Inorg. Chem. **2006**, *45*, 9480–9486

Inorganic Chemistry
Article

An Isomeric Pair of Fluoride-Bridged Cyclic Dimolybdenum Triads

F. Albert Cotton,*,† Chun Y. Liu,*,†,‡ Carlos A. Murillo,*,† and Qinliang Zhao†

Department of Chemistry and Laboratory for Molecular Structure and Bonding, P.O. Box 3012, Texas A&M University, College Station, Texas 77842-3012, and Department of Chemistry, Tongji University, Shanghai 200092, P. R. China

Received August 11, 2006

A pair of isomeric cyclic triads containing three quadruply bonded [Mo_2] units, [Mo_2(cis-DAniF)$_2$]$^{2+}$ (DAniF = *N*,*N'*-di-*p*-anisylformamidinate), bridged by six fluoride anions, has been synthesized and crystallographically characterized. For the α isomer, the three [Mo_2] units are oriented in two orthogonal directions. Two of them are structurally equivalent and parallel to each other, but oriented perpendicular to the third one. The β isomer is a triangle with three geometrically identical [Mo_2] units, parallel to each other, as the vertices. Thus, the β isomer possesses idealized D_{3h} symmetry while the α isomer only has C_{2v} symmetry. These two isomers do not interconvert in boiling THF or toluene or under irradiation with ultraviolet light, but oxidation of the α isomer first generates an α^+ species that changes to β^+. The two isomers have very similar electrochemical behavior, both showing three reversible one-electron redox processes for the [Mo_2] centers and similar potential separations ($\Delta E_{1/2}$). The first and second redox couples are well separated (ca. 390–410 mV), while the second and third ones are separated by only about 150 mV.

Introduction

Supramolecular chemistry based on extended ligand coordination to metal ions is an active research area.[1] The diverse binding modes of metal units and the vast array of organic and/or inorganic fragments that can be used as ligands has resulted in countless well-defined discrete molecules and infinite networks with various sizes, shapes, topologies, and dimensions.[2] In addition to fundamental interest, studies in this field are expected to lead to the development, through molecular design, of new functional materials that may be used in applications such as chemical storage,[3] sensors,[4] and catalysis.[5]

In our recent studies on dimetal-containing supramolecular compounds, much attention has been devoted to linkers capable of linking multiple, covalently bonded dimetal units (e.g., Mo_2^{4+}, Rh_2^{4+}, and Ru_2^{4+}).[6] By careful selection of the linker, it is possible to control the molecular structure, regulate the electronic configuration, and modify the chemical properties of the assembled compounds. In addition to organic linkers such as dicarboxylate[7]and diamidate,[8] a variety of inorganic species have been used to link two

---

* To whom correspondence should be addressed. E-mail: cotton@tamu.edu (F.A.C.); cyliu05@gmail.com (C.Y.L.); murillo@tamu.edu (C.A.M.).

† Texas A&M University.

‡ Tongji University.

(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, K. 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) Gianneschi, N. C.; Masar III, M. S.; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825.

(3) (a) Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431. (b) Sudik, A. C.; Millward, A. R.; Ockwig, N. W.; Cote, A. P.; Kim, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 7110. (c) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670.

(4) (a) Maspoch, D.; Ruiz-Molina, D.; Wurst, K.; Domingo, N.; Cavallini, M.; Biscarini, F.; Tejada, J.; Rovira, C.; Veciana, J. *Nat. Mater.* **2003**, *2*, 190. (b) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762.

(5) (a) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (b) Janiak, C. *Dalton Trans.* **2003**, 2781.

(6) (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.

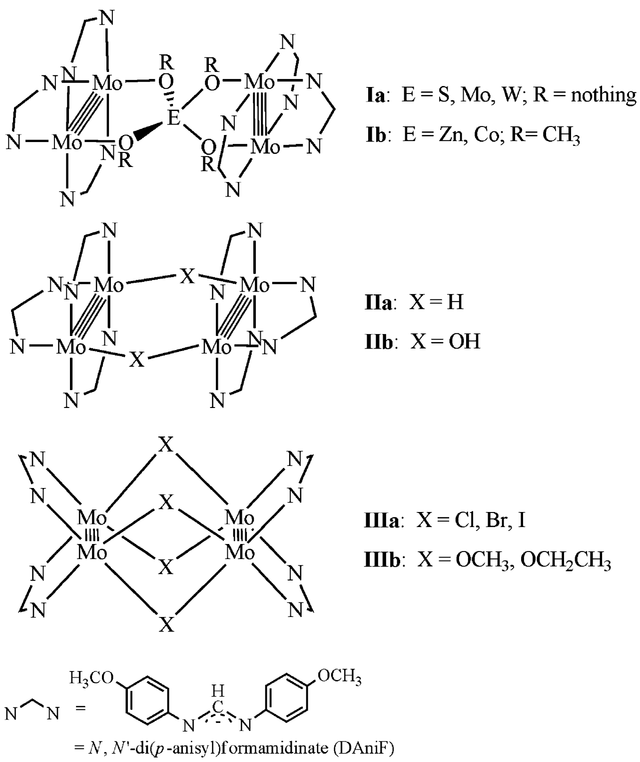
(7) (a) Cotton, F. A.; Donahue, J. P.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 1234. (b) Cotton, F. A.; Donahue, P. J.; Murillo, C. A. *J. Am. Chem. Soc.* **2003**, *125*. 5436. (c) Cotton, F. A.; Donahue, P. J.; Murillo, C. A.; Pérez, L. M. *J. Am. Chem. Soc.* **2003**, *125*, 5486. (d) Cotton, F. A.; Donahue, J. P.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 2229. (e) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2003**, *42*, 4619. (f) Cotton, F. A.; Daniels, L. M.; Donahue, J. P.; Liu, C. Y.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 1354.

