

# Quadridentate Bridging $\text{EO}_4^{2-}$ (E = S, Mo, W) Ligands and Their Role as Electronic Bridges

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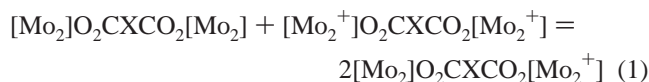
Three compounds containing two quadruply bonded  $\text{Mo}_2(\text{DAniF})_3$  ( $\text{DAniF} = N,N'$ -di-*p*-anisylformamidinate) units linked by tetrahedral  $\text{EO}_4^{2-}$  anions (E = S, Mo, W) have been prepared and characterized by crystallography and NMR. The linkers in these  $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-EO}_4)$  compounds hold the  $\text{Mo}_2$  units in an approximately perpendicular orientation and mediate strong electrochemical communication between them. Each of the three compounds shows two quasireversible ( $\mu\text{-SO}_4$ ) or fully reversible ( $\mu\text{-MoO}_4$ ,  $\mu\text{-WO}_4$ ) features in its cyclic voltammogram corresponding to successive oxidation of each of its  $\text{Mo}_2$  units. The  $\Delta E_{1/2}$  values are the largest thus far measured for  $\text{Mo}_2\text{-X-Mo}_2$  bridged complexes and may be sufficiently large to permit isolation of the singly oxidized species.

## 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.<sup>1</sup> 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 I,  $[\text{Mo}_2]\text{O}_2\text{C-X-CO}_2\text{-}[\text{Mo}_2]$ , where  $[\text{Mo}_2]$  represents  $\text{Mo}_2\{(p\text{-MeOC}_6\text{H}_4\text{N})_2\text{CH}\}_3^+$  and X is some type of linker, usually but not necessarily an organic group.<sup>2</sup> We have also made a series of  $[\text{Mo}_2(\text{DAniF})_2(\mu\text{-O}_2\text{C-X-CO}_2)]_4$  squares,<sup>4</sup> and  $[\text{M}_2(\text{DAniF})_2(\mu\text{-O}_2\text{C-X-CO}_2)]_3$  triangles<sup>5</sup> (M = Mo and

Rh), and also tridimensional complexes having octahedra of  $\text{M}_2$  units (M =  $\text{Mo}^6$  and  $\text{Rh}^7$ ) 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, assemblies having infinite tubes,<sup>8</sup> and also interlocking lattices and double helices.<sup>9</sup>

A major point of interest concerning the electrochemistry of compounds of type I was the ability of the various bridging dicarboxylate ligands to communicate the effect of oxidation of the dimetal unit at one end to the dimetal unit at the other end.<sup>2</sup> This was measured by determining the separation of the first and second oxidation potentials and calculating from these the comproportionation constants,  $K_c$ , according to the expression  $K_c = e^{\Delta E_{1/2}/25.69}$ , where  $\Delta E_{1/2}$  is the separation of potentials for successive one-electron processes in millivolts. The comproportionation constant is the equilibrium constant for the following reaction:



In the limit of no communication,  $K_c$  will have the value 4, but as communication improves  $K_c$  increases. Among the dicarboxylate linkers used, the highest degree of communication occurred for the oxalate ion, in which there is no X, the two  $\text{CO}_2^-$  units being directly connected. Where X is a poor transmitter of the effect of oxidation from one  $\text{Mo}_2$  unit to the other (e.g.,  $\text{CH}_2$ ,  $\text{C}_2\text{H}_4$ , etc.), a plot of  $\Delta E_{1/2}$  versus  $d^2$  is linear ( $d$  = distance between the centers of the  $\text{Mo}_2$  units), consistent with an essentially electrostatic (Coulombic) effect.

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- (1) See, for example: (a) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3843. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853 and references therein. (c) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417 and references therein. (d) Espinet, P.; Soulantica, K.; Charmant, J. P. H.; Orpen, A. G. *Chem. Commun.* **2000**, 915. (e) Navarro, J. A. R.; Lippert, B. *Coord. Chem. Rev.* **1999**, *185–186*, 653. (f) Whang, D.; Kim, K. *J. Am. Chem. Soc.* **1997**, *119*, 451. (g) Mann, S. Huttner, G.; Zsolnai, L.; Heinze, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2808. (h) Scherer, M.; Caulder, D. L.; Johnson, D. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 1588. (i) Lai, S.-W.; Chan, M. C.-W.; Peng, S.-M.; Che, C.-M. *Angew. Chem., Int. Ed.* **1999**, *38*, 669. (j) Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289. (k) Klausmeyer, K. K.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 2705.
- (2) Cotton, F. A.; Donahue, J. P.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 1234.
- (3) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 472.
- (4) (a) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 4538. (b) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 478. (c) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A.; Yu, S.-Y. *J. Chem. Soc., Dalton Trans.* **2001**, 502.
- (5) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 575.

