

The Simplest Supramolecular Complexes Containing Pairs of Mo₂(formamidinate)₃ Units Linked with Various Dicarboxylates: Preparative Methods, Structures, and Electrochemistry

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Twelve compounds containing two quadruply bonded Mo₂(DAniF)₃ (DAniF = *N,N'*-di-*p*-anisylformamidinate) units linked by dicarboxylate anions have been prepared in high purity and good yields. All of these compounds have been characterized by crystallography and NMR. The dinuclear pairs display electrochemical behavior which is controlled by the nature of the bridging dicarboxylate group. As described by the linkers, the compounds are oxalate, **1**; acetylene dicarboxylate, **2**; fumarate, **3**; tetrafluorophthalate, **4**; carborane dicarboxylate, **5**; ferrocene dicarboxylate, **6**; malonate, **7**; succinate, **8**; propane-1,3-dicarboxylate, **9**; tetrafluorosuccinate, **10**; bicyclo[1.1.1]-pentane-1,3-dicarboxylate, **11**; and *trans*-1,4-cyclohexanedicarboxylate, **12**.

Introduction

The use of metal atoms (or ions) as key elements in the assembly of supramolecular arrays has emerged as an area of great interest, and much effort has been devoted to the assemblage of molecules having a great variety of polygons and polyhedra.¹ In most of the work done in other laboratories, the metal-containing moiety has been a *cis*-ML₂ (M = Pd^{II}, Pt^{II}) unit, where the L ligands (or bidentate L₂ ligand) are neutral. Since the linkers, usually diamines, are also neutral, the polygons or polyhedra containing *n* metal moieties have charges of 2*n*+, usually upward of 8+. Only in a very few cases has a neutral metal moiety, e.g., Re(CO)₃Cl,² been used, together with neutral linkers, thus leading to a neutral product. In these compounds, no change in the charge is in general possible because oxidation or reduction would lead to disintegration of the assembly. This work is driven by the search for novel materials, distinguished by special magnetic properties,³ micro- and mesoporous structures,⁴ or catalytic properties.⁵

We recognized some time ago that many of the same general types of molecular architectures can be constructed by using partially complexed M₂ units as can be constructed with M units. However, with the use of M₂ units one may obtain compounds with desirable properties not readily available with the mononuclear units. Of the many differences expected between these two classes of compounds, one would be related to the charge of the end species. With dinuclear species the charge can be reduced to zero. Furthermore, the presence of dinuclear units are expected to facilitate redox processes, and indeed they do.

We have already shown in preliminary reports that by using suitably chosen M₂ units and linkers, one can obtain a variety of product geometries, among which are simple pairs of M₂ units,⁶ triangular arrays,⁷ square arrays,⁷ and three-dimensional arrays.⁸ In our continuing studies, we have examined each of these types, and others, in much greater depth, and this is the first in a series of reports presenting our extensive results.

In this report we focus on molecules in which two M₂ units are joined by a bifunctional linker. We further restrict this report to systems in which the bifunctional linkers are *dianions of dicarboxylic acids* and the dimetal units contain Mo. We employ here a particularly stable and convenient quadruply bonded dimetal unit, Mo₂(DAniF)₃⁺, shown as **I**,⁶ and henceforth symbolized by [Mo₂]. A schematic representation of all molecules described here with corresponding linkers is shown as **II**. In this paper we shall describe (1) the syntheses of 12 such molecules, encompassing a very broad range of linkers,

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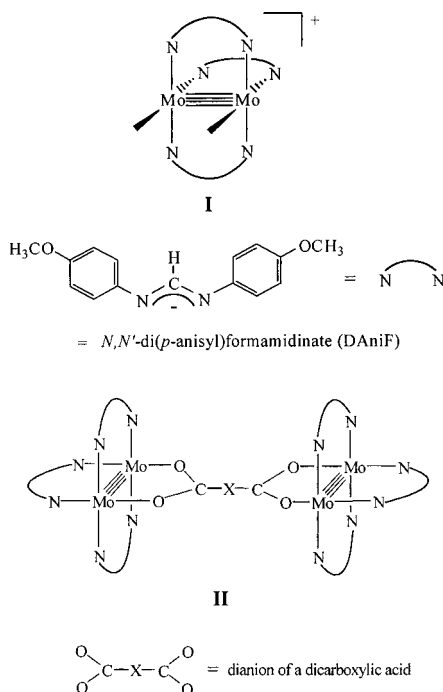
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(2) the crystal structures of all 12 compounds, and (3) the electrochemistry of these 12 compounds.



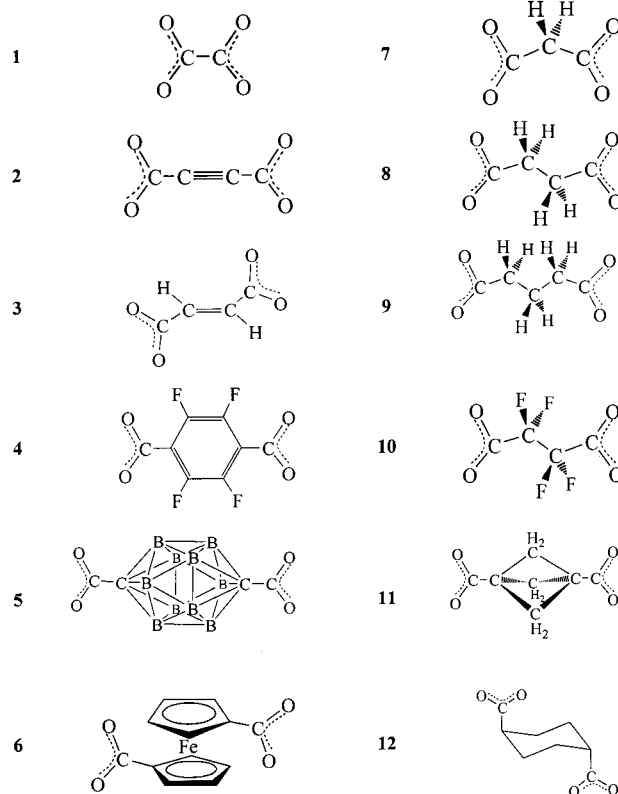
It is to be emphasized that an understanding of the variables involved in the synthesis of the relatively simple compounds reported here provides the essential groundwork for our forthcoming reports on more elaborate molecules. Furthermore, the electrochemistry reported here for the simplest type of dicarboxylate-bridged system shall also provide a basis for interpretation of the results for more elaborate systems currently under study. Chart 1 presents a numbered list of the 12 dicarboxylate linkers. The corresponding type **II** compounds will be numbered in a similar fashion.

Experimental Section

Materials and Methods. All manipulations and procedures were conducted under N₂ using either a N₂ drybox or standard Schlenk line techniques. Solvents were distilled and degassed prior to use; MeCN was twice distilled under N₂, first from activated molecular sieves and then from CaH₂, CH₂Cl₂ was dried and distilled from P₂O₅, MeOH and EtOH were dried and distilled from Mg turnings, and Et₂O and hexanes were dried and distilled from Na/K-benzophenone. Mo₂(DAniF)₃-Cl₂ (DAniF = *N,N'*-di-*p*-anisylformamidinate) was prepared by the literature method,⁹ and all tetrabutylammonium and tetraethylammonium dicarboxylate salts were prepared and isolated as white solids by neutralizing the corresponding diacid with 2 equiv of Et₄NOH or Bu₄N⁺OH followed by careful drying in vacuo. All other reagents (NaHBET₃, Zn dust) were purchased from commercial sources and used as received.