(8) (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.

10.1021/ic061525g CCC: $33.50

© 2006 American Chemical Society
Published on Web 10/19/2006

Scheme 1



dimetal units, typically, $[Mo_2(DAniF)_n]^{(4-n)+}$ ($n = 2$ or 3), where DAniF = *N*,*N*′-di-*p*-anisylformamidinate. These include polyatomic anions EO_4^{2-} (E = S, Mo, and W),[9] $M(OCH_3)_4^{2-}$ (M = Zn or Co),[10] single atom halides X (e.g., Cl^-, Br^-, and I^-),[11] hydride H^-,[12] hydroxide OH^-,[11a] and alkoxides ^-OR (R = CH_3, CH_2CH_3).[13] Compounds with a great variety of conformations and binding patterns, as shown in Scheme 1, have been obtained. This diversity has allowed better understanding of the impact of the linker on the electronic interaction between dimetal units. For instance, a tetrahedral inorganic linker, e.g., $M(OCH_3)_4^{2-}$ (M = Zn or Co) (**Ib**), brings together two [Mo_2] units perpendicular to each other, which severely limits electron delocalization over the two dimetal centers because of the lack of metal−ligand π-orbital interaction.[10b] When single atoms such as H^- (**IIa**) serve as bridges, the distances between the two dimetal centers may be greatly reduced so that strong electronic interaction attributable to direct metal−metal orbital interactions is observed.[12]

We have shown that assemblies of dimolybdenum units, $[Mo_2(cis\text{-DAniF})_2]^{2+}$, with the halogen atoms Cl^-, Br^-, and I^-, produce quadruply bridged tetranuclear compounds of the general formula $[Mo_2(cis\text{-DAniF})_2]_2(\mu\text{-X})_4$ (**IIIa**).[11a] However, in considering the possibility of using the first member of the halogen family, F^-, in the same way, it must be kept in mind that it differs in many ways from other halogens because of its small size and high electronegativity.[14] In many organometallic fluorides, fluorine functions as the structure-directing element capable of connecting from two to four nonmetal or metal atoms.[15] In these compounds, the compositions and molecular structures are highly diversified, ranging from discrete small molecules to supramolecular arrays. When a fluorine atom bridges two single metal atoms, linear or bent binding patterns may be expected. While the linear bridges support cyclic tetramers M_4F_4 (M = Mo, Ru, Yb, Al, Ti, etc.),[16] the bent bridging mode occurs in cyclic M_3F_3 trinuclear species (M = Al, Sc, Sm, etc.).[17] A valid generalization, however, is that the fluorine atom is far more inclined than the other halogen atoms to form linear or nearly linear bridges.

In the present work, fluoride anions, F^-, have been found to cause the assembly of dimolybdenum units $[Mo_2(cis\text{-DAniF})_2]^{2+}$, represented for simplicity as [Mo_2], to form cyclic triads. The compounds that have been synthesized and crystallographically characterized include α-$[Mo_2(cis\text{-DAniF})_2]_3(\mu\text{-F})_6$ (**1**), β-$\{[Mo_2(cis\text{-DAniF})_2]_3(\mu\text{-F})_6\}(BPh_4)$ (**2** or β^+), and β-$[Mo_2(DAniF)_2]_3(\mu\text{-F})_6$ (**3**). Compounds **1** and **3** are geometric isomers that do not interconvert even in boiling THF or toluene, nor photochemically. The idealized symmetries for the two isomers are C_{2v} and D_{3h} for the α and β species, respectively (Scheme 2).

Experimental Section

Materials and Methods. Solvents were purified under argon using a Glass Contour solvent purification system or distilled over appropriate drying agents under nitrogen. All synthetic operations were conducted under N_2 using Schlenk line techniques. The starting material, $[Mo_2(cis\text{-DAniF})_2(NCCH_3)_4](BF_4)_2$, was prepared according to a published method.[18] Commercially available chemicals were used as received except for potassium fluoride, which was heated

---

[9] Cotton, F. A.; Donahue, J. P.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 2229.

[10] (a) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2003**, *42*, 4619. (b) Cotton, F. A.; Dalal, N. S.; Liu, C. Y.; Murillo, C. A.; North, J. M.; Wang, X. *J. Am. Chem. Soc.* **2003**, *125*, 12945.

[11] (a) Cotton, F. A.; Daniels, L. M.; Guimet, I.; Henning, R. W.; Jordan IV, G. T.; Lin, C.; Schultz, A. J.; Murillo, C. A. *J. Am. Chem. Soc.* **1998**, *120*, 12531. (b) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Wang, X. *Chem. Commun.* **2003**, 2190. (c) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Zhao, Q. *Inorg. Chem.* **2006**, *45*, ASAP.

[12] (a) Cotton, F. A.; Daniels, L. M.; Jordan IV, G. T.; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **1998**, *120*, 3398. (b) Cotton, F. A.; Donahue, J. P.; Huang, P.; Murillo, C. A.; Villagrán, D. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2606.

[13] Cotton, F. A.; Li, Z.; Liu, C. Y.; Murillo, C. A.; Zhao, Q. *Inorg. Chem.* **2006**, *45*, 6387.

[14] (a) Politzer, P.; Timberlake, J. W. *J. Org. Chem.* **1972**, *37*, 3557. (b) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley and Sons: New York, 1999.

[15] Roesky, H. W.; Haiduc, I. *J. Chem. Soc., Dalton Trans.* **1999**, 2249.

