

Dynamic equilibrium between cyclic oligomers. Thermodynamic and structural characterization of a square and a triangle†

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A dynamic equilibrium has been found in CDCl_3 between a neutral molecular square, $[\text{cis-Mo}_2(\text{DAniF})_2]_4(\text{O}_2\text{CC}_6\text{F}_4\text{CO}_2)_4$ (**1**) and triangle, $[\text{cis-Mo}_2(\text{DAniF})_2]_3(\text{O}_2\text{CC}_6\text{F}_4\text{CO}_2)_3$ (**2**) (DAniF = the anion of *N,N'*-di-*p*-anisylformamidine). The two components have been crystallographically characterized and solution studies by ^1H and ^{19}F NMR spectra of the concentration- and the temperature-dependence of the equilibrium have been performed. The conversion of three moles of molecular squares **1** to four moles of molecular triangles **2** has an equilibrium constant of $1.98(7) \times 10^{-4}$ at 23.7°C . At this temperature, the ΔG° for the conversion of three moles of squares to four moles of triangles is 21.0 kJ mol^{-1} . The conversion is enthalpically disfavored ($\Delta H^\circ = 23.5\text{ kJ mol}^{-1}$), but entropically favored ($\Delta S^\circ = 8.2\text{ J K}^{-1}\text{ mol}^{-1}$).

Introduction

The self-assembly of supramolecular arrays by combining cationic metal fragments with neutral or anionic linkers has attracted much attention lately.¹ Through the proper choice of metal-containing units and bi- or multidentate linkers, a remarkable variety of supramolecular architectures has been realized, including triangles, squares, other polygons, helices, and polyhedra, as well as 2D and 3D infinite structures. Many of the structures have been designed using the guiding principles of coordination chemistry with attention to the angle subtended by the spectator ligands, the geometric preferences of the linkers, and the flexibility of all components.

Since 1998, numerous publications from this laboratory have pursued the general theme by employing dimetal units (*e.g.*, Mo_2^{4+} , Rh_2^{4+} , Ru_2^{n+} , $n = 4, 5$) as corner pieces and various organic (*e.g.*, $-\text{O}_2\text{CRCO}_2^-$, diamidates) or inorganic (*e.g.*, Cl^- , OH^- , SO_4^{2-}) entities as linkers.² An advantage of this approach is that the products are usually neutral molecules which can be subjected to electrochemical as well as ordinary chemical oxidation.^{2e} It is also possible to make species that have interesting magnetic^{2c} and chiral properties.^{2d}

Structurally, three principal types of products arise when the $[\text{M}_2]$ units (that is dimetal cores suitably insulated against further undesired reactions) and bidentate ligands **L** are combined in a 1 : 1 ratio. These are molecular squares, $([\text{M}_2]\text{L})_4$; molecular triangles; $([\text{M}_2]\text{L})_3$; molecular loops, $([\text{M}_2]\text{L})_2$. The most common $[\text{M}_2]$ corner piece used is the *cis*- $\text{Mo}_2(\text{DAniF})_2^{2+}$ moiety (where DAniF is the anion derived from *N,N'*-di-*p*-anisylformamidine). When the linkers are linear and rigid, such as oxalate or fumarate ions, there is a tendency to generate squares because

of the preferred 90° angle displayed by the $[\text{M}_2]$ unit.³ A few triangles have been obtained when the linker is flexible⁴ (*e.g.*, with cyclohexane-1,4-dicarboxylate). When the linker is intrinsically bent, loops are frequently observed (*e.g.*, with homophthalate, or malonate).⁵ With the very long, bent linker *m*- $\text{O}_2\text{CCH}(\text{CH}_3)\text{O}-\text{C}_6\text{H}_4-\text{OCH}(\text{CH}_3)\text{CO}_2^{2-}$ a macrocyclic ring is formed.^{5c}

To suppose that the synthesis of any one $([\text{M}]\text{L})_n$ or $([\text{M}_2]\text{L})_n$ composition will necessarily give only one result, or, in other words, one and only one value of *n*, has been well recognized as an underestimation of the subtlety of Nature.⁶ In particular, the existence of equilibria in solution between squares and triangles was postulated as early as 1996.⁷ However, the first case in which the solution equilibrium was documented unequivocally by the actual isolation and structural characterization of both the square and the triangle of the same composition was reported by us in 1999.⁸

In this first fully proven case of equilibrating molecular squares and molecular triangles, the species were $[\text{cis-Rh}_2(\text{DAniF})_2(\text{O}_2\text{CCO}_2)]_n$ ($n = 3$ and 4). It was shown that at equilibrium in approximately one millimolar solution, the molar ratio of squares and triangles was not far from unity, but quantitative results have never been obtained. The reason for this is that the only means of distinguishing between the squares and triangles in solution was based on differences between their cyclic voltammograms,⁹ but those overlapped so extensively that it was difficult to deconvolute them in a quantitatively acceptable manner.

