Inorg. Chem. **2001,** *40,* 575−577

A Neutral Triangular Supramolecule Formed by Mo_2^{4+} Units

F. Albert Cotton,*,[†] Chun Lin,[†] and Carlos A. Murillo*,[†,‡]

Department of Chemistry and Laboratory for Molecular
Structure and Bonding, P.O. Box 300012, Texas A&M
University, College Station, Texas 77842-3012, and
Department of Chemistry, University of Costa Rica,
Ciudad Universitaria, Costa Rica

Received August 22, 2000

Introduction

Recently there has been a lot of activity in the area of supramolecular chemistry using mononuclear metal-containing units to produce various types of polygons such as triangles, squares, and more complex units.[1] Frequently these materials have high ionic charges and are not electrochemically active.

Our quest has been the preparation of neutral supramolecular units built from corner pieces containing dimetal units linked by divalent anions such as dicarboxylates. We have prepared a large number of complexes of the type $[Mo_2(DAniF)_3]_2(\mu\text{-}O_2C{-}X{-}CO_2)$, where DAniF = *N*,*N*′-di-*p*-anisylformamidinate and X is some type of linker, usually, but not necessarily, an organic group.[2] We have also made a series of squares having the formula $[M_2(DAniF)_2(\mu\text{-}O_2C{-}X{-}CO_2)]_4$,[3] where M = Mo and Rh, and also tridimensional complexes having octahedra of M_2 units, M = Mo[4] and Rh,[5] joined by four 1,3,5-benzenetricarboxylate (trimesate) anions. For compounds having dirhodium units, it is possible to make both equatorial and axial connections to produce sheetlike structures and assemblies having infinite tubes.[6]

While studying the dirhodium molecular square with oxalate linkers, $[Rh_2(DAniF)_2(\mu\text{-}O_2C{-}R'{-}CO_2)]_4$, we found that depending on the reaction conditions it was also possible to isolate, in pure form, a molecular triangle of the same empirical formula, namely, $[Rh_2(DAniF)_2(\mu\text{-}O_2C{-}CO_2)]_3$. Furthermore, an equilibrium between these two species was found in solution.[3] No such molecular triangle was known before having metal−metal bound units derived from paddlewheel complexes, although there is a triangular compound having three singly bonded $Ru_2(CO)_4(CH_3CN)_2$ units linked by tartrate dianions[7] and another one with dicobalt units of the type $Co_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)$ linked by diacetylide groups.[8] There are also ionic complexes having the formula $\{[\textit{trans}\text{-}Mo_2(O_2CCF_3)_2(\mu\text{-dppa})]_3(\mu_6\text{-}CO_3)(\mu_2\text{-}X)_3\}F$ [X = Cl, Br, or I; dppa = *N*,*N*-bis(diphenylphosphino)amine].[9] More prevalent are triangles with mononuclear units as corners.[10]

Experimental Section

General Considerations. All the syntheses were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and then distilled under nitrogen following conventional methods. Chemicals were purchased from Aldrich and used as received. The tetrabutylammonium salt was prepared by neutralizing the dicarboxylic acid with 1.0 M Bu^n_4NOH in MeOH solution, followed by vacuum drying at 40−50 °C for 24 h. The compound $[\textit{cis}\text{-}Mo_2(DAniF)_2(CH_3CN)_4](BF_4)_2$ was prepared by following published procedures.[11] Elemental analysis was performed by Canadian Microanalytical Service, Delta, British Columbia. The cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer in 0.10 M $Bu^n_4NPF_6$ solution (CH_2Cl_2) with Pt working and auxiliary electrodes and a Ag/AgCl reference electrode, and scan rates of 100 mV s^{-1}. All the potential values are referred to the Ag/AgCl electrode, and under the present experimental conditions, the $E_{1/2}(Fc^+/Fc)$ was consistently measured at 440 mV.