Physical Measurements. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia. ¹H NMR spectra were recorded on a Varian XL-200E NMR spectrometer, with chemical shifts (δ) referenced to CH₂Cl₂ or to CHCl₃. The cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer in 0.1 M Bu₄NPF₆ solution (CH₂Cl₂) with Pt working and auxiliary electrodes, a Ag/AgCl reference electrode, and a scan rate of 100 mV/s. All the potential values are referenced to the Ag/AgCl electrode, and under the present experimental conditions, the E_{1/2}(Fc⁺/Fc) was consistently measured at 440 mV.

Chart 1. Dicarboxylate Linkers in [Mo₂(DAniF)₃]₂O₂CXCO₂[Mo₂(DAniF)₃] Compounds



X-ray Structure Determinations. Single crystals suitable for X-ray diffraction analysis of all compounds were grown by diffusion of hexanes into a CH₂Cl₂ solution of the corresponding product. Single-crystal X-ray work on compounds **1–6** and **9–12** was performed on a Nonius FAST diffractometer utilizing the program MADNES.¹⁰ In each case, a suitable crystal was mounted on the tip of a quartz fiber with a small amount of silicone grease or epoxy and transferred to a goniometer head. Cell parameters were obtained from an autoindexing routine and were refined with 250 reflections within a 2θ range of 18.1–41.6°. Cell dimensions and Laue symmetry for all crystals were confirmed with axial photographs. All data were corrected for Lorentz and polarization effects. Data were processed using an ellipsoid-mask algorithm (the program PROCOR¹¹), and the program SORTAV¹² was used to correct for absorption. Data for **7** and **8** were collected using a Bruker SMART 1000 CCD area detector system using ω scans of 0.3 deg/frame with 30 s frames such that 1271 frames were collected for a hemisphere of data. The first 50 frames were re-collected at the end of the data collection to monitor for crystal decay, but no significant decomposition was observed. Cell parameters were determined using the program SMART.¹³ Data reduction and integration were performed with the software package SAINT,¹⁴ which corrects for Lorentz polarization, while absorption corrections were applied by using the program SADABS.¹⁴

In all structures, the positions of some or all of the non-hydrogen atoms were found via direct methods using the SHELXTL software.¹⁵

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- (13) SMART for Windows NT, version 5.059; Bruker Analytical X-ray Systems: 1997–1998.
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For all structures, subsequent cycles of least squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. All hydrogen atoms were added in calculated positions and refined isotropically as riding atoms with displacement parameter values equal to 1.2 times those of the carbon atoms to which they are attached. Cell parameters and refinement results for all compounds are summarized in Table 1, while key metrical parameters are collected in Tables 2 and 3.

Preparation of Compounds. The dicarboxylate-bridged molecules $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-O}_2\text{CXCO}_2)$, Chart 1, were prepared by one of two general methods, which are detailed below.

Method A. A solution of $\text{Mo}_2(\text{DAniF})_3\text{Cl}_2$ (154 mg, 0.150 mmol) and an excess of the bis(tetrabutylammonium) dicarboxylate (0.450 mmol) in 60 mL of CH_2Cl_2 was treated with NaHBEt_3 (1.0 mmol), which produced visible evolution of H_2 and effected a lightening of the solution color. The reaction mixture was stirred for 24 h at ambient temperature and then was concentrated to dryness in vacuo. The resulting residue was washed with Et_2O (10 mL), EtOH (2×20 mL), H_2O (2×10 mL), and EtOH (10 mL). Extraction of the remaining solid with CH_2Cl_2 (3×7 mL), filtration, concentration of the combined extracts (4 mL), and layering of the CH_2Cl_2 concentrate with hexanes produced crystalline material within 24–48 h. The crystalline product was collected by filtration and dried in vacuo.

Method B. A solution of $\text{Mo}_2(\text{DAniF})_3\text{Cl}_2$ (0.500 g, 0.490 mmol) in 60 mL of MeCN was treated with Zn dust (7.5 g). The resulting suspension was stirred vigorously for 1.5 h. The excess Zn dust was then separated from the yellow solution by filtration through packed Celite into a flask containing the bis(tetraethylammonium) dicarboxylate salt (0.490 mmol). The Celite was washed with an additional 5 mL portion of MeCN. Within a few minutes of stirring, the filtrate developed a voluminous precipitate. Stirring was sustained for 1 h, and the volume of the mixture was then reduced to 20 mL. The MeCN was removed by filtration, and the remaining solid was washed with an additional 10 mL portion of MeCN followed by 10 mL of Et_2O . The solid product was dried briefly under vacuum, extracted with 4×3 mL of CH_2Cl_2 , and filtered. Layering of the filtrate with hexanes produced crystalline material within 24–48 h. The crystalline product was collected by filtration and dried in vacuo.

$[\text{Mo}_2(\text{DAniF})_3]_2(\text{O}_2\text{CCO}_2)$ (**1**). Method A: 53.6% yield. ^1H NMR δ (ppm in CD_2Cl_2): 8.52 (s, 2H, $-\text{NCHN}-$), 8.47 (s, 4H, $-\text{NCHN}-$), 6.56 (m, 32H, aromatic), 6.45 (d, 8H, aromatic), 6.23 (d, 8H, aromatic), 3.67 (s, 24H, $-\text{OCH}_3$), 3.64 (s, 12H, $-\text{OCH}_3$).

$[\text{Mo}_2(\text{DAniF})_3]_2(\text{O}_2\text{CC}\equiv\text{CCO}_2)$ (**2**). Method B: 70.6% yield. (Note: Compound **2** can only be prepared following method B. Furthermore, successful preparation requires use of *exactly* $1/2$ equiv of $(\text{Et}_4\text{N})_2(\text{O}_2\text{CC}\equiv\text{CCO}_2)$ per equivalent of $\text{Mo}_2(\text{DAniF})_3\text{Cl}_2$.) ^1H NMR δ (ppm in CDCl_3): 8.49 (s, 4H, $-\text{NCHN}-$), 8.41 (s, 2H, $-\text{NCHN}-$), 6.63 (d, 16H, aromatic), 6.54 (d, 16H, aromatic), 6.43 (d, 8H, aromatic), 6.19 (d, 8H, aromatic), 3.72 (s, 24H, $-\text{OCH}_3$), 3.65 (s, 12H, $-\text{OCH}_3$). Anal. Calcd for $\text{C}_{94}\text{H}_{90}\text{Mo}_4\text{N}_{12}\text{O}_{16}$: C, 55.68; H, 4.47; N, 8.29. Found: C, 55.71; H, 4.49; N, 8.07.

$[\text{Mo}_2(\text{DAniF})_3]_2(\text{trans-O}_2\text{CC}(\text{H})\text{C}(\text{H})\text{CO}_2)$ (**3**). Method A: 41.2% yield. ^1H NMR δ (ppm in CD_2Cl_2): 8.47 (s, 4H, $-\text{NCHN}-$), 8.41 (s, 2H, $-\text{NCHN}-$), 7.36 (s, 2H, $-\text{C}(\text{H})\text{C}(\text{H})-$), 6.64 (d, 16H, aromatic), 6.53 (d, 16H, aromatic), 6.42 (d, 8H, aromatic), 6.21 (d, 8H, aromatic), 3.70 (s, 24H, $-\text{OCH}_3$), 3.62 (s, 12H, $-\text{OCH}_3$).