Nature has now presented us with a more auspicious opportunity to carry out a full thermodynamic characterization of a system of interconverting squares and triangles. We now describe the system represented by eqn. (1) and (2).



$$K = \frac{[\text{triangles}]^4}{[\text{squares}]^3} \quad (2)$$

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† Electronic supplementary information (ESI) available: Fig. S1 and S2: Thermal ellipsoid plots for the molecular structures of square **1** and triangle **2** showing ethanol molecules close to the $[\text{Mo}_2]$ units. See DOI: 10.1039/b604928a

In this system, both the triangular and the square molecules have been characterized by X-ray crystallography.

Results and discussion

Syntheses and structural results

Quadruply bonded Mo_2^{4+} paddlewheel compounds usually have eclipsed configurations with negligible torsion angles and each paddle forms an angle of about 90° with its neighbors. The Mo_2^{4+} precursor to the supramolecules reported here, $[\text{cis-Mo}_2(\text{DAniF})_2(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$, is normal in these respects and thus has an obvious tendency to form molecular squares when it reacts with rigid linear dicarboxylate dianions.³ In a previous study,³ we have described the reaction of this molybdenum precursor with the perfluoroterephthalate dianion, which was regarded as a rigid and linear linker. Because no suitable crystal had been obtained, the structure of the product was assumed to be a molecular square by analogy to the structures of a series of compounds with dicarboxylate linkers that were being reported.³

Recently, a molecular triangle, $[\text{cis-Mo}_2(\text{DAniF})_2]_3(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)_3$, was isolated from a reaction of the precursor and a solution containing terephthalate dianions as linkers.¹⁰ This surprising result prompted us to revisit the reaction of $[\text{cis-Mo}_2(\text{DAniF})_2(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ with the perfluoroterephthalate analogue that had been reported earlier to produce only squares.³ A reaction in ethanol led to the formation of a deep red precipitate in high yield which turned out to be a mixture of two species, *i.e.*, a molecular square **1** and a molecular triangle **2**, as suggested by the NMR spectra, and later confirmed by X-ray crystallography.

The molecular square **1** was obtained exclusively as plate-like, dark-red crystals suitable for X-ray crystal structure analysis from a solution in CH_2Cl_2 that was layered with ethanol as described in the Experimental section. Crystals of **2** suitable for an X-ray study were grown as a minor product together with crystals of **1** when a larger volume of CH_2Cl_2 was used to recrystallize the molecular square.

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with an inversion center located at the center of the molecule ($Z = 1$). It can be described as a molecular square which has four Mo_2 units at the corners linked by four perfluoroterephthalate groups (Fig. 1). The area of the square formed by the core is $11.2 \times 11.2 \text{ \AA}^2$. In the crystal structure, the C_6F_4 rings are tilted, but the ^1H and ^{19}F NMR spectra in CDCl_3 solution are consistent with only highly symmetric species, suggesting that those rings are torsionally free. Each dimolybdenum unit consists of an eclipsed paddlewheel arrangement, with two cisoid formamidinate paddles and two carboxylate paddles from the perfluoroterephthalate groups. As shown in Table 1 the two crystallographically independent quadruply bonded Mo–Mo distances (2.117(2) and 2.114(2) Å) are in the normal range. There is one ethanol molecule located in one axial position of each Mo_2 unit. The crystallographically independent Mo– O_{EtOH} distances (2.53(1) and 2.58 Å, for Mo(1) and Mo(3), respectively) are short enough to imply more than a mere van der Waals contact between Mo and O atoms (about 3.00 Å). There are three disordered ethanol molecules located inside the square. Other molecules from the crystallization solution fill additional interstices in the unit cell.