Preparation of $[\textit{cis}\text{-}Mo_2(DAniF)_2]_3(\textit{trans}\text{-}1,4\text{-}O_2CC_6H_{10}CO_2)_3$ (1). To a stirred solution of $[\textit{cis}\text{-}Mo_2(DAniF)_2(CH_3CN)_4](BF_4)_2$ (104 mg, 0.100 mmol) in 20 mL of CH_3CN was added $(Bu^n_4N)_2(\textit{trans}\text{-}1,4\text{-}O_2CC_6H_{10}CO_2)$ (65.5 mg, 0.100 mmol) in 10 mL of CH_3CN. An immediate reaction took place with formation of a bright yellow precipitate, which was collected by filtration, washed several times with CH_3CN, and dried under vacuum. The crude product was extracted with CH_2Cl_2 (2 × 5 mL). Hexanes were then carefully layered on the top of the solution to afford a yellow crystalline material after several days. The yield was essentially quantitative. ^1H NMR δ (ppm, in CD_2Cl_2): 8.43 (s, 6H, −NC*H*N−), 6.63 (dd, 48H, aromatic), 3.70 (s, 36H, $-OCH_3$), 2.91 (br, 6H, cyclohexyl), 2.30 (m, 12H, cyclohexyl), 1.89 (m, 12H, cyclohexyl). Anal. for **1**, $C_{114}H_{120}Mo_6N_{12}O_{24}$, calcd (found): C, 52.30 (51.95); H, 4.62 (4.60); N, 6.42 (6.35). Electrochemistry: An irreversible oxidation at E_{pa} of 510 mV vs Ag/AgCl.

Crystallographic Procedures. Single-crystal X-ray data on compound **1** were collected on a Bruker SMART 2000 CCD detector system. Cell parameters were measured using the SMART[12] software. Data were corrected for Lorentz and polarization effects using the program SAINT.[13] Absorption corrections were applied using SADABS.[14]

The positions of some of the non-hydrogen atoms were found via direct methods by employing the program package SHELXTL.[15]

---

* To whom correspondence should be addressed. E-mail: cotton@tamu.edu or murillo@tamu.edu.

[†] Texas A&M University.

[‡] University of Costa Rica.

(1) See for example: (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853 and references therein. (b) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417 and references therein. (c) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483 and references therein.

(2) Cotton, F. A.; Donahue, J. P.; Lin, C.; Murillo, C. A. *Inorg. Chem.*, accepted.

(3) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 4538.

(4) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *Chem. Commun.* **1999**, 841.

(5) Cotton, F. A.; Lin, C.; Murillo, C. A. Unpublished results.

(6) Cotton, F. A.; Lin, C.; Murillo, C. A. *Chem. Commun.* **2001**, 11.

(7) Süss-Fink, G.; Wolfender, J.-L.; Neumann, F.; Stoeckli-Evans, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 429.

(8) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 4966.

(9) Suen, M.-C.; Tseng, G.-W.; Chen, J.-D.; Keng, T.-C.; Wang, J.-C. *Chem. Commun.* **1999**, 1185.

(10) For some recent references, see for example: (a) Duhme-Klair, A.-K.; Vollmer, G.; Mars, C.; Frohlich, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1626 and references therein. (b) Bonnefous, C.; Bellec, N.; Thummel, R. P. *Chem. Commun.* **1999**, 1243. (c) Lai, S.-W.; Chan, M. C.-W.; Peng, S.-M.; Che, C.-M. *Angew. Chem., Int. Ed.* **1999**, *38*, 669. (d) Sun, S.-S.; Lees, A. J. *Inorg. Chem.* **1999**, *38*, 4181. (e) Neels, A.; Stoeckli-Evans, H. *Inorg. Chem.* **1999**, *38*, 6164. (f) Habereder, T.; Warchhold, M.; Nöth, H.; Severin, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 3225. (g) See also ref 1a.

(11) Chisholm, M. H.; Cotton, F. A.; Daniels, L. M.; Folting, K.; Huffman, J.; Iyer, S.; Lin, C.; Macintosh, A. M.; Murillo, C. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1387.

(12) *SMART V5.5 Software for the CCD Detector System*; Bruker Analytical Instruments Division: Madison, WI, 1998.

(13) *SAINT, V5.06 Software for the CCD Detector System*; Bruker Analytical Instruments Division: Madison, WI, 1997.

(14) SADABS. Program for absorption correction using the Bruker CCD based on the Blessing's method: *Acta Crystallogr.* **1995**, *A51*, 33.

(15) *SHELXTL*, version 5.03; Siemens Industrial Automation Inc.; Madison, WI, 1994.