$[\text{Mo}_2(\text{DAniF})_3]_2(\text{O}_2\text{CCF}_4\text{CO}_2)$ (**4**). Method A: 46.5% yield. ^1H NMR δ (ppm in CD_2Cl_2): 8.52 (s, 2H, $-\text{NCHN}-$), 8.51 (s, 4H, $-\text{NCHN}-$), 6.66 (d, 16H, aromatic), 6.57 (d, 16H, aromatic), 6.46 (d, 8H, aromatic), 6.25 (d, 8H, aromatic), 3.70 (s, 24H, $-\text{OCH}_3$), 3.64 (s, 12H, $-\text{OCH}_3$). Anal. Calcd for $\text{C}_{98}\text{H}_{90}\text{F}_4\text{Mo}_4\text{N}_{12}\text{O}_{16}$: C, 54.71; H, 4.22; N, 7.81. Found: C, 54.48; H, 4.33; N, 7.63.

$[\text{Mo}_2(\text{DAniF})_3]_2(\text{O}_2\text{CCB}_{10}\text{H}_{10}\text{CCO}_2)$ (**5**). Method A: 62.4% yield. ^1H NMR δ (ppm in CD_2Cl_2): 8.44 (s, 2H, $-\text{NCHN}-$), 8.34 (s, 4H, $-\text{NCHN}-$), 6.65 (d, 16H, aromatic), 6.51 (d, 16H, aromatic), 6.44 (d, 8H, aromatic), 6.18 (d, 8H, aromatic), 3.77 (br, $-\text{B}_{10}\text{H}_{10}-$), 3.70 (s, 24H, $-\text{OCH}_3$), 3.63 (s, 12H, $-\text{OCH}_3$).

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

Table 1. Crystallographic Data^a for Compounds 1–12

formula	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	α , deg	β , deg	γ , deg	<i>V</i> , Å ³	space group	$R1, ^b wR2^c$
1·2CH ₂ Cl ₂	13.998(2)	17.441(3)	20.229(1)		97.40(1)		4898(1)	$P2_1/c$	0.052, 0.121
2·2.5CH ₂ Cl ₂ ·C ₆ H ₁₄ · $1/2$ Et ₂ O	10.409(4)	16.299(4)	32.533(6)	86.23(2)	89.69(1)	84.83(2)	5486(3)	$P1$	0.093, 0.207
3·1.75CH ₂ Cl ₂	10.458(1)	34.382(2)	27.257(1)		99.41(1)		9669(1)	$P2_1/c$	0.066, 0.150
4·2CH ₂ Cl ₂ ·C ₆ H ₁₄	9.791(1)	15.756(2)	18.090(3)	76.65(1)	79.61(1)	87.63(1)	2670.8(6)	$P1$	0.068, 0.167
5·2.9CH ₂ Cl ₂	15.718(1)	17.786(1)	20.059(2)		92.76(1)		5601.2(7)	$P2_1/c$	0.077, 0.190
6·2CH ₂ Cl ₂	11.525(2)	13.101(1)	20.178(4)	72.68(3)	87.93(3)	65.33(1)	2629.4(7)	$P1$	0.063, 0.144
7·CH ₂ Cl ₂	10.2875(9)	26.534(2)	33.857(3)		90.565(2)		9241(1)	$P2_1/n$	0.077, 0.148
8·2CH ₂ Cl ₂ ·2C ₆ H ₁₄ · $1/2$ H ₂ O	17.792(2)	19.467(2)	31.665(3)		104.360(2)		10624(2)	$P2_1/n$	0.069, 0.166
9·1.5CH ₂ Cl ₂	10.6542(4)	13.422(3)	35.848(9)	94.062(4)	91.78(1)	106.90(1)	4893(2)	$P1$	0.046, 0.126
10·3.5CH ₂ Cl ₂ ·C ₆ H ₁₄	17.431(4)	19.630(4)	31.801(6)		104.83(3)		10519(4)	$P2_1$	0.051, 0.127
11·4CH ₂ Cl ₂	16.604(2)	17.407(9)	18.95(1)	76.89(3)	81.14(4)	81.24(3)	5232(4)	$P1$	0.084, 0.204
12·3.5CH ₂ Cl ₂ ·C ₆ H ₁₄	19.548(2)	17.413(3)	32.123(5)		93.19(1)		10918(3)	$P2_1/n$	0.077, 0.198

^aData were obtained with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). ^b $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $wR2 = [\sum |w(F_o^2 - F_c^2)| / \sum w(F_o^2)]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\text{max}(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

Table 2. Selected Interatomic Distances (Å) for Compounds 1–12

	1	2	3	4	5	6	7	8	9	10 ^a	11	12
<i>d</i> , Å ^b	6.953	9.537	9.194	11.300	11.605	10.953	7.647	9.209	9.013	9.061	10.297	9.784
Mo(1)–Mo(2)	2.0900(7)	2.095(2)	2.0860(5)	2.0903(9)	2.0883(9)	2.087(1)	2.089(1)	2.0920(8)	2.0837(7)	2.087(1)	2.082(1)	2.088(1)
Mo(3)–Mo(4)		2.095(2)	2.0870(6)				2.088(1)	2.0904(9)	2.0876(7)	2.086(1)	2.088(1)	2.087(1)
Mo(1)–O(1)	2.145(3)	2.145(7)	2.123(3)	2.124(5)	2.149(5)	2.126(5)	2.136(6)	2.124(4)	2.133(3)	2.175(6)	2.130(6)	2.134(7)
Mo(2)–O(2)	2.115(3)	2.124(7)	2.140(3)	2.163(5)	2.134(5)	2.139(5)	2.141(6)	2.138(5)	2.149(4)	2.156(6)	2.140(6)	2.130(7)
Mo(3)–O(3)		2.150(7)	2.132(3)				2.128(6)	2.142(5)	2.135(4)	2.169(6)	2.123(6)	2.126(8)
Mo(4)–O(4)		2.139(7)	2.165(3)				2.151(6)	2.122(4)	2.123(4)	2.155(6)	2.154(6)	2.173(7)
Mo(1)–N(1)	2.119(4)	2.14(1)	2.147(4)	2.144(6)	2.170(7)	2.141(6)	2.143(7)	2.130(6)	2.154(4)	2.126(7)	2.151(9)	2.187(8)
Mo(1)–N(3)	2.137(4)	2.13(1)	2.135(4)	2.108(6)	2.135(6)	2.122(5)	2.133(8)	2.117(5)	2.119(4)	2.113(7)	2.134(8)	2.16(1)
Mo(1)–N(5)	2.130(4)	2.11(1)	2.161(3)	2.156(6)	2.148(5)	2.142(6)	2.164(7)	2.158(6)	2.164(4)	2.146(7)	2.138(8)	2.145(8)
Mo(2)–N(2)	2.168(5)	2.13(1)	2.145(4)	2.137(6)	2.143(6)	2.140(6)	2.140(5)	2.143(6)	2.126(4)	2.159(7)	2.144(5)	2.163(8)
Mo(2)–N(4)	2.135(4)	2.126(9)	2.151(4)	2.122(6)	2.125(6)	2.134(6)	2.119(5)	2.133(6)	2.128(4)	2.134(8)	2.123(8)	2.130(9)
Mo(2)–N(6)	2.155(4)	2.15(1)	2.137(3)	2.129(6)	2.130(6)	2.163(6)	2.128(7)	2.123(6)	2.128(4)	2.132(7)	2.141(8)	2.135(8)
Mo(3)–N(7)		2.13(1)	2.150(4)				2.140(7)	2.137(6)	2.136(5)	2.139(7)	2.132(8)	2.179(9)
Mo(3)–N(9)		2.122(9)	2.115(4)				2.127(7)	2.127(6)	2.122(4)	2.119(8)	2.118(8)	2.136(9)
Mo(3)–N(11)		2.155(9)	2.161(4)				2.131(8)	2.144(6)	2.141(5)	2.149(7)	2.169(8)	2.122(9)
Mo(4)–N(8)		2.15(1)	2.147(4)				2.133(7)	2.135(6)	2.141(5)	2.140(7)	2.137(8)	2.134(8)
Mo(4)–N(10)		2.126(9)	2.123(4)				2.148(5)	2.116(6)	2.127(4)	2.125(7)	2.118(8)	2.141(8)
Mo(4)–N(12)		2.153(9)	2.147(4)				2.160(7)	2.152(6)	2.145(5)	2.137(7)	2.115(8)	2.147(9)
Selected Bond Distances for Bridging Dicarboxylate												
		C(3)–C(4)	C(3)–C(4)						C(1)–C(3)	C(1)–C(3)	C(2)–C(4) ^c	
		1.18(2)	1.372(7)						1.498(8)	1.53(1)	1.87(1)	C(1)–C(3)
C(1)–C(1A)	C(1)–C(3)	C(1)–C(3)	C(1)–C(3)	C(1)–C(2)	C(1)–C(2)	C(1)–C(2)	1.50(1)	C(3)–C(4)	C(2)–C(4)	C(2)–C(4)	C(1)–C(2)	1.52(2)
1.51(1)	1.44(2)	1.480(6)	1.480(6)	1.49(1)	1.50(1)	1.47(1)	C(2)–C(3)	1.50(1)	1.496(8)	1.53(1)	1.48(1)	C(2)–C(6)
	C(2)–C(4)	C(2)–C(4)	C(2)–C(4)				1.52(1)			C(3)–C(4)	C(3)–C(4)	1.51(2)
	1.45(2)	1.486(7)	1.486(7)							1.56(1)	1.49(1)	