[16] (a) Edwards, A. J.; Peacock, R. D.; Small, R. W. H. *Am. Chem. Soc.* **1962**, 4486. (b) Holloway, J. H.; Peacock, R. D.; Small, R. W. H. *Am. Chem. Soc.* **1964**, 644. (c) Peacock, R. D.; Marshall, C. J.; Russell, D. R.; Wilson, I. L. *J. Chem. Soc., Chem. Commun.* **1970**, 1643. (d) Burns, C. J.; Berg, D. J.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 272. (e) Gundersen, G.; Haugen, T.; Haaland, A. *J. Chem. Soc., Chem. Commun.* **1972**, 708. (f) Weidlein, J.; Krieg. V. *J. Organomet. Chem.* **1968**, *11*, 9. (g) Yu, P.; Montero, M. L.; Barnes, C. E.; Roesky, H. W.; Usón, I. *Inorg. Chem.* **1998**, *37*, 2595. (h) Troyanov, S. I.; Varga, V.; Mach, K. *J. Organomet. Chem.* **1991**, *402*, 201. (i) Palacios, F.; Royo, P.; Serrano, J. L.; Balcázar, J. L.; Fonseca, I.; Florencio, F. *J. Organomet. Chem.* **1989**, *375*, 51.

[17] (a) Waezsada, S. D.; Liu, F. Q.; Murphy, E. F.; Roesky, H. W.; Teichert, M.; Usón, I.; Schmidt, H. G.; Albers, T.; Parisini, E.; Noltemeyer, M. *Organometallics* **1997**, *16*, 1260. (b) Bottomley, F.; Paez, D. E.; White, P. S. *J. Organomet. Chem.* **1985**, *291*, 35. (c) Schumann, H.; Keitsch, M. R.; Winterfeld, J.; Demtschuk, J. *J. Organomet. Chem.* **1996**, *525*, 279.

Scheme 2

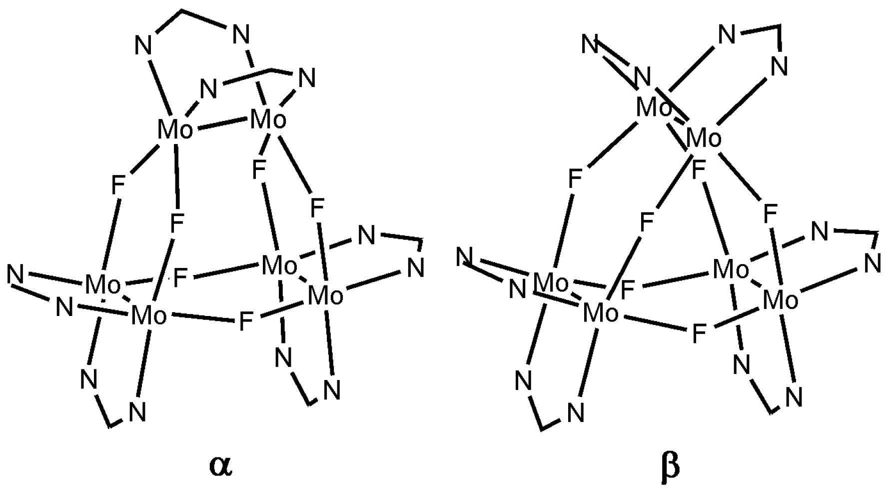


Table 1. X-ray Crystallographic Data

	$\mathbf{1}\cdot2CH_2Cl_2$	$\mathbf{2}\cdot2CH_2Cl_2$	$\mathbf{3}\cdot2CH_2Cl_2\cdot C_6H_{14}$
empirical formula	$C_{92}H_9Cl_4F_6Mo_6N_{12}O_{12}$	$C_{116}H_{114}BCl_4F_6Mo_6N_{12}O_{12}$	$C_{98}H_{108}Cl_4F_6Mo_6N_{12}O_{12}$
fw	2391.23	2710.44	2477.40
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	14.146(2)	19.923(3)	24.15(1)
b, Å	14.286(2)	28.670(4)	16.360(6)
c, Å	26.043(4)	20.496(3)	26.45(1)
α, deg	76.605(3)	90	90
β, deg	76.147(3)	98.590(3)	90.387(7)
γ, deg	70.266(3)	90	90
V Å^3	4744(1)	11576(3)	10449(7)
Z	2	4	4
λ, Å	0.71073	0.71073	0.71073
d_{calcd}, g/cm^3	1.674	1.555	1.575
μ, mm^{-1}	0.960	0.797	0.874
R1^a (wR2^b)	0.0525 (0.1018)	0.0761 (0.1057)	0.1194 (0.2074)

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

at 350 °C under vacuum overnight before use. Ferrocenium tetraphenylborate, $[FeCp_2]BPh_4$, was prepared immediately prior to use.[19]

Characterization Measurements. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ. Electronic spectra were measured on a Shimadzu UV-2501PC spectrometer in CH_2Cl_2 solution. NMR spectra were recorded on a Mercury 300 spectrometer with chemical shifts (δ) referenced to the protonated residue in $CDCl_3$ for ^{1}H NMR and to CCl_3F in CD_2Cl_2 for ^{19}F NMR. Cyclic voltammograms and differential pulse voltammograms were recorded on a BAS 100 electrochemical analyzer with Pt working and auxiliary electrodes, Ag/AgCl reference electrode, scan rate of 100 mV/s, and 0.1 M Bu_4NPF_6 as electrolyte. Under these electrochemical conditions, the $E_{1/2}$ for the ferrocene/ferrocenium couple (Fc/Fc$^+$) was measured at 440 mV.

