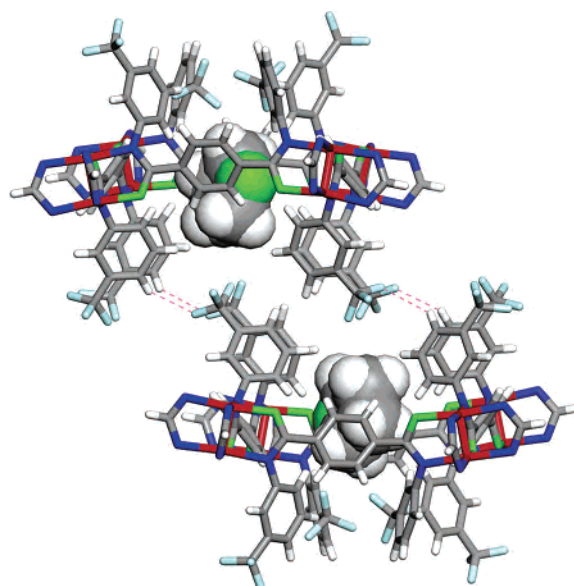


Figure 6. Bimolecular cage of **3** formed by intermolecular F \cdots H interactions in the solid state, in which two THF molecules are encapsulated. All *p*-anisyl groups and hydrogen atoms have been omitted for clarity.

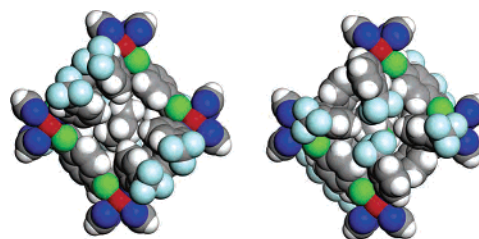


Figure 7. Space-filling models for **3** showing the encapsulated THF molecule. The figure at the left is a view from the top of the molecule whereas that on the right is a view from the bottom.

differs from most of the bimolecular capsules previously studied in that most are purely organic compounds, whereas compound **3** is a metal complex. Furthermore, encapsulation of THF appears to be quite selective, as early attempts at the crystallization of compound **3** from solvent mixtures that did not contain THF produced crystals that lost solvent so rapidly that structural determination was precluded. However, when a mixture of tetrahydrofuran, toluene, and hexane was used as the crystallization medium, the crystals of **3**·THF had sufficient stability for allowing mounting of the crystals on a goniometer head without solvent loss.

The structures of all four compounds reported here clearly show that the substituents of the amidate group have a significant impact on the geometric architectures of the product. Furthermore, the formation of these superstructures

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and their host/guest behavior exemplify the general factors that underlie molecular organization, such as size, shape, and geometrically compatible binding forces.^{29,30}

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Supporting Information Available: X-ray crystallographic files in CIF format for **1a**·3CH₂Cl₂, **2**, and **3**·THF and a table in pdf (Table S1) listing intermolecular F···H interactions in the crystal structures of **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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