Table 1 Selected bond lengths (Å) and angles ($^\circ$) for the molecular square **1**: $2\text{CH}_2\text{Cl}_2 \cdot 9\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$

Mo(1)–Mo(2)	2.117(2)	Mo(4)–N(8)	2.125(8)
Mo(3)–Mo(4)	2.114(2)	Mo(1)–O(9)	2.145(7)
Mo(1)–N(1)	2.113(9)	Mo(1)–O(13)	2.152(7)
Mo(1)–N(3)	2.123(8)	Mo(2)–O(14)	2.119(7)
Mo(2)–N(2)	2.139(8)	Mo(2)–O(10)	2.135(7)
Mo(2)–N(4)	2.113(8)	Mo(3)–O(15A)	2.147(7)
Mo(3)–N(5)	2.114(9)	Mo(3)–O(11)	2.152(7)
Mo(3)–N(7)	2.125(8)	Mo(4)–O(16A)	2.132(7)
Mo(4)–N(6)	2.116(9)	Mo(4)–O(12)	2.150(7)
N(1)–Mo(1)–N(3)	95.0(3)	N(5)–Mo(3)–N(7)	91.1(4)
N(3)–Mo(1)–O(9)	89.2(3)	N(5)–Mo(3)–O(15A)	88.8(3)
N(1)–Mo(1)–O(13)	89.0(3)	N(7)–Mo(3)–O(11)	92.2(3)
O(9)–Mo(1)–O(13)	86.8(3)	O(15A)–Mo(3)–O(11)	87.7(3)
N(4)–Mo(2)–O(10)	89.0(3)	N(6)–Mo(4)–N(8)	91.9(3)
O(14)–Mo(2)–O(10)	86.4(3)	N(6)–Mo(4)–O(16A)	89.6(3)
N(4)–Mo(2)–N(2)	95.3(3)	N(8)–Mo(4)–O(12)	90.9(3)
O(14)–Mo(2)–N(2)	88.6(3)	O(16A)–Mo(4)–O(12)	87.4(3)

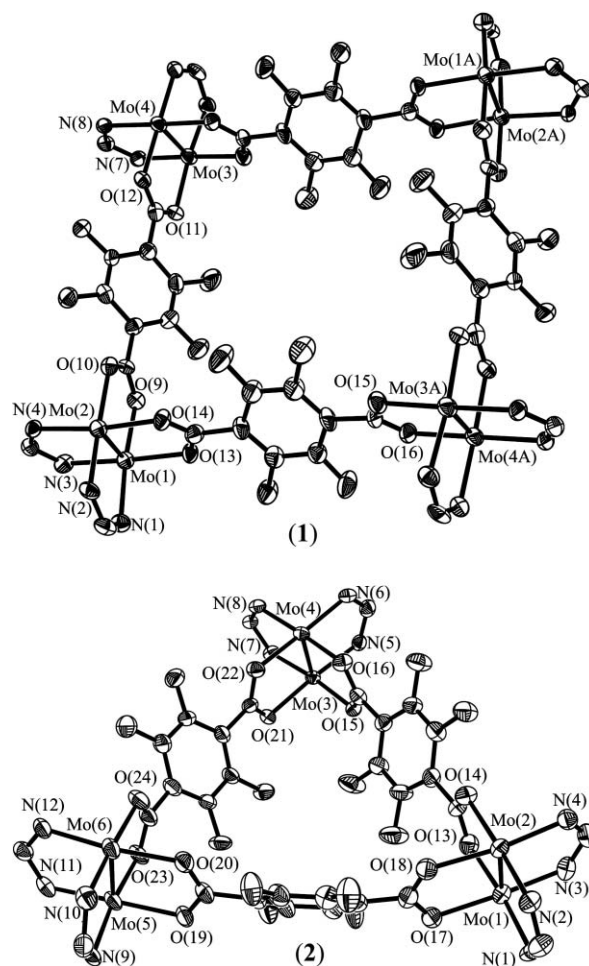


Fig. 1 Core structures of the molecular square **1** and the triangle **2**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, anisyl groups and axial and interstitial molecules are omitted for clarity.

Complex **2** also crystallizes in the triclinic space group $P\bar{1}$ but with $Z = 2$. Its core structure is presented in Fig. 1 and selected distances and angles are given in Table 2. In contrast to the square **1**, this compound contains only three paddlewheel

Table 2 Selected bond lengths (Å) and angles (°) for the molecular triangle 2·3.5CH₂Cl₂·3.5C₂H₅OH·H₂O