X-ray Structure Determinations. Single crystals suitable for X-ray analyses were obtained by diffusion of hexanes into CH_2Cl_2 solutions of the corresponding compound. Each crystal was mounted on the tip of a cryoloop attached to the goniometer head. Data for $\mathbf{1}\cdot2CH_2Cl_2$, $\mathbf{2}\cdot2CH_2Cl_2$, and $\mathbf{3}\cdot2CH_2Cl_2\cdot C_6H_{14}$ were collected at −60 °C on a BRUKER SMART 1000 CCD area detector system. Cell parameters were determined using the program SMART.[20] Data reduction and integration were performed with the software package SAINT,[21] and absorption corrections were applied by using SADABS.[22] Using the program package SHELXTL,[23] the structures were solved by direct methods and refined. Non-hydrogen atoms, except for those of disordered parts and solvent molecules, were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions. Crystallographic data are presented in Table 1, and selected bond distances and angles are listed in Table 2.

Preparation of α-[Mo$_2$(*cis*-DAniF)$_2$]$_3$(μ-F)$_6$, 1, Method A. To a flask containing $[Mo_2(cis\text{-DAniF})_2(NCCH_3)_4](BF_4)_2$ (0.624 g, 0.600 mmol) and an excess amount of tris(dimethylamino)sulfur(trimethylsilyl)difluoride (0.600 g, 2.14 mmol) was added 20 mL of acetonitrile. The resultant solution was stirred at room temperature for 4 h, yielding a light yellow solid. The supernatant solution was decanted, and the solid was washed with acetonitrile (2 ×

---

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

(19) Ferrocenium tetraphenylborate, $[FeCp_2]BPh_4$, was prepared by mixing a solution of ferrocenium chloride in ethanol and a solution with an excess of $NaBPh_4$ in the same solvent. A grayish-blue precipitate formed immediately. After being stirred for 0.5 h, the solid was filtrated and washed with a small amount of ethanol and then dried under vacuum. Because this compound appeared to be light sensitive, it was prepared immediately prior to use and stored in a dark vial.

(20) *SMART for Windows NT*, Version 5.618: Bruker AXS, Inc.: Madison, WI, 2001.

(21) *SAINT, Data reduction Software*, version 6.36A.; Bruker AXS, Inc.: WI, 2001.

(22) *SADABS, Area Detector Absorption and other Corrections Software*, version 2.05; Bruker AXS, Inc.: Madison, WI, 2000.

(23) Sheldrick, G. M. *SHELXL*, Version 6.12; Bruker AXS, Inc.: Madison, WI, 2002.

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

	1·$2CH_2Cl_2$	**2**·$2CH_2Cl_2$	**3**·$2CH_2Cl_2$·C_6H_{14}
Mo(1)−Mo(2)	2.1055(6)	2.1585(6)	2.118(2)
Mo(3)−Mo(4)	2.1082(6)	2.1355(6)	2.119(2)
Mo(5)−Mo(6)	2.1159(5)	2.1369(6)	2.119(2)
Mo(1)−F(1)	2.095(2)	2.032(3)	2.085(8)
Mo(1)−F(5)	2.108(2)	2.043(3)	2.099(7)
Mo(2)−F(2)	2.098(2)	2.086(3)	2.119(8)
Mo(2)−F(6)	2.104(2)	2.044(3)	2.116(7)
Mo(3)−F(1)	2.104(2)	2.049(3)	2.107(8)
Mo(3)−F(3)	2.107(2)	2.093(3)	2.127(7)
Mo(4)−F(2)	2.099(2)	2.102(3)	2.116(8)
Mo(4)−F(4)	2.112(2)	2.083(3)	2.101(7)
Mo(5)−F(3)	2.112(2)	2.089(3)	2.095(7)
Mo(5)−F(4)	2.117(2)		
Mo(5)−F(5)		2.064(3)	2.101(8)
Mo(6)−F(4)		2.083(3)	2.125(7)
Mo(6)−F(5)	2.119(2)		
Mo(6)−F(6)	2.119(2)	2.069(3)	2.109(7)
F(1)−Mo(1)−F(5)	82.59(9)	84.3(1)	82.8(3)
F(2)−Mo(2)−F(6)	83.42(9)	83.9(1)	83.3(3)
F(1)−Mo(3)−F(3)	82.28(9)	85.0(1)	82.4(3)
F(2)−Mo(4)−F(4)	83.09(9)	81.9(1)	81.4(3)
F(3)−Mo(5)−F(4)	83.10(9)		
F(3)−Mo(5)−F(5)		83.2(1)	82.4(3)
F(6)−Mo(6)−F(5)	82.72(9)		
F(6)−Mo(6)−F(4)		85.1(1)	83.1(3)
Mo(1)−F(1)−Mo(3)	148.3(1)	142.9(1)	141.4(4)
Mo(2)−F(2)−Mo(4)	146.0(1)	144.1(1)	141.5(4)
Mo(3)−F(3)−Mo(5)	128.6(1)	140.8(1)	141.5(4)
Mo(4)−F(4)−Mo(5)	128.0(1)		
Mo(4)−F(4)−Mo(6)		143.0(1)	141.5(4)
Mo(1)−F(5)−Mo(5)		143.7(1)	141.4(4)
Mo(1)−F(5)−Mo(6)	128.2(1)		
Mo(2)−F(6)−Mo(6)	128.8(1)	142.8(1)	140.2(4)