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

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

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

(9) Cotton, F. A.; Lin, C.; Murillo, C. A. *J. Chem. Soc., Dalton Trans.* **2001**, 499.

**Table 1.** Crystallographic Data for  $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-EO}_4)$  Complexes (E = S, Mo, W)

	$[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-SO}_4) \cdot 2\text{CH}_2\text{Cl}_2 \cdot \text{C}_6\text{H}_{14}$	$[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-MoO}_4) \cdot \text{ClCH}_2\text{CH}_2\text{Cl} \cdot 0.5\text{C}_6\text{H}_{14}$	$[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-WO}_4) \cdot \text{ClCH}_2\text{CH}_2\text{Cl} \cdot 0.5\text{C}_6\text{H}_{14}$
empirical formula	$\text{C}_{98}\text{H}_{108}\text{Cl}_4\text{Mo}_4\text{N}_{12}\text{O}_{16}\text{S}$	$\text{C}_{95}\text{H}_{101}\text{Cl}_2\text{Mo}_5\text{N}_{12}\text{O}_{16}$	$\text{C}_{95}\text{H}_{101}\text{Cl}_2\text{Mo}_4\text{N}_{12}\text{O}_{16}\text{W}$
fw	2267.58	2217.48	2305.36
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> , Å	15.224(4)	12.606(5)	12.595(3)
<i>b</i> , Å	17.860(6)	12.946(6)	12.931(3)
<i>c</i> , Å	20.030(5)	28.658(9)	28.781(7)
$\alpha$ , deg	87.83(2)	91.02(4)	90.93(2)
$\beta$ , deg	79.72(1)	94.18(3)	94.22(3)
$\gamma$ , deg	69.76(1)	94.60(3)	94.70(2)
<i>V</i> , Å <sup>3</sup>	5026(2)	4648(3)	4658(2)
<i>Z</i>	2	2	2
<i>T</i> , °C	−60	−60	−60
$\lambda$ , Å	0.71073	0.71073	0.71073
<i>d</i> <sub>calcd.</sub> , g/cm <sup>3</sup>	1.498	1.584	1.644
$\mu$ , mm <sup>−1</sup>	0.684	0.786	1.884
<i>R</i> 1 <sup>a</sup> ( <i>wR</i> 2 <sup>b</sup> )	0.070 (0.167)	0.064 (0.135)	0.079 (0.173)

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

In view of these results, we asked ourselves whether communication would not be further increased by eliminating the C–C bond, that is, by fusing the two carbon atoms into one. Of course, this cannot actually be done, but the idea of having two  $\text{EO}_2^-$  units sharing the same E atom can be implemented by using an  $\text{EO}_4^{2-}$  ion, such as  $\text{SO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$  or  $\text{WO}_4^{2-}$ . Of course, another difference arises in the change from  $^-\text{O}_2\text{CCO}_2^-$  to an  $\text{EO}_4^{2-}$  ion, namely, that in the latter case the two di-metal units must be perpendicular rather than parallel. We present here a report on the preparation, structural characterization, and electrochemical behavior of three  $[\text{Mo}_2]\text{O}_2\text{EO}_2[\text{Mo}_2]$  molecules in which the aforementioned tetrahedral oxo anions are used.

## Experimental Section

**Materials and Methods.** All manipulations and procedures were conducted under  $\text{N}_2$  using either a  $\text{N}_2$  drybox or standard Schlenk line techniques. Solvents were distilled and degassed prior to use. Acetonitrile was twice distilled under  $\text{N}_2$ , first from activated molecular sieves and then from  $\text{CaH}_2$ ;  $\text{CH}_2\text{Cl}_2$  was dried and distilled from  $\text{P}_2\text{O}_5$ ; and  $\text{Et}_2\text{O}$  and hexanes were distilled from Na/K-benzophenone. 1,2-Dichloroethane was filtered through anhydrous  $\text{Na}_2\text{SO}_4$  and degassed by  $\text{N}_2$  bubbling prior to use. The compound  $[\text{Mo}_2(\text{DAniF})_3]_2$  ( $\text{DAniF} = N,N'$ -di-*p*-anisylformamidinate) was prepared according to a literature procedure;<sup>10</sup>  $(\text{Bu}^n\text{N})_2\text{SO}_4$  was prepared by neutralization of  $\text{Bu}^n\text{NHSO}_4$  with 1 equiv of  $\text{Bu}^n\text{NOH}$  followed by careful drying in vacuo. Similarly,  $(\text{Et}_4\text{N})_2\text{MO}_4$  (M = Mo, W) were prepared by treating  $(\text{NH}_4)_2\text{MO}_4$  with 2 equiv of  $\text{Et}_4\text{NOH}$ . Other reagents such as  $\text{Bu}^n\text{NHSO}_4$ ,  $(\text{NH}_4)_2\text{MO}_4$  (M = Mo, W),  $\text{Bu}^n\text{NOH}$  (1.0 M in MeOH),  $\text{Et}_4\text{NOH}$  (20 wt % in  $\text{H}_2\text{O}$ ), and Zn dust were purchased from commercial sources and used as received.