Mo(1)–Mo(2)	2.115(1)	Mo(6)–N(12)	2.110(7)
Mo(3)–Mo(4)	2.119(1)	Mo(1)–O(13)	2.145(6)
Mo(6)–Mo(5)	2.111(1)	Mo(1)–O(17)	2.147(6)
Mo(1)–N(1)	2.107(7)	Mo(2)–O(14)	2.153(5)
Mo(1)–N(3)	2.115(7)	Mo(3)–O(15)	2.147(5)
Mo(2)–N(2)	2.101(7)	Mo(2)–O(18)	2.147(6)
Mo(2)–N(4)	2.115(7)	Mo(3)–O(21)	2.190(5)
Mo(3)–N(5)	2.136(6)	Mo(4)–O(22)	2.114(5)
Mo(3)–N(7)	2.128(6)	Mo(4)–O(16)	2.134(5)
Mo(4)–N(6)	2.100(6)	Mo(5)–O(19)	2.147(5)
Mo(4)–N(8)	2.086(6)	Mo(5)–O(23)	2.133(6)
Mo(5)–N(9)	2.107(7)	Mo(6)–O(24)	2.151(6)
Mo(5)–N(11)	2.114(7)	Mo(6)–O(20)	2.152(6)
Mo(6)–N(10)	2.109(7)		
N(1)–Mo(1)–N(3)	95.3(3)	N(8)–Mo(4)–N(6)	94.0(2)
N(3)–Mo(1)–O(13)	89.1(2)	N(8)–Mo(4)–O(22)	89.8(2)
N(1)–Mo(1)–O(17)	91.3(3)	N(6)–Mo(4)–O(16)	91.8(2)
O(13)–Mo(1)–O(17)	83.9(2)	O(22)–Mo(4)–O(16)	83.7(2)
N(2)–Mo(2)–N(4)	94.1(3)	N(9)–Mo(5)–N(11)	94.9(2)
N(2)–Mo(2)–O(18)	91.6(2)	N(11)–Mo(5)–O(23)	90.1(2)
N(4)–Mo(2)–O(14)	90.0(2)	N(9)–Mo(5)–O(19)	89.5(2)
O(18)–Mo(2)–O(14)	84.1(2)	O(23)–Mo(5)–O(19)	85.0(2)
N(7)–Mo(3)–N(5)	93.8(2)	N(10)–Mo(6)–N(12)	95.0(3)
N(5)–Mo(3)–O(15)	91.4(2)	N(12)–Mo(6)–O(24)	89.3(2)
O(15)–Mo(3)–O(21)	83.8(2)	N(10)–Mo(6)–O(20)	90.4(3)
N(7)–Mo(3)–O(21)	91.0(2)	O(24)–Mo(6)–O(20)	85.1(2)

dimolybdenum units. The midpoints of the Mo₂ bonds define a triangle with the average distance between vertices being 11.2 Å. The perfluoroterephthalate linkers are again tilted. Compared to compound **1**, the solid structure of **2** shows evidence of being strained, *i.e.*, the perfluoroterephthalate linkers are bowed, whereas they are relatively linear in the square. The quadruply bonded Mo–Mo distances are 2.115(1), 2.119(1) and 2.111(1) Å, which are indistinguishable from those in the square. There is an ethanol molecule close to one of the axial positions of each dimolybdenum unit. The Mo–O distances are about 2.54 Å.

The crystal packing of these compounds is interesting. As shown in Fig. 2, the square molecules of **1** and the triangular molecules of **2** create square and triangular channels, respectively. The space inside the channels is large enough to include some small molecules. Indeed, disordered ethanol molecules are found in **1**, and disordered ethanol molecules and water molecules are both found in **2**.

NMR studies

When solutions of **1** were first prepared from crystalline material at ambient temperature, there was a set of signals in the ¹H NMR spectrum that corresponded to a main species but also a set of less intense signals that suggested the presence of a second species. It was observed that the relative amounts changed with time. When the experiments were repeated, samples were prepared in a dry-box and quickly cooled to –70 °C. The sample was kept at this temperature until it was placed in the ¹H NMR instrument and then was allowed to reach ambient temperature (*ca.* 22 °C). Under such conditions the spectrum showed only one set of signals that corresponded to a highly symmetric species, logically believed to be the molecular square **1**. The signals consisted of one singlet at 8.52 ppm for the methine protons, one singlet at 3.70 ppm for the OCH₃ groups, and only a pseudo-singlet centered