10 mL) and then dried under vacuum. Yield: 0.300 g (74%). This material was used for the preparation of **2** without further purification. A yellow crystalline product was obtained by diffusion of hexanes into a dichloromethane solution of the product. ^{1}H NMR (ppm in $CDCl_3$): 8.79 (s, 2H, −NC*H*N−), 8.65 (s, 2H, −NC*H*N−), 8.19 (s, 2H, −NC*H*N−), 6.73 (m, 8H, aromatic), 6.52 (m, 8H, aromatic), 6.42−6.27 (m, 32H, aromatic), 3.68 (s, 12H, −OC*H*$_3$), 3.64 (s, 12H, −OC*H*$_3$), 3.63 (s, 12H, −OC*H*$_3$). ^{19}F NMR (ppm in CD_2Cl_2): −242.9(s, 4F), −244.9 (s, 2F). UV−vis (λ_{max}, nm) (ϵ, M^{-1} cm^{-1}): 404 (5.6×10^3), 479 (2.8×10^3). Anal. Calcd for $C_{91}H_{92}Cl_2F_6Mo_6N_{12}O_{12}$ (**1**·CH_2Cl_2): C, 47.39; H, 4.02; N, 7.29. Found: C, 47.24; H, 4.02; N, 7.36.

Preparation of α-[Mo$_2$(*cis*-DAniF)$_2$]$_3$(μ-F)$_6$, 1, Method B. [Mo$_2$(*cis*-DAniF)$_2$($NCCH_3$)$_4$](BF_4)$_2$ (0.416 g, 0.400 mmol) and KF (0.322 g, 4.00 mmol) were mixed in 20 mL of acetonitrile. The mixture was stirred at ca. 60−70 °C for 5 h, producing a yellow precipitate. The supernatant solution was decanted. The solid was washed with acetonitrile (2 × 10 mL) and dried under vacuum. The crude product was dissolved in ca. 15 mL of dichloromethane. The solution was allowed to pass though a Celite-packed frit. The filtrate was layered with 40 mL of hexanes. Yield of yellow crystals: 0.05 g (18%).

Preparation of {β-[Mo$_2$(*cis*-DAniF)$_2$]$_3$(μ-F)$_6$}(BPh_4), 2. A yellow solution of **1** (0.140 g, 0.063 mmol) in 10 mL of CH_2Cl_2 and a blue solution having 1 equiv of [FeCp$_2$]BPh$_4$ (0.032 g, 0.063 mmol) in 15 mL of CH_2Cl_2 were prepared separately and cooled to −78 °C. The two solutions were mixed by transferring the oxidizing reagent to the dimolybdenum complex at low temperature using a cannula to produce a dark brown solution. After the resultant solution was stirred at −78 °C for 30 min, a copious amount of precooled hexanes was added by a syringe to produce a dark brown precipitate. The supernatant solvent was then decanted, and the solid residue was washed with 20 mL of hexanes. The solid was dissolved in dichloromethane, and the solution was layered with hexanes to obtain a dark crystalline product. Yield: 0.104 g (63% based on **2**·CH_2Cl_2). UV−vis (λ_{max}, nm) (ϵ, M^{-1} cm^{-1}): 478 (3.1×10^3), 619 (1.1×10^3). Anal. Calcd for $C_{115}H_{112}BCl_2F_6Mo_6N_{12}O_{12}$ (**2**·CH_2Cl_2): C, 52.61; H, 4.30; N, 6.40. Found: C, 52.29; H, 3.92; N, 6.32.

Preparation of β-[Mo$_2$(*cis*-DAniF)$_2$]$_3$(μ-F)$_6$, 3. To a flask containing dark brown {β-[Mo$_2$(*cis*-DAniF)$_2$]$_3$(μ-F)$_6$}PF$_6$ [24] (0.237 g, 0.100 mmol) and a large excess of Al dust (1.50 g, 55.6 mmol) was added 20 mL of acetonitrile. The mixture was stirred at room temperature for about 5 h, yielding a yellow solid. After the supernatant brown solution was decanted, the solid mixture was washed with a small amount of acetonitrile. The residue was extracted with 10 mL of CH_2Cl_2 followed by filtration via a Celite-packed column to remove the Al dust. After the volume of the filtrate was reduced under vacuum to ca. 5 mL, a mixture of isomeric hexanes (40 mL) was added by syringe to produce a light yellow precipitate. This solid was collected by filtration and dried under vacuum. Yield: 0.152 g (68%). Crystalline material for analysis was obtained by diffusion of hexanes into a dichloromethane solution. ^{1}H NMR (ppm in $CDCl_3$): 8.78 (s, 6H, −NC*H*N−), 6.59 (d, 24H, aromatic), 6.38 (d, 24H, aromatic), 3.63 (s, 36H, −OC*H*$_3$). ^{19}F NMR (ppm in CD_2Cl_2): −249.4(s, 6F). UV−Vis (λ_{max}, nm) (ϵ, $M^{-1}cm^{-1}$): 409 (5.4×10^3), 476 (1.8×10^3). Anal. Calcd for $C_{91}H_{92}Cl_2F_6Mo_6N_{12}O_{12}$ (**3**·CH_2Cl_2): C, 47.39; H, 4.02; N, 7.29. Found: C, 47.87; H, 4.08; N, 7.22.

Study of the $\alpha \rightarrow \alpha^+ \rightarrow \beta^+ \rightarrow \beta$ Conversion Process. A yellow solution of **1** (α) in 10 mL of CH_2Cl_2 and a blue solution having 1 equiv of [FeCp$_2$]PF$_6$ in 15 mL of CH_2Cl_2 were prepared separately and cooled to −78 °C. The two solutions were mixed by transferring via cannula that of the oxidizing agent into that having the dimolybdenum complex at low temperature. The brown solution of α^+ was stirred at −78 °C for 30 min to ensure that the reaction had gone to completion. The solution was then transferred to a flask which contained 2 equiv of the reducing agent ($Bu^n{}_4N$)BH_4. The color of the solution changed immediately to yellowish brown. This solution was stirred at −78 °C for 0.5 h, and the solvent was then removed under vacuum. Both ^{1}H and ^{19}F NMR spectra of the residue showed that the reduced product is the α species. A similar procedure was repeated using resting temperatures of −20 and 0 °C for 20 and 1.0 h, respectively (vide infra).