^a Values are for one of two molecules in the asymmetric unit. ^b *d* = distance between centroids of Mo₂ units. ^c Nonbonded distance.

Table 3. Selected Angles (deg) for Compounds 1–12

	1	2	3	4	5	6	7	8	9	10 ^a	11	12
Φ , deg ^b	0	3.4	10.9	0	0	0	39.4	19.3	44.0	13.9	9.4	18.4
O(1)–Mo(1)–N(1)	85.1(2)	86.6(3)	85.9(1)	85.4(2)	90.1(2)	87.9(2)	85.9(2)	87.6(2)	85.8(2)	84.0(3)	84.2(3)	85.8(3)
O(1)–Mo(1)–N(3)	176.8(2)	175.1(4)	174.7(1)	173.3(2)	175.4(2)	174.2(2)	175.4(3)	174.5(2)	173.7(2)	175.5(2)	175.5(3)	176.6(3)
O(1)–Mo(1)–N(5)	86.3(2)	85.8(4)	87.8(1)	86.9(2)	85.5(2)	85.5(2)	88.9(3)	84.6(2)	85.7(2)	86.5(2)	89.5(3)	87.9(3)
O(2)–Mo(2)–N(2)	84.8(2)	86.0(3)	86.0(1)	84.9(2)	88.3(2)	86.5(2)	86.6(3)	87.8(2)	84.0(2)	84.5(2)	85.2(3)	83.2(3)
O(2)–Mo(2)–N(4)	173.2(2)	175.4(4)	175.6(1)	177.4(2)	175.1(2)	176.5(2)	175.0(3)	175.4(2)	177.0(2)	174.8(2)	174.6(3)	174.3(3)
O(2)–Mo(2)–N(6)	85.6(2)	86.4(3)	87.1(1)	87.7(2)	85.4(2)	85.2(2)	87.7(3)	84.8(2)	86.3(2)	85.6(3)	91.4(3)	87.4(3)
O(3)–Mo(3)–N(7)		86.2(3)	84.8(1)				85.2(3)	86.7(2)	85.3(2)	84.0(2)	84.8(3)	84.3(3)
O(3)–Mo(3)–N(9)		175.9(3)	174.8(1)				174.1(3)	176.6(2)	176.6(2)	175.2(2)	173.6(3)	173.9(3)
O(3)–Mo(3)–N(11)		84.7(3)	86.9(1)				89.5(3)	86.3(2)	86.2(2)	87.1(2)	87.3(3)	85.2(3)
O(4)–Mo(4)–N(8)		86.0(3)	86.4(1)				86.5(3)	86.4(2)	85.4(2)	85.8(3)	85.5(3)	83.4(3)
O(4)–Mo(4)–N(10)		175.3(3)	175.7(1)				177.0(3)	174.4(2)	174.6(2)	174.8(2)	176.3(3)	176.6(3)
O(4)–Mo(4)–N(12)		86.0(3)	86.1(1)				88.2(3)	85.5(2)	87.1(2)	87.0(2)	88.1(3)	86.6(3)
N(1)–Mo(1)–N(5)	168.1(2)	171.2(4)	171.7(1)	171.9(2)	173.9(3)	171.6(2)	173.1(3)	170.7(2)	171.3(2)	169.5(3)	171.3(3)	172.1(3)
N(2)–Mo(2)–N(6)	170.2(2)	170.8(4)	171.5(1)	169.8(2)	171.2(3)	170.3(2)	172.4(3)	170.7(2)	167.3(2)	168.7(3)	174.3(3)	169.4(4)
N(7)–Mo(3)–N(11)	169.7(3)	170.4(2)					172.9(3)	170.7(2)	169.4(2)	169.6(3)	171.1(3)	168.9(4)
N(8)–Mo(4)–N(12)	170.2(4)	170.9(2)					172.4(3)	170.6(2)	171.4(2)	170.9(3)	170.7(3)	168.0(3)
Selected Bond Angles for Bridging Dicarboxylate												
	C(1)–C(3)–C(4)						C(1)–C(3)–C(2)		C(1)–C(3)–C(4)–C(2) ^c			
	177(1)						120.4(8)		164.3			
	C(2)–C(4)–C(3)								C(1)–C(3)–C(4)–C(2) ^c		C(2)–C(5)–C(4)	
	177(1)								175.3		74.0(7)	
			C(1)–C(3)–C(4)								C(2)–C(6)–C(4)	
			117.8(4)								74.8(7)	
			C(2)–C(4)–C(3)								C(2)–C(7)–C(4)	
			123.0(5)								74.5(7)	

^a Values are for one of two molecules in the asymmetric unit. ^b Φ = twist angle between Mo₂ axes. ^c Torsion angle.

[Mo₂(DAniF)₃]₂(O₂CFcCO₂) (**6**). Method A: 57.5% yield. ¹H NMR δ (ppm in CD₂Cl₂): 8.54 (s, 4H, -NCHN-), 8.47 (s, 2H, -NCHN-), 6.63 (br, 32H, aromatic), 6.43 (d, 8H, aromatic), 6.21 (d, 8H, aromatic), 5.04 (t, 4H, Cp rings), 4.22 (t, 4H, Cp rings), 3.67 (s, 24H, -OCH₃), 3.64 (s, 12H, -OCH₃).

[Mo₂(DAniF)₃]₂(O₂CCH₂CO₂) (**7**). Method B: 52.0% yield. ¹H NMR δ (ppm in CDCl₃): 8.41 (s, 2H, -NCHN-), 8.24 (s, 4H, -NCHN-), 6.44 (m, 40H, aromatic), 6.18 (d, 8H, aromatic), 4.55 (s, 2H, O₂CCH₂CO₂), 3.66 (s, 12H, -OCH₃), 3.62 (s, 24H, -OCH₃).