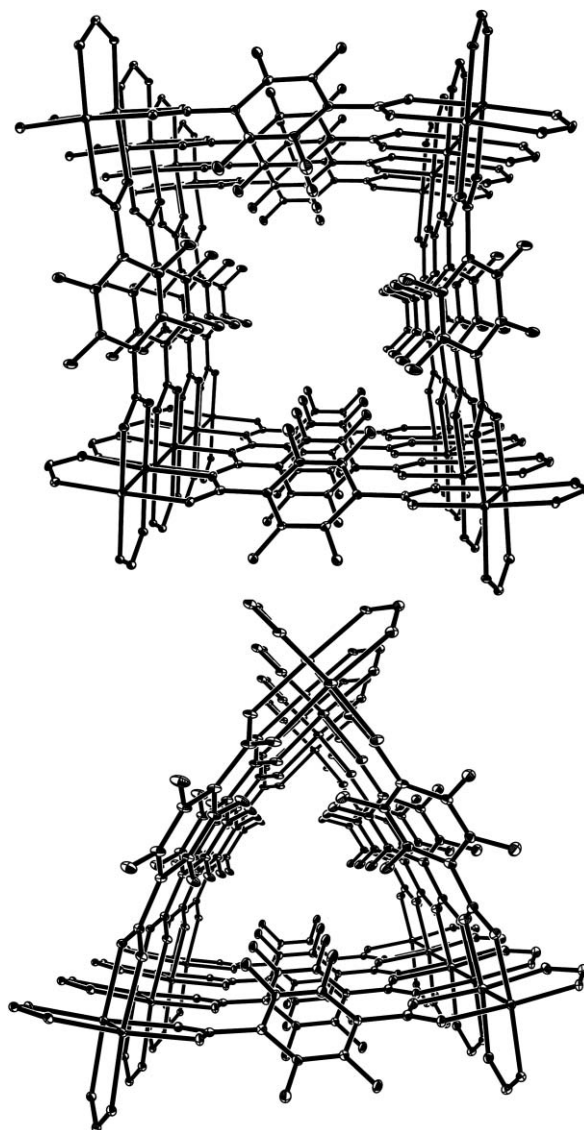


Fig. 2 Crystal packing of the molecular square **1** and the triangle **2**. Hydrogen atoms, anisyl groups and solvent molecules are omitted for clarity.

at 6.66 ppm for the aromatic protons. Under similar conditions, the ¹⁹F NMR spectrum showed a singlet at –64.00 ppm. These features are consistent with the molecular structure found in the solid state. However, after some time the spectra had changed, with an additional set of signals appearing in the ¹H NMR spectrum. These were singlets at 8.54 ppm for methine groups and at 3.70 ppm for OCH₃ groups, and a multiplet centered at 6.69 ppm which can be assigned to aromatic protons of anisyl groups. In the ¹⁹F NMR spectrum, another singlet also appeared with the passing of time at –63.60 ppm. After more than 10 h at ambient temperature, the spectra did not further change indicating that equilibrium had been attained.

Each of the signals in the second set was shifted downfield relative to the corresponding signal for **1**, and could be assigned to a new symmetrical species. By comparison with the NMR spectra taken immediately after dissolving crystals of **2**, this new species was identified as the molecular triangle. Similarly to **1**, the NMR

spectra from solutions of **2** changed as time passed giving rise after several hours to the same final result as that just described. In other words, a dynamic equilibrium is established in solution between molecular squares and triangles, as shown in eqn (1).

The attainment of equilibrium is significantly affected by the presence of water. Although a similar equilibrium constant was observed, the rate of reaction was increased by the addition of water. The water molecules most likely act as a catalyst in the process of reaching equilibrium in which bond breaking between molybdenum units and carboxylate linkers must occur. It is possible that water molecules form bonds at equatorial positions of the intermediate(s) when the Mo–O bonds are severed, and stabilize the intermediate(s). It is also possible that interconversion would not occur if solutions absolutely free of H₂O (or some other donor molecules) could be prepared.

NMR studies of concentration dependence

Because the signals in the ¹H NMR spectra for **1** and **2** are very close and there is some overlap, proton NMR spectra are not as useful for a study of the equilibrium as ¹⁹F NMR spectra, where the signals for the fluorine atoms of **1** and **2** are well separated. Thus the latter allow the measurement of the molar ratios simply by integration of the signals, as shown in Fig. 3. The molar fractions at equilibrium, *X*, of **1** and **2** as a function of total concentration of [Mo₂] are given in Table 3. The ratio of **1** to **2** varies as a function of concentration. At 8.47 mmol kg⁻¹, 68.5% of the dimolybdenum units are present as part of **1**, and this percentage decreases to 50.4% when the concentration is 0.53 mmol kg⁻¹. This indicates that **1** is entropically disfavored because it is assembled from more building blocks than **2**. The average of the equilibrium constants in these solutions is found to be 1.98(7) × 10⁻⁴, and therefore Δ*G*⁰ for reaction (1) is 21.0(1) kJ mol⁻¹, or 7.0 kJ mol⁻¹ per mole of squares converted to triangles.