Results and Discussion

Structural Considerations. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with the molecule residing on a general position ($Z = 2$). The molecule consists of three dimolybdenum units, [Mo$_2$(*cis*-DAniF)$_2$]$^{2+}$, bridged by six fluoride anions, as shown by the core structure at the top of Figure 1. The molecular structure of **1** is a significant departure from precedent, in that the structures of other compounds containing [Mo$_2$] units bridged by halide anions were all “dimer of dimers” structures with two parallel $Mo_2{}^{4+}$ units, and had the general formula [Mo$_2$(*cis*-DAniF)$_2$]$_2$(μ-X)$_4$ (X = Cl^-, Br^-, and I^-) (**IIIa**).[11] There is also a report of two triply bonded $Mo_2{}^{6+}$ units coupled by four F^- anions

---

[24] The compound {β-[Mo$_2$(*cis*-DAniF)$_2$]$_3$(μ-F)$_6$}PF$_6$ was made similarly to **2** but using [FeCp$_2$]PF$_6$ instead of [FeCp$_2$]BPh$_4$. The structure of {β-[Mo$_2$(*cis*-DAniF)$_2$]$_3$(μ-F)$_6$}PF$_6$ is similar to that of **2**. Anal. Calcd for $C_{90}H_{90}F_{12}Mo_6N_{12}O_{12}P$: C, 45.68; H, 3.83; N, 7.10. Found: C, 45.87; H, 4.02; N, 7.36.

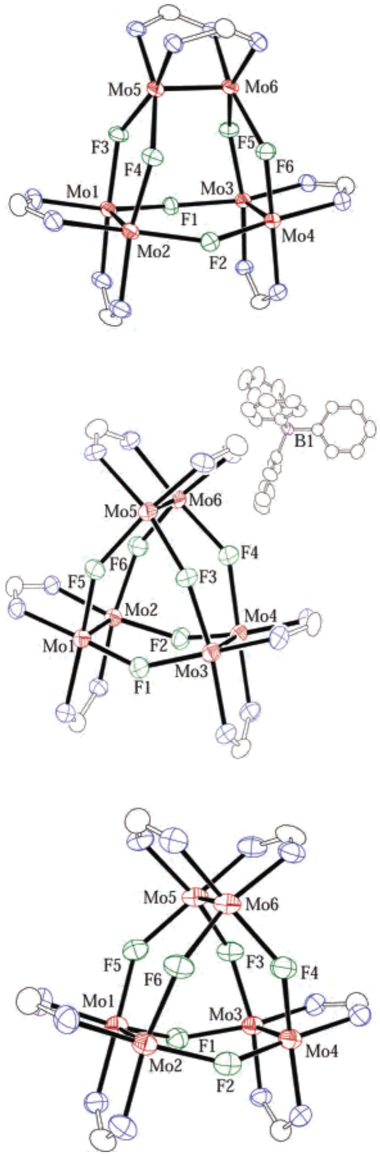


Figure 1. Core structures of **1**$\cdot$2CH_2Cl_2 (top), **2**$\cdot$2CH_2Cl_2 (center), and **3**$\cdot$2$CH_2Cl_2\cdot C_6H_{14}$ (bottom) drawn with ellipsoids at the 40% probability level. All *p*-anisyl groups and hydrogen atoms have been omitted for clarity.

in $[Mo_2(OBu^t)_4]_2(\mu\text{-}F)_4$ in which the dimetal units are orthogonal to each other.[25] In **1**, the three dimetal units are oriented in two orthogonal directions. Two of them are structurally equivalent and parallel to each other, but mutually perpendicular to the third one. The six fluorine atoms bridging six molybdenum atoms give rise to five-membered rings, $\overline{\text{M—F—Mo—Mo—F}}$, on two sides of the molecule and a six-membered ring, $\overline{\text{Mo—Mo—F—Mo—Mo—F}}$, on the other. There is an idealized 2-fold axis that passes through the center of the six-membered ring and the midpoint of the Mo(5)—Mo(6) bond. In addition, there are two idealized mirror planes perpendicular to each other that intersect at the C_2 axis, and the overall structure has idealized C_{2v} symmetry. This structural motif is designated the α form.

In the α form, the bond distances for the two parallel dimetal units are essentially the same (2.1055(6), 2.1082(6) Å), while the third one, 2.1159(5) Å, is but slightly (0.009 Å) longer. The separations between midpoints of the $[Mo_2]$ units are all ca. 4.0 Å despite the difference in binding modes. As expected, there are two sets of Mo—F—Mo angles. Such angles between the two parallel $[Mo_2]$ units, about 147°, are significantly larger than those that connect to the perpendicular Mo_2^{4+} unit, which are about 128°. In $[Mo_2(OBu^t)_4]_2(\mu\text{-}F)_4$, in which fluoride anions bridge two perpendicular Mo_2^{6+} units, the Mo—F—Mo angles are 123—125°.[25] It should be noted that, in the fluorine-bridged clusters, the Mo—F—Mo angles are considerably larger than the Mo—X—Mo angles found in the halide-bridged dimolybdenum dimers, which range from 87° to 91°.[11] This is in agreement with the well-known fact that, when the small fluorine atoms serve as bridges, they tend toward a more linear binding mode which increases the distance and reduces the repulsion between metal atoms.