10.1021/ic000963z CCC: $20.00

Table 1. Crystal and Structure Refinement Data for **1**·4.9CH$_2$Cl$_2$

compd	[*cis*-Mo$_2$(DAniF)$_2$]$_3$(*eq,eq*−1,4-O$_2$CC$_6$H$_{10}$CO$_2$)$_3$·4.9CH$_2$Cl$_2$
formula	$C_{118.9}H_{129.8}Cl_{9.8}Mo_6N_{12}O_{24}$
fw	3034.00
space group	*C*2/*c*
a, Å	34.412(3)
b, Å	34.012(3)
c, Å	22.489(2)
β, deg	93.273(2)
vol, Å^3	26279(4)
Z	8
T, °C	193(2)
λ, Å	0.71073
ρ_{calcd}, g cm^{-3}	1.534
μ, mm^{-1}	0.825
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.141, 0.291
R1, wR2	0.220, 0.366

[a] $R1 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. [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 Distances (Å) for **1**

Mo(1)−Mo(2)	2.809(2)	Mo−O (av)	2.147[5]
Mo(3)−Mo(4)	2.077(3)	Mo−N (av)	2.13[1]
Mo(5)−Mo(6)	2.098(3)		

Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. All hydrogen atoms were used in calculated positions. One DAniF$^-$ group and one *p*-MeOPh group exhibit a slight disorder. The disordered groups were each refined as a pair, comprising a major and a minor orientation, but the members of each pair were constrained to have the same bond distances and angles. The major orientation of the group containing atom N(7) had an occupancy of 0.61, and that of the group containing atom O(11) was 0.55. Due to the weak data set resulting from disorder and the large cell, only the molybdenum atoms were refined anisotropically. Other details of data collection and refinement for **1** are given in Table 1.[16] Selected atomic distances are provided in Table 2. Other crystallographic data are available as Supporting Information.

Results and Discussion

Preparation. The compound reported here was obtained in essentially quantitative yield following a method (eq 1) in which [*cis*-Mo$_2$(DAniF)$_2$(CH$_3$CN)$_4$](BF$_4$)$_2$ reacts with the tetrabutylammonium salt of the dicarboxylic acid in essentially stoichiometric amounts using acetonitrile as solvent. The yellow

$$3[\textit{cis}\text{-Mo}_2(\text{DAniF})_2(\text{CH}_3\text{CN})_4](\text{BF}_4)_2 + 3(\text{NBu}^{n}{}_4)_2(\textit{trans}\text{-1,4-O}_2\text{CC}_6\text{H}_{10}\text{CO}_2)\xrightarrow{\text{CH}_3\text{CN}} [\textit{cis}\text{-Mo}_2(\text{DAniF})_2]_3[\textit{eq,eq}\text{-1,4-O}_2\text{CC}_6\text{H}_{10}\text{CO}_2]_3 + 6(\text{NBu}^{n}{}_4)(\text{BF}_4) \quad (1)$$

crystalline material is moderately soluble in common organic solvents. Its ^{1}H NMR spectrum, which shows only one type of DAniF ligand and one type of dicarboxylate bridge, is consistent with the presence of a highly symmetrical species in solution.

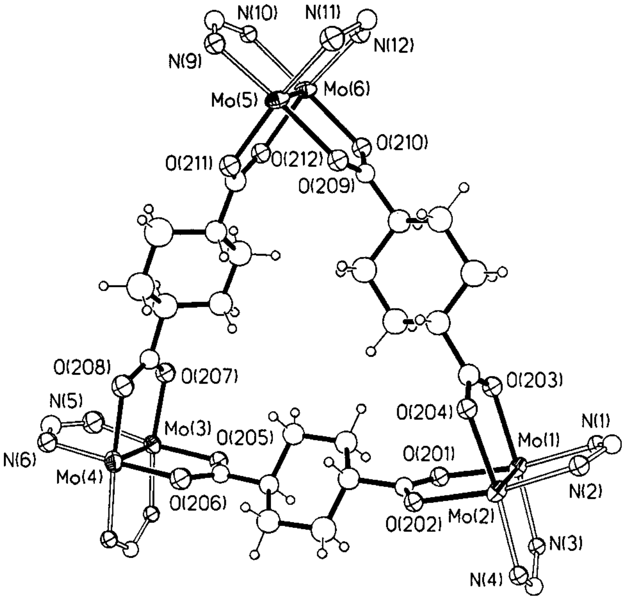

Figure 1. The core of the molecular structure of [*cis*-Mo$_2$(DAniF)$_2$]$_3$-[*eq,eq*-1,4-O$_2$CC$_6$H$_{10}$CO$_2$]$_3$ in **1**·4.9CH$_2$Cl$_2$ with non-hydrogen atoms drawn at the 40% probability level and hydrogen atoms shown as arbitrarily sized circles. For clarity the *p*-anisyl group on each N atom has been removed.