**Physical Measurements.** Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia.  $^1\text{H}$  NMR spectra were recorded on a Varian XL-200E NMR spectrometer, with chemical shifts ( $\delta$ ) referenced to  $\text{CH}_2\text{Cl}_2$  or to  $\text{CHCl}_3$ . The cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer in 0.1 M  $\text{Bu}^n\text{NPF}_6$  solution ( $\text{CH}_2\text{Cl}_2$ ) 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  $E_{1/2}(\text{Fc}^+/\text{Fc})$  was consistently measured at 440 mV.

**X-ray Structure Determinations.** Single crystals of all compounds suitable for X-ray diffraction analysis were grown by diffusion of hexanes into a  $\text{CH}_2\text{Cl}_2$  (**1**) or 1,2-dichloroethane (**2**, **3**) solution of the corresponding product. Single-crystal X-ray work on compounds **1–3** was performed on a Nonius FAST diffractometer utilizing the program MADNES.<sup>11</sup> In each case, a suitable crystal was mounted on the tip of a quartz fiber with a small amount of silicone grease and transferred

to a goniometer head. Cell parameters were obtained from an autoindexing routine and were refined with 250 reflections within a  $2\theta$  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 PROCOR<sup>12</sup>), and the program SORTAV<sup>13</sup> was used to correct for absorption.

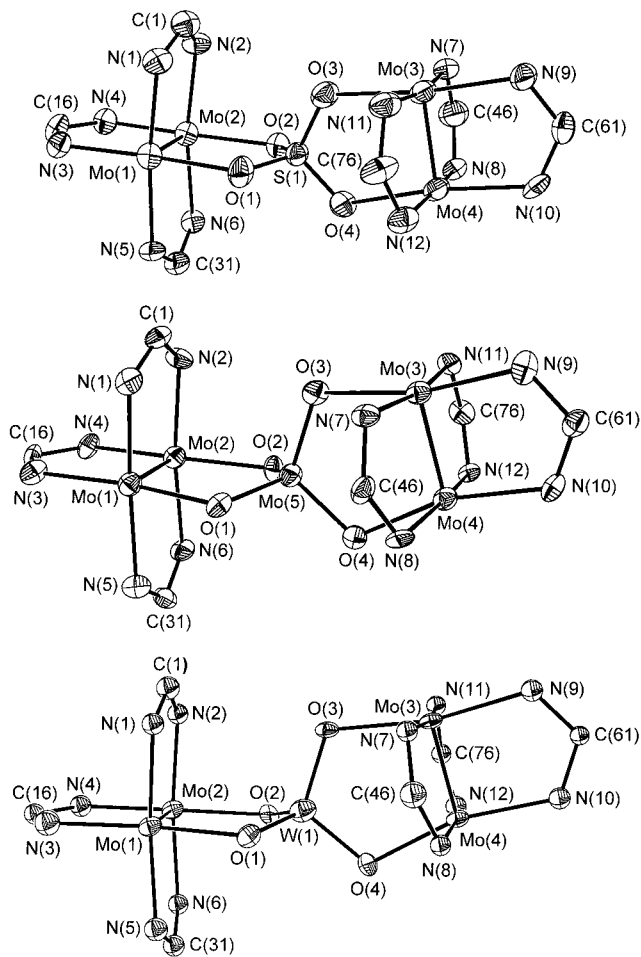
For all structures, the positions of some or all of the non-hydrogen atoms were found via direct methods using the SHELXTL software suite.<sup>14</sup> Subsequent cycles of least squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters except for **3**, in which only the five metal atoms and the tungstate oxygen atoms were refined anisotropically owing to the limited quality of the data. All hydrogen atoms were added in calculated positions and refined isotropically as riding atoms with the carbon atoms to which they were attached. Cell parameters and refinement results for all compounds are summarized in Table 1.