The molecular structure of **1** evidently persists in solution, as shown by the ^{1}H NMR spectrum. The six methine protons, one from each of the DAniF ligands, are present as three singlets (8.19—8.79 ppm) in a ratio of 1:1:1, in agreement with the idealized C_{2v} symmetry of the molecule. There are also three singlets at 3.68, 3.64, and 3.63 ppm, respectively, in a ratio of 1:1:1, which account for the 24 protons of the methoxy groups on the ligands of the two parallel $[Mo_2]$ units in two orientations and the 12 hydrogen atoms from the third unit. Although the two DAniF ligands that support each of the two parallel Mo_2^{4+} units are not in the same chemical environment, these signals are not resolved under our experimental conditions. The ^{19}F NMR spectrum presents two resonances in the ratio of 2:1, at −243 and −245 ppm, as expected for a solution structure that is the same as that in the solid state.

Compound **2** was prepared by oxidation of **1** using 1 equiv of the oxidizing reagent $[FeCp_2]BPh_4$, which gives high-quality single crystals.[26] The molecule of **2** resides on a general position of the monoclinic $P2_1/c$ space group. As shown at the center of Figure 1, the structure of the cation in **2** differs from that of the precursor **1** in that it is a triangle with three geometrically identical $[Mo_2(cis\text{-DAniF})_2]^{2+}$ units as the vertices. All three dimolybdenum units are parallel to each other, as well as to an idealized C_3 axis that passes through the center of the triangle. Addition of a plane and three C_2 axes perpendicular to the C_3 axis gives an idealized D_{3h} symmetry for the molecule. This structural motif of the molecule will henceforth be designated the β form. Clearly, a structural rearrangement of the cyclic triad from the α (C_{2v}) to the β (D_{3h}) form occurs during or quickly following the removal of one electron from **1**.

The neutral compound **3**, an isomer of **1**, was obtained by reduction of **2**. As shown at the bottom of Figure 1, it has a β structural motif, like its precursor **2**. Thus, **3** is a geometric isomer of **1** that possesses idealized D_{3h} symmetry instead

---

(25) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7100.

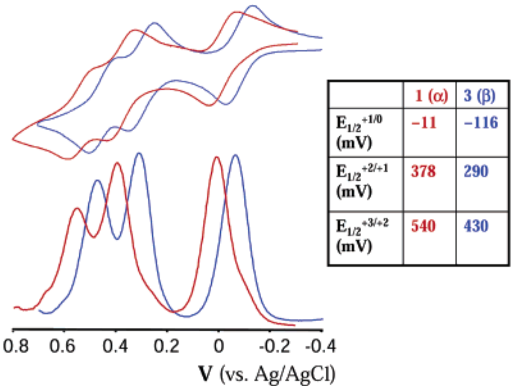
(26) Although the compounds with counterions such as BF_4^- and PF_6^- may be synthesized using the corresponding ferrocenium salt, the quality of their crystals is not as good.

of C_{2v} symmetry. In **3**, the three Mo−Mo bond distances, ca. 2.12 Å, fall in the range of Mo−Mo quadruply bonded units having two bridging ligands.[27] The six Mo−F−Mo angles are all about 141°, similar to those found in **2**. The center-to-center separation between two [Mo_2] units is about 4.0 Å.

The D_{3h} symmetry of **3** is retained in solution as confirmed by the ^{1}H and ^{19}F NMR spectra. In the ^{1}H NMR spectrum, there is only one resonance for the methine protons, a singlet at 8.78 ppm, and a singlet at 3.63 ppm for the methoxy groups. For the six equivalent bridging fluorine atoms, the ^{19}F resonance occurs as a singlet at −249 ppm.

Syntheses. With the use of the designed building block [Mo_2(*cis*-DAniF)$_2$($NCCH_3$)$_4$]$^{2+}$, which has been used frequently in this laboratory as a corner piece for the construction of various cyclic [Mo_2]-containing supramolecules,[6] the preparation of **1**, α-[Mo_2(*cis*-DAniF)$_2$]$_3$(μ-F)$_6$, proceeds in a straightforward and convenient manner. Acetonitrile serves well as the solvent because the low solubility of the neutral product in this polar solvent provides an additional driving force to the reaction. Alcohol solvents such as methanol or ethanol should be avoided because the alkoxide anions are capable of bridging [Mo_2] units, forming compounds such as [Mo_2(*cis*-DAniF)$_2$]$_2$(μ-OR)$_4$ (**IIIb**).[13] As fluoride sources, either organic compounds such as tris(dimethylamino)sulfur(trimethylsilyl)difluoride or inorganic salts such as KF can be used. However, the former provided substantially higher yields than those obtained from reactions using KF. To achieve high yield and purity, it is essential that all the solvents and reagents be rigorously dry. If trace amounts of H_2O are present, the hydroxide anion may partially replace some bridging fluorine atoms. Water is also known to promote a side reaction that leads to the formation of the paddlewheel compound Mo_2(DAniF)$_4$. Unlike reactions with the other halides, Cl^-, Br^-, and I^-, that give [Mo_2(*cis*-DAniF)$_2$]$_2$(μ−X)$_4$ (**IIIa**) compounds, direct assembly of dimolybdenum units with fluoride sources yields exclusively the cyclic triad **1**. The reason for this difference in behavior is that the fluorine atoms are far more inclined than the other halogen atoms to form linear or nearly linear bridges.[14b]