[Mo₂(DAniF)₃]₂(O₂CCH₂CH₂CO₂) (**8**). Method B: 90.5% yield. ¹H NMR δ (ppm in CDCl₃): 8.45 (s, 4H, -NCHN-), 8.39 (s, 2H, -NCHN-), 6.64 (d, 16H, aromatic), 6.53 (d, 16H, aromatic), 6.43 (d, 8H, aromatic), 6.21 (d, 8H, aromatic), 3.72 (s, 24H, -OCH₃), 3.65 (s, 12H, -OCH₃), 3.50 (s, 4H, -O₂CH₂CH₂CO₂-). Anal. Calcd for C₉₄H₉₄-Mo₄N₁₂O₁₆: C, 55.57; H, 4.66; N, 8.27. Found: C, 55.22; H, 4.72; N, 8.09.

[Mo₂(DAniF)₃]₂(O₂CCH₂CH₂CH₂CO₂) (**9**). Method B: 71.2% yield. ¹H NMR δ (ppm in CDCl₃): 8.43 (s, 2H, -NCHN-), 8.35 (s, 4H, -NCHN-), 6.51 (m, 32H, aromatic), 6.45 (d, 8H, aromatic), 6.22 (d, 8H, aromatic), 3.67 (s, 12H, -OCH₃), 3.62 (s, 24H, -OCH₃), 3.02 (t, 4H, -O₂CCH₂CH₂CH₂CO₂-), 2.44 (q, 2H, -O₂CCH₂CH₂CH₂CO₂-). Anal. Calcd for C₉₅H₉₆Mo₄N₁₂O₁₆: C, 55.78; H, 4.73; N, 8.22. Found: C, 55.14; H, 4.70; N, 7.92.

[Mo₂(DAniF)₃]₂(O₂CCF₂CF₂CO₂) (**10**). Method B: 46.9% yield. ¹H NMR δ (ppm in CDCl₃): 8.49 (s, 2H, -NCHN-), 8.45 (s, 4H, -NCHN-), 6.63 (d, 16H, aromatic), 6.60 (d, 16H, aromatic), 6.47 (d, 8H, aromatic), 6.23 (d, 8H, aromatic), 3.71 (s, 24H, -OCH₃), 3.68 (s, 12H, -OCH₃).

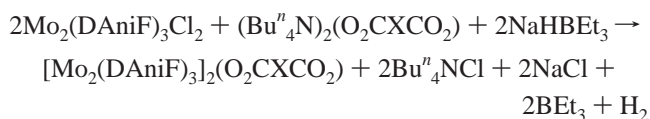
[Mo₂(DAniF)₃]₂(O₂CC(CH₂)₃CCO₂) (**11**). Method B: 51.7% yield. ¹H NMR δ (ppm in CDCl₃): 8.46 (s, 2H, -NCHN-), 8.38 (s, 4H, -NCHN-), 6.66 (d, 16H, aromatic), 6.55 (d, 16H, aromatic), 6.46 (d, 8H, aromatic), 6.23 (d, 8H, aromatic), 3.73 (s, 24H, -OCH₃), 3.67 (s, 12H, -OCH₃), 2.60 (s, 6H, C(CH₂)₃C). Anal. Calcd for C₉₇H₉₆-Mo₄N₁₂O₁₆: C, 56.29; H, 4.68; N, 8.12. Found: C, 55.71; H, 4.78; N, 8.22.

[Mo₂(DAniF)₃]₂(O₂CC(H)(CH₂CH₂)₂C(H)CO₂) (**12**). Method B: 74.4% yield. ¹H NMR (ppm in CDCl₃): 8.48 (s, 2H, -NCHN-), 8.42 (s, 4H, -NCHN-), 6.69 (d, 16H, aromatic), 6.58 (d, 16H, aromatic), 6.49 (d, 8H, aromatic), 6.27 (d, 8H, aromatic), 3.75 (s, 24H, -OCH₃), 3.69 (s, 12H, -OCH₃), 2.69 (br, 2H, -O₂CC(H)-), 2.35 (m, 4H, *eq* C-H in O₂CC(H)CH₂-), 1.84 (m, 4H, *ax* C-H in O₂C(H)CH₂-). Anal. Calcd for C₉₈H₁₀₀Mo₄N₁₂O₁₆: C, 56.44; H, 4.83; N, 8.06. Found: C, 56.48; H, 4.95; N, 8.29.

Results

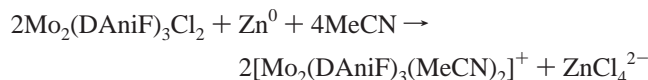
Preparative Methods. Two distinct procedures were used to introduce the Mo₂(DAniF)₃⁺ components of the bridged assembly. A common feature is the introduction of the dicarboxylate linker as the tetraethylammonium or tetrabutylammonium salt. All of these were easily prepared by neutralizing the diacids with aqueous R₄NOH and were isolated as white anhydrous powders that were easy to weigh and handle.

The first compounds we made were prepared using method A which proceeds by the stoichiometry indicated in the following equation:



In practice, however, use of an excess of the dicarboxylate dianion appears to be critical, possibly because precipitation of sodium dicarboxylate dianion upon introduction of NaHBEt₃ interferes with the reaction stoichiometry. This procedure suffers from the additional problem that NaHBEt₃ is a reagent incompatible with bridging units sensitive to reduction. For example, in the reaction with acetylene dicarboxylate, the linker

is reduced to fumarate as shown by comparison of the NMR and cell dimensions with those of an authentic sample of **3**. Furthermore, [Mo₂(DAniF)₃]₂(μ-H)₂⁹ can be observed as a competing, albeit minor, byproduct when method A is followed. Thus we were forced to find a more general method and found that use of [Mo₂(DAniF)₃(CH₃CN)₂]BPh₄⁻ fulfilled our expectations. This was prepared using Zn metal as the reducing agent. Furthermore, it was found that isolation of the latter was not necessary for the success of the coupling reaction. Consequently the coupling process can be simplified by converting Mo₂(DAniF)₃Cl₂ to the highly soluble [Mo₂(DAniF)₃(CH₃CN)₂]⁺ cation by in situ reduction with zinc in acetonitrile according to the following stoichiometry:¹⁶



The subsequent coupling of the dicarboxylate dianion with [Mo₂(DAniF)₃(MeCN)₂]⁺ is a facile process driven forward by precipitation of the product as a neutral molecule. The soluble ZnCl₄²⁻ species can be easily eliminated during the filtration and washing of the product.

Here again, use of an excess of (Et₄N)₂dicarboxylate appears to be helpful. A notable exception is the reaction with (Et₄N)₂(O₂CC≡CCO₂), which requires the use of *exactly* 1/2 equiv of the dicarboxylate anion per equivalent of Mo₂(DAniF)₃-Cl₂. When an excess of the linker is used and the temperature is not kept below 25 °C, decarbonization of the linker is observed.¹⁷ As indicated above, compound **2** cannot be prepared following method A. A carefully controlled method B is the only way found, so far, for its preparation. Our observations indicate that method B is a decisively cleaner and more general protocol.

In every case the ¹H NMR results indicate that the bulk sample is very pure. Furthermore the spectra in solution are fully consistent with the structures of the compounds.

Structures. Because the structural results are so voluminous, we reserve most of the details for deposit. Figure 1 presents the 12 structures, with the formamidate ligands shown only as N-C-N chains. Generally, two [Mo₂] units are linked by the dicarboxylate dianions with the Mo-Mo axes nearly parallel to each other; the larger deviations of 39.4° and 44.0° are those for **7** and **9**, respectively (see Table 3). Depending on the nature of the dicarboxylate group, the two Mo₂⁴⁺ units and the linker can be nearly in a plane or forming a step. Interestingly, in the succinate, **8**, and the corresponding fluorinated analogue, **10**, there are considerable structural variations with **8** having a more planar core than **10**.