To characterize the equilibrium further, we have also studied it as a function of temperature using the van't Hoff method.¹¹ In Fig. 4, values of -ln *K* over the temperature range 30 to 53 °C are plotted vs. 1/*T*, giving a satisfactorily linear relationship. From the slope of this line we find that Δ*H*⁰ for reaction (1) is 23.5 kJ mol⁻¹. By extrapolation of the line to 1/*T* = 0, the standard entropy change Δ*S*⁰ of reaction (1) is found to be 7.9 J mol⁻¹ K⁻¹. Alternatively, and we believe more accurately, by inserting the values for Δ*G*⁰ at 296.85 K (21.0 kJ mol⁻¹) and Δ*H*⁰ (23.5 kJ mol⁻¹) into the equation Δ*G*⁰ = Δ*H*⁰ - *T*Δ*S*⁰, we obtain a value of Δ*S*⁰ = 8.4 J mol⁻¹ K⁻¹. Since an objective assignment of uncertainties is moot we will take a weighted average in which the latter is given twice the weight and conclude that Δ*S*⁰ = 8.2 ± 0.3 J mol⁻¹ K⁻¹.

Table 3 Equilibrium constant as a function of the molar fraction, *X*, of **1** and **2** with concentrations measured in CDCl₃ at 23.7 °C

[Mo ₂] ^a /mmol kg ⁻¹	<i>X</i> ₁	<i>X</i> ₂	<i>K</i> ^b (× 10 ⁻⁴)
8.47	0.685	0.315	2.05
4.23	0.643	0.357	2.04
2.26	0.606	0.393	1.90
1.06	0.555	0.445	1.92
0.53	0.504	0.496	1.98

^a [Mo₂] represents the concentration of the *cis*-Mo₂(DAniF)₂²⁺ unit. ^b *K* = [2]⁴/[1]³.

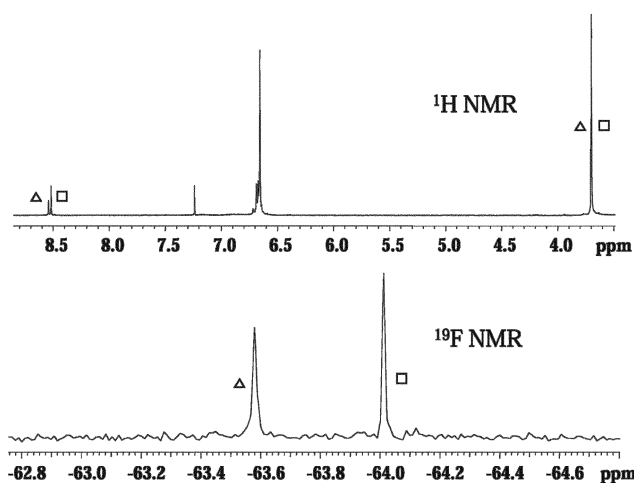


Fig. 3 Examples of ¹H and ¹⁹F NMR spectra showing the equilibrium between **1** and **2**. Note that the signals for the squares and triangles in the ¹⁹F NMR spectrum are well separated.

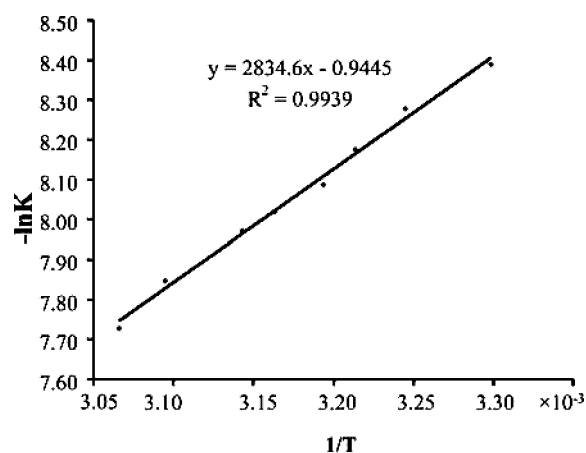


Fig. 4 van't Hoff plot for the equilibrium of the molecular square [cis-Mo₂(DAniF)₂]₄(O₂CC₆F₄CO₂)₄ and molecular triangle [cis-Mo₂(DAniF)₂]₃(O₂CC₆F₄CO₂)₃. In this plot the slope corresponds to the enthalpy term Δ*H*⁰/*R*, and the *y*-intercept represents the value of -Δ*S*⁰/*R*.