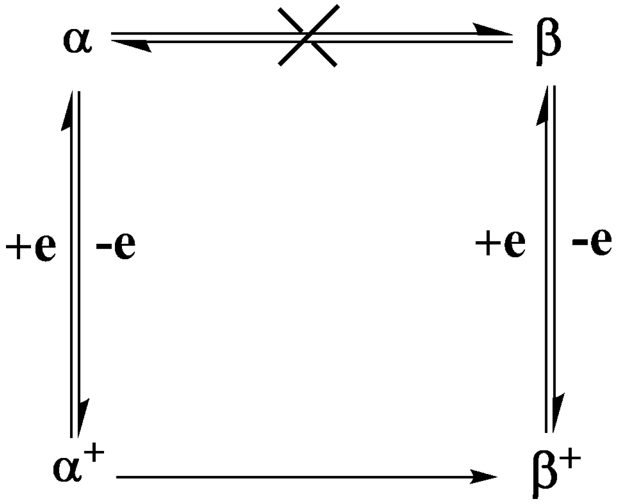
The isolation of products from chemical oxidation of compounds having two or more linked dimolybdenum units has not frequently been accomplished, even for compounds that show reversible electrochemical redox processes. For example, dicarboxylate-linked Mo_2 compounds have not yet given isolable products upon addition of oxidizing reagents. In some cases, the compound Mo_2(DAniF)$_4$ has been isolated, although how it forms is not known. In other cases, however, we have successfully oxidized at low temperature a series of dimolybdenum pairs by using a mild oxidizing reagent, such as ferrocenium hexafluorophosphate.[10a,11b] By employing similar reaction conditions, oxidation of the neutral compound **1** afforded **2** in good yield. Compound **2** is the first mixed-valent supramolecular complex with three [Mo_2] units. Electrochemical measurements of **1**, shown in Figure 2, suggested that the ferrocenium cation, $FeCp_2^+$, with a potential of 0.45 V (vs Ag/AgCl in CH_2Cl_2) would be capable of oxidizing two dimolybdenum centers. Thus, to obtain a pure singly oxidized compound, it was critical to precisely control the stoichiometry of the reactants. As mentioned earlier, compound **2** differs from **1** not only in oxidation state but also in molecular geometry, and under the preparative conditions, oxidation of **1** with an α structure does not allow the isolation of an α$^+$ product.



	1 (α)	3 (β)
$E_{1/2}^{+1/0}$ (mV)	−11	−116
$E_{1/2}^{+2/+1}$ (mV)	378	290
$E_{1/2}^{+3/+2}$ (mV)	540	430

Figure 2. Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of **1** and **3** in CH_2Cl_2. Experimental values (vs Ag/AgCl) are shown in the inset.

Scheme 3



Reduction of **2** with aluminum metal in acetonitrile produced a yellow precipitate which was identified as another neutral compound, **3**, which was shown to be an isomer of **1** with a β structure. It should be noted that the method applicable for the preparation of a given isomer produces none of the other. Direct assembly generates only **1** and no **3**, while reduction of **2** gives only **3** but no **1**.

α−*β* Geometry Transformation. As mentioned earlier, the two neutral isomeric compounds, **1** and **3** in α and β forms, respectively, must be synthesized in different ways. Direct assembly from the molybdenum building block and a source of F^- anions gives exclusively the α isomer, while the β isomer, **3**, was isolated by reduction of the monocation in **2**, which has the same geometric form and may be denoted β^+. Formation of molecule **1** is kinetically favored over **3** in the initial preparative reaction, while neither **1** nor **3** is

---

(27) Cotton, F. A.; Daniels, L. M.; Hillard, E. A.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 2466.

structurally labile. The molecular identity for each of them is retained both in the solid state and in solution. No interconversion was observed under refluxing THF, CH_2Cl_2, or toluene for about 6 h. Addition of $Bu^n{}_4NPF_6$ to the refluxing solutions had no effect. No interconversion was observed either after 3 h upon irradiation of a toluene solution with a UV lamp having a wavelength of 350 nm.

In view of these facts, the key question to be answered is: Does the β^+ ion arise in a way that is concerted with the oxidation of the neutral α molecule, or is there an α^+ ion that is first formed as a discrete though short-lived intermediate? An answer to this question has been obtained by a series of experiments designed to provide semiquantitative estimates of the lifetime of an α^+ intermediate, if one existed. The first such experiment was carried out at −78 °C, which is the temperature used in the synthesis of **2**. After a solution of **1** was treated at that temperature with 1 equiv of $[FeCp_2]PF_6$, the oxidized solution was allowed to stand at −78 °C for 5 h and then reduced with an excess of $(Bu^n{}_4N)BH_4$. Both ^1H and ^{19}F NMR spectra showed that **1**, with its α form structure was regenerated without a trace of the β isomer, **3**. In a second experiment, after oxidation of **1** at −78 °C the solution was allowed to warm to −20 °C and remain at that temperature for 20 h before the reduction was carried out, about 20% α^+ had converted to β^+, as shown by the ratio of the signals in the NMR spectra of α and β forms. At 0 °C, all of the α^+ rearranged to β^+ after 1 h. These reactions show that the $\alpha \rightarrow \alpha^+$ and $\beta^+ \rightarrow \beta$ processes take place readily and fast even at −78 °C, while $\alpha^+ \rightarrow \beta^+$ is temperature and time dependent, as shown in Scheme 3.

Acknowledgment. We thank the National Science Foundation, the Robert A. Welch Foundation, and Texas A&M University for financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for **1**$\cdot 2CH_2Cl_2$, **2**$\cdot 2CH_2Cl_2$, and **3**$\cdot 2CH_2Cl_2 \cdot C_6H_{14}$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC061525G