The structure of **12** is a little surprising. As can be seen in Figure 1, the conformer obtained is the axial-axial (*ax-ax*) one, whereas, with large substituents (as in the classic case of 1,4-di-*tert*-butylcyclohexane) the equatorial-equatorial (*eq-eq*) conformation is normally expected. Evidently, the net effect of both intra- and intermolecular forces (i.e., crystal packing forces) favors the *ax-ax* conformation in the crystal. As will

(16) [Mo₂(DAniF)₃(MeCN)₂]⁺ has been crystallographically characterized as the [BPh₄]⁻ salt, details of which will be communicated at a later time. Also, crystalline (Buⁿ₄N)₂(ZnCl₄) has been isolated and structurally characterized by X-ray diffraction, thereby providing further evidence for the reaction stoichiometry. (Buⁿ₄N)₂(ZnCl₄)·2C₆H₆ crystallizes in the space group I42d with cell parameters *a* = *b* = 14.711(2) Å, *c* = 23.499(5) Å, and *V* = 5086(1) Å³.

(17) The elimination of CO₂ has been demonstrated by the isolation in good yield of crystalline Mo₂(DAniF)₃(O₂CC≡C-H), the structure of which has been determined and will be described elsewhere.

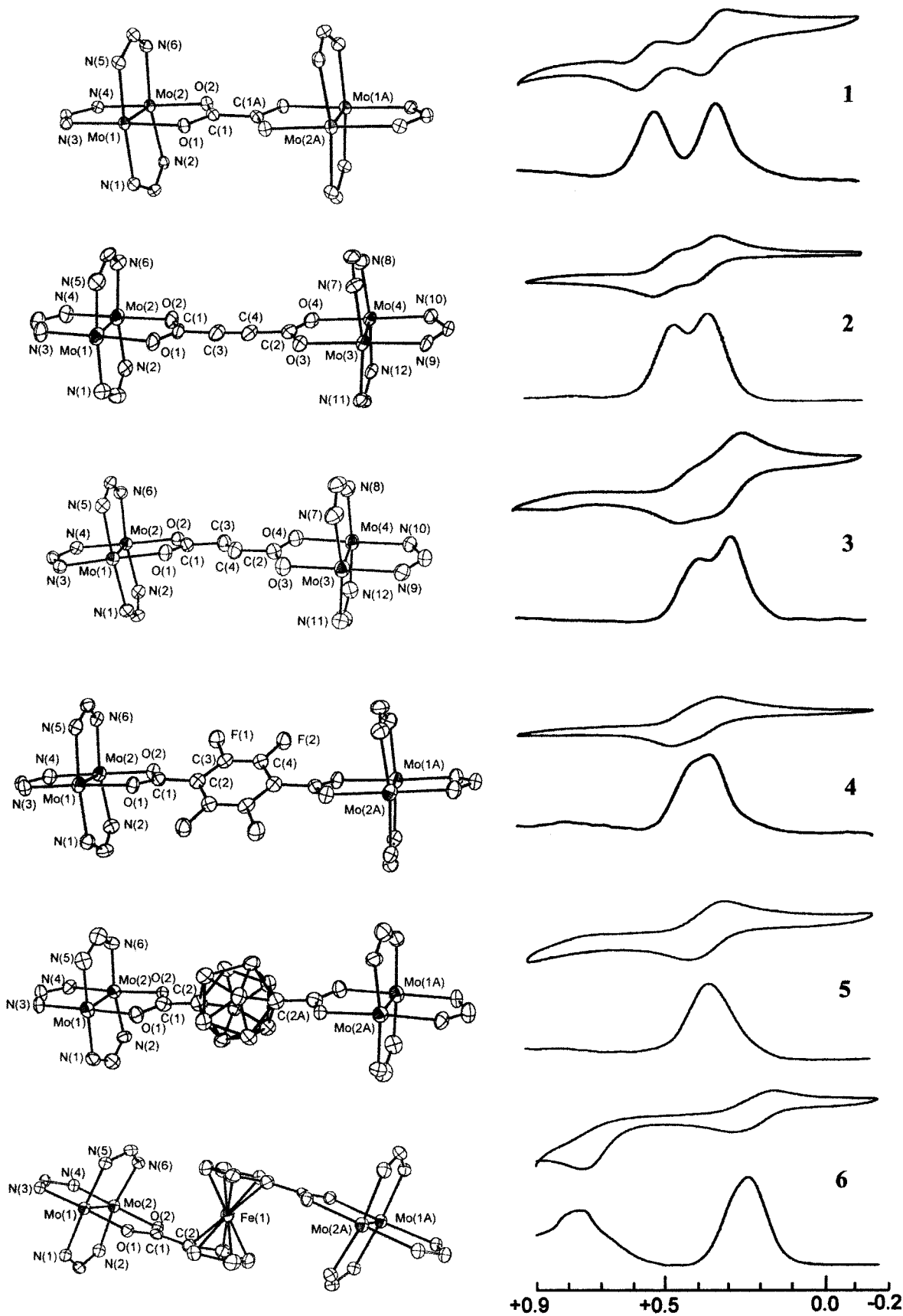


Figure 1. The core structures of the 12 $[\text{Mo}_2(\text{DAniF})_3](\text{O}_2\text{CXCO}_2)$ compounds. Displacement ellipsoids are given at the 40% probability level. The *p*-anisyl group attached to each N atom and all hydrogen atoms have been omitted for clarity. To the right of each structure, the number of each compound and the cyclic voltammogram (above) and differential pulse voltammogram, DPV (below), are shown.