Structure. The molecular structure is shown in Figure 1. There are three quadruply bonded Mo$_2$(DAniF)$_2$ units linked by three [*eq,eq*-1,4-O$_2$CC$_6$H$_{10}$CO$_2$]$^{2-}$ dianions. The midpoints of the Mo$_2$ bonds define a triangle with the average distance between vertexes being 11.16 Å. The Mo−Mo distances of 2.077(3), 2.089(2), and 2.098(3) Å fall in the range of other quadruply-bonded dimolybdenum complexes.[20] Other distances such as those for Mo−N and Mo−O bonds are as expected, but some are affected by crystallographic disorder.

It is interesting to compare the conformation of the 1,4-cyclohexanedicarboxylate dianion in compound **1** with that found in the previously reported [Mo$_2$(DAniF)$_3$]$_2$(O$_2$CC$_6$H$_{10}$-CO$_2$) compound.[2] *trans*-1,4-C$_6$H$_{10}$(CO$_2$)$_2$ can exist in two conformations, one with both CO$_2$ groups axial (*ax,ax*) and the other with both CO$_2$ groups equatorial (*eq,eq*). In compound **1** we find the *eq,eq* conformation, whereas in the previous case the conformation was *ax,ax*. Accordingly, the average distance between the centers of the two Mo$_2$ units in **1** (11.16 Å) is much greater than it was in the previous case (9.78 Å). That, in turn, should lead to reduced coupling between the Mo$_2$ units. It was not possible to determine how many electrons were involved in the highly irreversible oxidation wave for **1**, but with essentially no coupling it could be that the +3 species was

---

(16) The values of R1 and wR2 for least squares refinement on F^2, calculated for data with $I > 2\sigma(I)$, 0.141 and 0.291, respectively, are larger than those normally obtained for small inorganic molecules. This is very common for supramolecules, where values of wR2 in the range 0.20−0.30[17] and above[18] have been published. It is a consequence of having very large unit cells, disordered appendages such as phenyl groups or alkyl groups, and large numbers of (usually disordered) solvent molecules. Despite these relatively poor figures of merit, crystal structures of these molecules are conclusive as to the general shape of the molecule, and having such a structure is better than having to rely only upon various sorts of indirect evidence (e.g., mass spectra, NMR), as is sometimes the case.[19]

(17) For some examples, see: (a) Iengo, E.; Milani, B.; Zangrando, E.; Geremia, S.; Alessio, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 1096. (b) Mann, S.; Huttner, G.; Zsolnai, L.; Heinze, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2808. (c) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *Chem. Commun.* **1996**, 1535. (d) Berseth, P. A.; Sokol, J. J.; Shores, M. P.; Heinrich, J. L.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 9655. (e) Whang, D.; Park, K.-M.; Heo, J.; Ashton, P.; Kim, K. *J. Am. Chem. Soc.* **1998**, *120*, 4899.

(18) See for example: Whang, D.; Kim, K. *J. Am. Chem. Soc.* **1997**, *119*, 451.

(19) See for example: (a) Olenyuk, B.; Whiteford, J. A.; Fechtenkotter, A.; Stang, P. J. *Nature* **1999**, *398*, 796. (b) See also ref 1.

(20) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Oxford University Press: Oxford, 1993.

produced and that the irreversibility is accounted for by the instability of such a highly oxidized species.

Each of the dinuclear units has the commonly found paddlewheel structure with nearly negligible torsion angles and each paddle being nearly 90° from its neighbors. Not surprisingly, this type of arrangement has previously given a number of molecular squares which have been prepared[3,21] following a preparative protocol identical to that described for **1** when more rigid linkers such as oxalate, fumarate, and tetrafluorophthalate were used. In **1** the flexibility of the linker allows for the formation of a molecular triangle instead.