From the values just discussed, we can write the following for conversion of 3 moles of the squares to 4 moles of triangles:

$$\Delta G^0 = 21.0 \text{ kJ mol}^{-1}$$

$$\Delta H^0 = 23.5 \text{ kJ mol}^{-1}$$

$$\Delta S^0 = 8.2 \text{ J mol}^{-1} \text{ K}^{-1}.$$

These values indicate that there is very little strain energy (*ca.* 1.8 kJ per edge) in the triangles relative to the squares, which is easily offset by a small entropy increase arising from the increased contributions from rotations and translations, both hindered by the fact that the molecules are immersed in solvent.

Summary

In this paper, we show that the preparations of both molecular triangles and squares having [Mo₂] units and perfluoroterephthalate

dianions as bridging linkers can be accomplished. In chloroform solution they exist in equilibrium. Both compounds have been characterized crystallographically making this one of the few examples^{6,8} in which both species in a dynamic equilibrium could be isolated and analyzed by X-ray work. Since the perfluoroterephthalate linkers are linear and relatively rigid, formation of molecular squares is not unexpected. Thus it was a pleasant surprise that the reaction of the [Mo₂] precursor and the dianion also produces the molecular triangle **2**. Multinuclear NMR studies confirm that conversion of squares to triangles is entropically favored but enthalpically disfavored with an equilibrium constant of $1.98(7) \times 10^{-4}$ at 23.7 °C. Per mole of square, the conversion to triangles has $\Delta G^0 = 7.0 \text{ kJ mol}^{-1}$, $\Delta H^0 = 7.9 \text{ kJ mol}^{-1}$, and $\Delta S^0 = 2.7 \text{ J mol}^{-1} \text{ K}^{-1}$.

Experimental

All manipulations and procedures were carried out under N₂ using either a drybox or standard Schlenk line. Solvents were distilled and degassed prior to use. The compound [cis-Mo₂(DAniF)₂(CH₃CN)₄](BF₄)₂ was prepared following a literature method.¹² The salt (Et₄N)₂(O₂CC₆F₄CO₂) was prepared and isolated as a colorless solid by neutralizing the corresponding diacid with 2 equiv. of 35% Et₄NOH in water. The solvent was removed and the solid was then thoroughly dried under vacuum. All other reagents were purchased from commercial sources and used as received.

Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia. NMR spectra were recorded on an INOVA-300 NMR spectrometer. The references used were the residual proton of CDCl₃ for the ¹H NMR spectra and CF₃COOH in CDCl₃ for the ¹⁹F NMR spectra.

Preparation of [cis-Mo₂(DAniF)₂]₄(O₂CC₆F₄CO₂)₄ (**1**)/[cis-Mo₂(DAniF)₂]₃(O₂CC₆F₄CO₂)₃ (**2**)

A mixture of [cis-Mo₂(DAniF)₂(CH₃CN)₄](BF₄)₂ (330 mg, 0.320 mmol) and (Et₄N)₂O₂CC₆F₄CO₂ (150 mg, 0.300 mmol) was

dissolved in 30 mL of CH₂Cl₂ and 2 mL of ethanol at room temperature. The resulting red solution was then layered with 30 mL of ethanol, giving dark red crystals of the square (**1**) over a period of two weeks. These crystals were pure **1** as shown by NMR. Yield: 210 mg, 72%. ¹H NMR (CDCl₃, δ, ppm): 8.52 (s, 8H, methine), 6.66 (pseudo-singlet, 64H, aromatic), 3.70 (s, 48 H, -OCH₃). ¹⁹F NMR (CDCl₃, δ, ppm): -64.00. Anal. Calc. for C₁₅₂H₁₂₀F₁₆Mo₈N₁₆O₃₂: C 48.41, H 3.21, N 5.95%. Found: C 48.23, H 3.17, N 5.64%. Prism-like crystals of **2** suitable for the X-ray work were found as a minor product together with plate-like crystals of **1** when larger volumes of CH₂Cl₂ and ethanol were used for the crystallization process described above for **1**. The crystals were manually separated. ¹H NMR (CDCl₃, δ, ppm): 8.54 (s, 6H, methine), 6.69. (m, 48H, aromatic), 3.70 (s, 36 H, -OCH₃). ¹⁹F NMR (CDCl₃, δ, ppm): -63.60. Anal. Calc. for C₁₁₄H₉₀F₁₂Mo₆N₁₂O₂₄: C 48.41, H 3.21, N 5.95%. Found: C 48.28, H 3.10, N 5.75%.