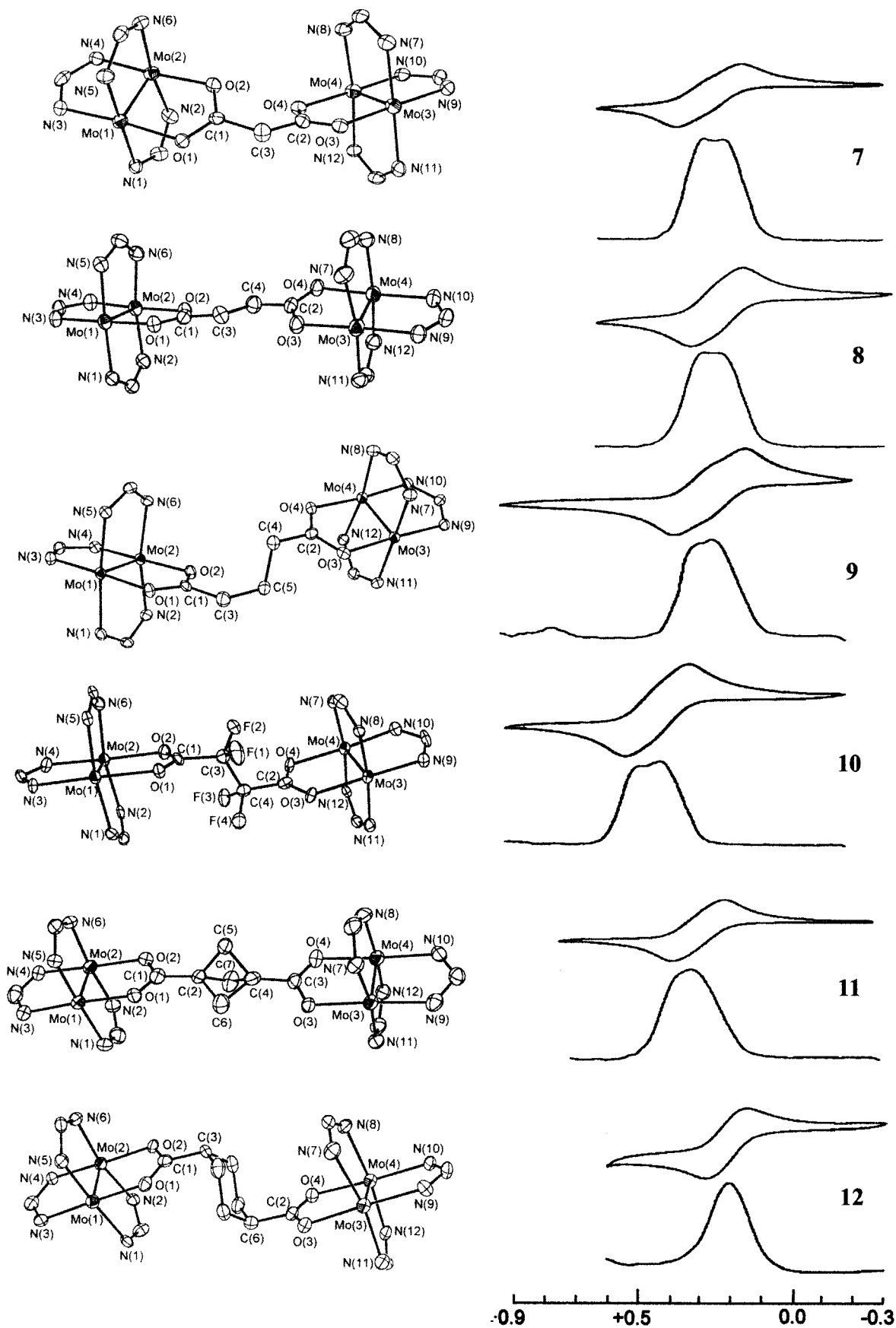


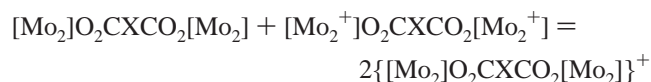
Figure 1. (continued)

be noted later, there are indications from the electrochemistry and ^1H NMR spectrum that the *eq-ec* conformation is favored in CHCl_3 solution.

Insofar as the dimensions of the $[\text{Mo}_2]$ units are concerned, the structures are all very similar (see Table 2). The Mo–Mo distances are all within the range 2.082(1)–2.095(2) Å, and the Mo–N and Mo–O distances also lie within very narrow ranges. All interatomic distances in the dicarboxylate linkers fall within normal ranges, e.g., the singly bonded C–C distances are close to 1.50 Å. Curiously, the C≡C bond in **2** retains the triple-bond character with a distance of 1.18(2) Å, and the C–C distance of 1.372(7) Å in **3** is also typical of a C=C double bond.

Besides the interatomic distances, another dimension given in Table 2 is the distance, d (Å), between the centers of the two $[\text{Mo}_2]$ units in each compound. These will be employed in the discussion of the electrochemical data. It may be noted here that not all of these distances will necessarily remain the same when the molecules are in a different environment, specifically, in solution. Almost certainly **1**, **2**, **3**, **4**, **5**, **7**, and **11** will not vary. It is unlikely that **6** will vary, but **8**, **9**, **10**, and **12** have enough conformational freedom to do so. This aspect of the structures will be relevant when the electrochemical results are discussed.

Electrochemical Data. The electrochemical results are shown in Figure 1, and numerical values are collected in Table 4. The $\Delta E_{1/2}$ values were measured by the method of Richardson and Taube.¹⁸ From each $\Delta E_{1/2}$ one may calculate the comproportionation constant K_c , that is, the equilibrium constant for the following reaction:



In this equation the oxidation states of individual dimolybdenum units, $[\text{Mo}_2]$ and $[\text{Mo}_2^+]$, have been specified on the left-hand side, but on the right-hand side we simply indicate that the entire unit has a +1 charge. How that charge is distributed, even formally, will have to be determined in each case.

Discussion

The work reported here demonstrates that it is possible to synthesize compounds of the type described with virtually any dicarboxylic acid desired, so long as its tetraalkylammonium salt can be prepared. The 12 compounds reported here have been deliberately chosen to present as broad a test of our synthetic methodology as possible.

Since the structures in general show no anomalous features, not a great deal of discussion is required. However, there are a few details that merit comment. The similarity of the Mo–Mo distances (vide supra) would have been expected on the basis of the fact that those in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$, and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ are all equal to within 0.01 Å,¹⁹ even though each of these molecules has four bridging carboxylate groups and the strengths of the corresponding acids vary over about 5 orders of magnitude. Likewise, $\text{Mo}_2(\text{diarylformamidinate})_4$ compounds, $\text{Mo}_2(\text{DArF})_4$, have Mo–Mo distances of 2.09 Å that vary by no more than ca. 0.01 Å, independently of the donor ability of the substituents on the aryl groups.²⁰ Therefore, when

Table 4. Electrochemical Data^a for Compounds **1–12**

compd	peak positions			$\Delta E_{1/2}$, mV ^c	K_c ^d
	$E_{1/2}(+/0)$, mV ^b	$E_{1/2}(2+/+)$, mV	$E_{1/2}(2+/0)$, mV		
1	260	472		223	5.9×10^3
2	325	433		150	3.4×10^2
3	217	334		137	2.1×10^2
4	315	356		87	30
5			328 ^e	69	15
6			192 ^e	75	19
7	225	285		108	67
8	225	285		100	49
9	217	262		112	78
10	410	495		121	1.1×10^2
11			261 ^e	95	40
12			213 ^e	69	15

^a The data were recorded on a BAS 100 electrochemical analyzer in 0.1 M Bu_4NPF_6 solution (CH_2Cl_2) with Pt working and auxiliary electrodes and a Ag/AgCl reference electrode. Scan rate is 100 mV/s for CV and 2 mV/s for DPV. All the potential values are referenced to Ag/AgCl, and under the present experimental conditions, the $E_{1/2}(\text{Fc}^+/\text{Fc})$ was consistently measured at 440 mV. ^b $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ from CV for **1**, **5**, **6**, **11**, and **12**; $E_{1/2} = E_{\text{p}} + E_{\text{pul}}/2$, $E_{\text{pul}} = 10$ mV from DPV for **3** and **4**; $E_{\text{pul}} = 50$ mV for **2**, **7**, **8**, **9**, and **10**. ^c $\Delta E_{1/2}$ as calculated using the DPV peak half-height method of Richardson and Taube, ref 18. ^d K_c , calculated from the formula $K_c = e^{\Delta E_{1/2}/25.69}$. See ref 23. ^e $E_{1/2}$ values for **5**, **6**, **11**, and **12** are average values for both redox couples, i.e., 2+/0.

there is only one varying carboxyl group and there are three invariant formamidinate ligands, no greater variation in Mo–Mo distances could be expected.

On the contrary, it has been shown that the electrochemical behavior of the $\text{Mo}_2(\text{DArF})_4$ complexes is very sensitive to small variations of the substituents. For example, for Ar = *p*-anisyl the oxidation potential $E_{1/2} = 244$ mV; for Ar = *p*- $\text{C}_6\text{H}_4\text{CF}_3$, $E_{1/2}$ is 795 mV, and for 3,5- $\text{C}_6\text{H}_3\text{Cl}_2$, E_{pa} is 1029 mV.²⁰ Consequently, at the onset of this study, we had no way to anticipate what could happen when pairs of $[\text{Mo}_2]$ units were oxidized. We have now found that, for $[\text{Mo}_2]\text{O}_2\text{CXCO}_2[\text{Mo}_2]$ molecules, there are indeed observable oxidation processes. These are reversible one- or two-electron oxidations that can be effected electrochemically. A major goal in future work will be to isolate and characterize these oxidized species, especially the singly oxidized ones. It is obvious that the compounds under study here will raise many of the same questions as were raised years ago in the work of Taube and others on the mixed-valence complexes of d^5 – d^6 metal centers.¹⁸ Since we have not yet isolated the mixed-valence species, nor even examined them spectroscopically in solution, we are not yet in a position to address these questions in detail, but we plan to do so in the future.