As mentioned earlier, there is one other neutral molecular triangle with dimetal units derived from paddlewheel complexes, [*cis*-$Rh_2(DAniF)_2]_3[O_2CCO_2]_3$, and in solution this exists in equilibrium with the corresponding square. It is appropriate to ask why there is such a difference between the rhodium system, with oxalate bridges, and the molybdenum case with cyclohexanedicarboxylate bridges. We believe the following points are relevant. With regard to the rhodium compounds, we note that the triangle shows evidence of being strained, i.e., the oxalate bridges are bowed, whereas they would normally be flat, and they are flat in the square. Thus, we conclude that the triangle is enthalpically disfavored, and its competitiveness with the square must be due to a more favorable entropy.

While it is true that the conversion of three molecules to four, eq 2, causes an increase in entropy of $R \ln(4/3) = 0.57$ cal K^{-1}

$$3\square \rightleftharpoons 4\triangle \tag{2}$$

mol^{-1}, this seems unlikely to be enough to offset the unfavorable enthalpy penalty. A more likely factor is solvent entropy. If the larger cavity in the square can trap and restrict the freedom of several solvent molecules, while the triangle cannot, this might provide the entropy change needed to drive reaction 2 to the right. In the case of square vs triangle for the dimolybdenum system, both may be able to trap and organize solvent molecules to a similar extent, thus reducing that as an entropy factor favoring the triangle. However, with the very flexible cyclohexanedicarboxylate bridge, there is unlikely to be any significant enthalpy factor favoring the square. Thus, the possibility of finding conditions under which the square counterpart of the dimolybdenum triangle with cyclohexanedicarboxylic acid exists is far from zero, although we have not yet succeeded in doing so. Perhaps a suitable template is required to favor its formation.

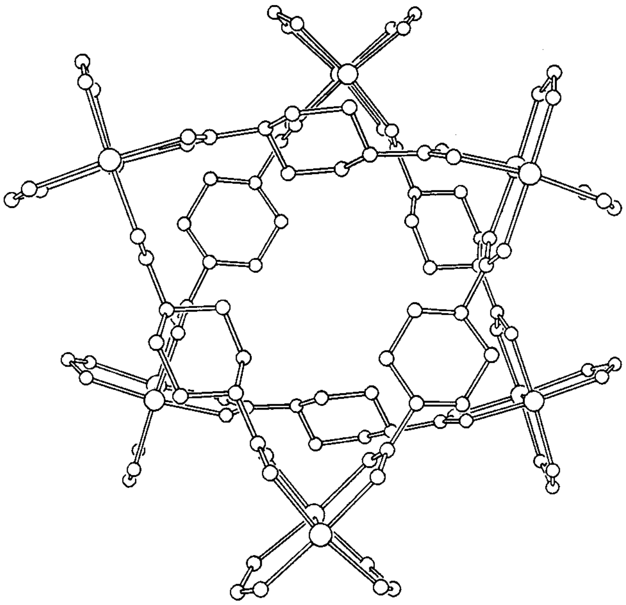

Figure 2. A drawing of the stacking of two molecules (with the *p*-anisyl group and hydrogen atoms removed). Notice the rotation of 60° between triangles. Thus the layers give an ABAB··· pattern, which leaves channels in the direction of the stacking.

The packing of the triangular molecules in **1** is also interesting. As shown in Figure 2, these are stacked in the crystal but with alternating orientations differing by about 60°. Thus, as the alternating layers stack a channel is formed, which is filled by disordered CH_2Cl_2 molecules.

Finally, we note that there is another class of molecular triangle containing Mo_2 units. These are the ionic complexes {[*trans*-$Mo_2(O_2CCF_3)_2(\mu$-dppa)$]_3(\mu_6\text{-}CO_3)(\mu_2\text{-}X)_3$}F, X = Cl, Br, or I,[9] in which each of the three Mo_2 units possesses three bridging ligands (two *trans*-O_2CCF_3 groups and one dppa molecule). The three units are then linked by a central μ_6-CO_3 dianion, and there are three μ_2-X groups bridging the axial positions of the Mo_2 units.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Supporting Information Available: An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000963Z

---

(21) (a) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.*, accepted. (b) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A.; Yu, S. Y. *J. Chem. Soc., Dalton Trans.*, submitted.