Equilibrium measurements by NMR

¹H and ¹⁹F NMR spectra were measured at 23.7 °C as a function of total concentration of the building block cis-Mo₂(DAniF)₂,¹³ which is abbreviated as [Mo₂]. For concentration-dependent NMR experiments at 23.7 °C, 30.1 mg of crystalline solid **1** was dissolved in $3.78 \times 10^3 \text{ mg}$ of CDCl₃ to give a solution in which the [Mo₂] concentration was 8.47 mmol kg⁻¹.¹⁴ Solutions of other concentrations, 4.23, 2.26, 1.06 and 0.53 mmol kg⁻¹, were prepared by successive dilutions of the first solution. ¹H and ¹⁹F NMR spectra at each concentration were measured before equilibration occurred and at appropriate intervals thereafter. The ratio of **1** to **2** was determined by integration of their signals in the ¹⁹F NMR spectra. The concentration of each compound was calculated by taking its fraction of the total concentration of the building block, and dividing by 4 for the molecular square **1** and by 3 for the molecular triangle **2**.

For the variable temperature NMR experiments a sample with a concentration of 2.7 mmol kg⁻¹ of the building block was used. The ¹H NMR and ¹⁹F spectra were recorded at 30, 35, 38,

Table 4 Crystallographic data

Compound	1·2CH ₂ Cl ₂ ·9C ₂ H ₅ OH·2H ₂ O	2·3.5CH ₂ Cl ₂ ·3.5C ₂ H ₅ OH·H ₂ O
Chemical formula	C ₁₇₂ H ₁₈₂ Cl ₄ F ₁₆ Mo ₈ N ₁₆ O ₄₃	C _{124.5} H ₁₂₀ Cl ₇ F ₁₂ Mo ₆ N ₁₂ O _{28.5}
<i>M_r</i>	4374.66	3293.12
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	12.792(6)	12.657(5)
<i>b</i> /Å	19.66(1)	20.015(7)
<i>c</i> /Å	20.81(1)	29.69(1)
<i>a</i> /°	85.705(9)	103.632(7)
<i>β</i> /°	89.699(8)	100.921(6)
<i>γ</i> /°	78.322(9)	97.011(6)
<i>V</i> /Å ³	5110(4)	7065(4)
<i>Z</i>	1	2
<i>D_c</i> /g cm ⁻³	1.422	1.548
<i>μ</i> (Mo-Kα)/mm ⁻¹	0.613	0.737
<i>T</i> /°C	188(2)	186(2)
GOF	1.094	1.141
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b (<i>I</i> > 2σ)	0.0989, 0.2473	0.0808, 0.2048

^a $R_1 = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$. ^b $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$.

40, 43, 45, 50 and 53 °C. After each measurement at a given temperature, the sample was allowed sufficient time to equilibrate. This was monitored by frequently recording NMR spectra at each temperature until the ratio of **1** to **2** no longer changed.

X-Ray structure determinations

For **1** and **2** diffraction data were collected at low temperature (ca. 187 K) on a Bruker SMART 100 CCD area detector. Cell parameters were determined using the program SMART.¹⁵ Data reduction and integration were performed with the software package SAINT,¹⁶ while absorption corrections were applied by using the program SADABS.¹⁷ The positions of the Mo atoms were found by direct methods using the program package SHELXTL.¹⁸ Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were not included in the structure refinement. Non-hydrogen atoms were refined with anisotropic displacement parameters except for the disordered atoms.

In each of these structures, a few *p*-anisyl groups and solvent molecules are disordered. In **1**, one crystallographically independent *p*-anisyl group shows two orientations in a ratio of 0.59 to 0.41. In **2**, three *p*-anisyl groups have two orientations with occupancy of 0.5 for each one. Other details of data collection and refinement for these compounds are listed in Table 4.

CCDC reference numbers 603498 and 603499 for **1**·2CH₂Cl₂·9C₂H₅OH·2H₂O and **2**·3.5CH₂Cl₂·3.5C₂H₅OH·H₂O, respectively.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604928a

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