As mentioned earlier, a major goal of the present study was to develop a synthetic approach to supramolecular compounds containing metal–metal bound corner pieces. In doing so, we prepared a large number of the simplest units. As an added bonus, and with the results now available, we can discuss some simple but basic questions concerning the electrochemical properties of our compounds. For comparison we will use some of the pioneering work on compounds of the Creutz–Taube type,²¹ where two octahedrally coordinated metal ions are linked by a diamine. We will be using the $\Delta E_{1/2}$ values or the related comproportionation constants; both of these are given in Table 4. In our discussion we will concentrate on the former, namely, what factor, or factors, determine the separation between the

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(21) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

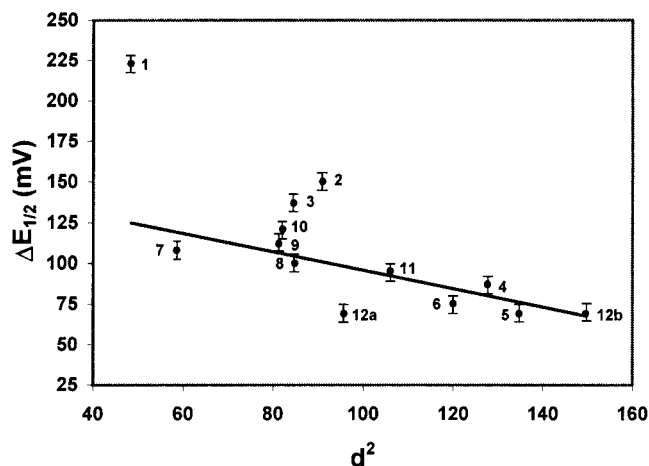


Figure 2. Variation of the $\Delta E_{1/2}$ as a function of the square of the distance (\AA^2) between the midpoints of the quadruply bonded M–M units. The best fit line excludes data points of the more polarizable linkers **1**, **2**, and **3**. For **12a** and **12b** see text.

two oxidation potentials, i.e., the $\Delta E_{1/2}$ values. We approach that question by looking first at the simplest possible relationship, namely, how the $\Delta E_{1/2}$ values vary with the distance between the [Mo₂] centers in the neutral molecules.

The first point to recognize is that if the linker is a very poor transmitter of the effect of oxidation of one Mo₂ unit to the other one, we might expect an essentially electrostatic (Coulombic) effect. This would mean that the $\Delta E_{1/2}$ values should vary inversely with d^2 , where d is the distance separating the centers of the two Mo₂⁴⁺ units. Figure 2 shows such a plot. Clearly eight of the points define a good straight line, with a correlation coefficient of 0.89. In other words, the data support the idea that, in these cases, there is no delocalization and little if any through-bond coupling. Considering the nature of the groups between the carboxylate groups in these eight cases, this is not surprising.

What about the four compounds that “do not fit”? In the case of **12**, there is the question about what the value of d may be for the molecule in solution. While in the crystal the *trans*-1,4-cyclohexyldicarboxylate linker has the carboxylate groups in an *ax-ax* conformation, it appears to change in solution to an *eq-eq* conformation. This change may be inferred by close inspection of the ¹H NMR signals corresponding to the *trans*-1,4-cyclohexyldicarboxylate linker, which show a broad signal of ~25 Hz at half-height for the two methine hydrogen atoms. If these methine hydrogen atoms were axially disposed, they would experience *ax-ax* couplings of 8–10 Hz and *ax-eq* couplings of 2–3 Hz with the vicinal CH₂ groups,²² which would be anticipated to produce a signal several tens of hertz wide, as observed. Were these hydrogen atoms in the equatorial conformation instead, all coupling constants (*ax-eq* and *eq-eq*) would be 2–3 Hz and combine to form a substantially narrower signal (10–12 Hz). The *ax-ax* and *eq-eq* conformations correspond to points **12a** and **12b**, respectively, and the latter fits quite well to the line in Figure 2. The distance for **12b** has been estimated, relative to that in **12a**, from models.

We are now left with compounds **1**, **2**, and **3** which all lie above the line. In the case of **1**, the oxalate, it seems extremely likely, a priori, that the monocation is delocalized, and its position in Figure 2 provides excellent support for this idea. Points **2** and **3** are clearly above the line but not nearly so much

as **1**. We propose that the monocations in these two cases are not fully delocalized, but that the short, unsaturated connectors –C≡C– and –CH=CH–, respectively, are significantly polarized when a charge is placed in one Mo₂ group. Such polarization should be greater for the triple bond, which is exactly what is seen.

Finally it may be noted that the small amount of scatter for the points that have been used to define the line is not surprising in view of the uncertainties in the $\Delta E_{1/2}$ values (which we estimate to be ±10 mV) and in the uncertainties as to the best mean value of d for molecules such as **6**–**10**, which all have some conformational freedom. All in all, the electrochemical results seem to make very good sense and to support a priori ideas as to where coupling and polarization phenomena should play the most important role.

Finally a few words about the comproportionation constants, K_c , derived from the electrochemical data (Table 4) are necessary. These constants are calculated using the expression²³

$$K_c = e^{\Delta E_{1/2}/25.69}$$

where $\Delta E_{1/2}$ is the separation of potentials for successive one-electron processes in millivolts.

In general, small $\Delta E_{1/2}$ values (and thus small K_c values) have been interpreted as being associated with a small degree of metal–metal interaction in homodinuclear complexes.²⁴ Conversely, larger $\Delta E_{1/2}$ values (larger K_c values) indicate increased M–M interactions, and for very large values the interaction might be so strong that electron delocalization can be prevalent in monooxidized species.

Accordingly, these intervalence compounds have been classified using the Robin–Day classification,²⁵ widely used by Creutz–Taube²¹ and others,²⁶ in one of three classes, beginning with class I where the compounds have complete charge localization. In class III compounds, the delocalization is very extensive and the metal units in each chromophore can be considered formally as having half the positive charge. Class II compounds are those more or less intermediate between the other two classes with detectable electronic interaction that partially mixes the character of the oxidized and reduced metal units through interaction with orbitals of the linker.²⁷

As shown in Table 4, the comproportionation constants of the 12 compounds described here vary from the essentially statistical value (4) to ca. 5.9×10^3 for **1**. The largest constant is associated with a $\Delta E_{1/2}$ value of 223 mV, and thus all compounds fall below the upper end for class II systems, which is normally associated with $\Delta E_{1/2}$ values of ca. 350 mV²⁸ or K_c of 8.3×10^5 .

As noted earlier, the K_c is a measurement of the stability of the non oxidized plus doubly oxidized species relative to the monooxidized species. Thus, this information is critically important in the planning of our next goal, that is, the isolation of some of the monooxidized species. One would expect that monooxidized complexes, with smaller K_c values, will be more

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difficult to isolate than those for which the K_c values are larger. A further report on this will be available at a later date.

In the meantime, the information we have gathered on the $[\text{Mo}_2]\text{O}_2\text{CXCO}_2[\text{Mo}_2]$ molecules will also be of importance, indeed indispensable, in understanding the behavior of more elaborate systems such as loops,²⁹ triangles,^{7b} squares,³⁰ and networks,^{8b} which are the subjects of recent reports from this laboratory. More importantly, however, is that the synthetic methodology used to prepare pairs of dimetal units can indeed be modified appropriately to prepare larger supramolecular species.

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Supporting Information Available: Twelve ORTEP drawings at 40% probability levels with complete atomic labeling in PDF, as well as X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs/acs/org>.

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