### Preparation of $[\text{Mo}_2(\text{AniF})_3]_2(\mu\text{-EO}_4)$ Complexes, E = S, Mo, W.

A suspension of  $[\text{Mo}_2(\text{DAniF})_3]_2$  (0.500 g, 0.486 mmol) and Zn dust (7.50 g) in MeCN was stirred under  $\text{N}_2$  for a period of 1.5 h. The excess Zn dust was removed from the heterogeneous mixture by filtration through packed Celite into a flask containing  $1/2$  equiv of  $(\text{Bu}^n\text{N})_2\text{SO}_4$ ,  $(\text{Et}_4\text{N})_2\text{MoO}_4$ , or  $(\text{Et}_4\text{N})_2\text{WO}_4$  (0.243 mmol). The Celite was washed with 5 mL of MeCN. The resulting orange solution was stirred for 1 h at ambient temperature and then concentrated in vacuo to a volume of 5 mL, whereupon a yellow (**1**) or orange (**2**, **3**) microcrystalline solid formed. The precipitate was isolated by filtration and washed with  $2 \times 1$  mL of MeCN followed by  $1 \times 5$  mL of  $\text{Et}_2\text{O}$ . The remaining solid was extracted with  $4 \times 2$  mL of  $\text{CH}_2\text{Cl}_2$  or 1,2-dichloroethane and filtered into a Schlenk tube. The filtrate was then layered with 1 mL of  $\text{Et}_2\text{O}$  followed by 50 mL of hexanes. After 72 h, the crystalline product was isolated by filtration and dried in vacuo.

**1:**  $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-SO}_4)$ , 77% yield.  $^1\text{H}$  NMR  $\delta$  (ppm in  $\text{CDCl}_3$ ): 8.60 (s, 4H,  $-\text{NCHN}-$ ), 8.24 (s, 2H,  $-\text{NCHN}-$ ), 6.61 (d, 16H, aromatic), 6.46 (d, 16H, aromatic), 6.40 (d, 8H, aromatic), 6.19 (d,

- (10) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **1998**, *120*, 3398.
- (11) Pflugrath, J.; Messerschmitt, A. MADNES, *Munich Area Detector (New EEC) System*, Version EEC 11/1/89, with enhancements by Nonius corporation, Delft, The Netherlands. A description of MADNES appears in the following: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, *20*, 306.
- (12) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 67. (b) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 916.
- (13) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.
- (14) SHELXTL, Version 5.03. Siemens Industrial Automation, Inc., Madison, WI.



**Figure 1.** The core structures of the three  $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-EO}_4)$  (E = S, Mo, W) compounds. Displacement ellipsoids are given at the 50% probability level. The *p*-anisyl group attached to each N atom and all hydrogen atoms have been omitted for clarity.

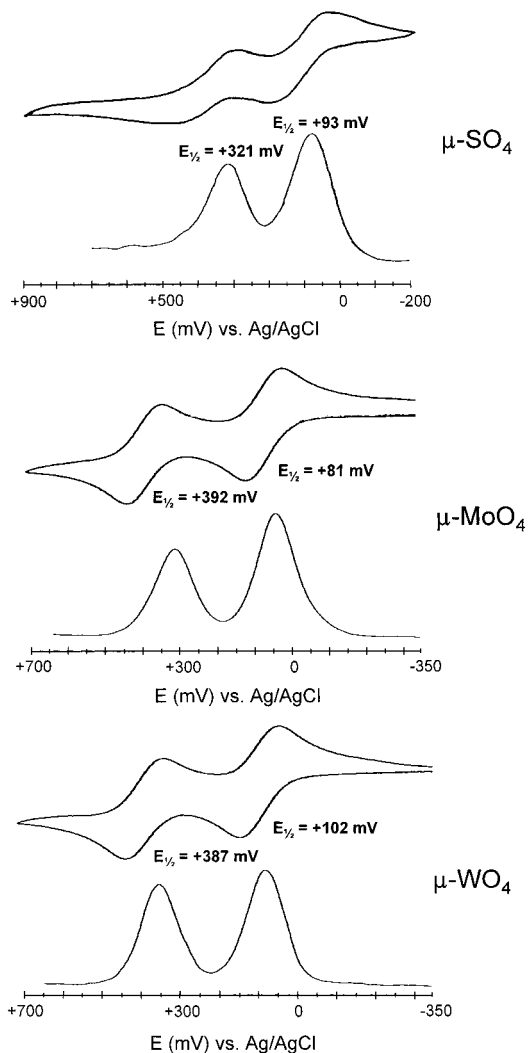
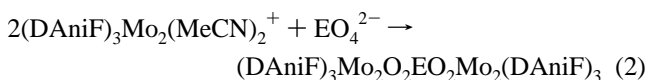
8H, aromatic), 3.66 (s, 24H,  $-\text{OCH}_3$ ), 3.64 (s, 12H,  $-\text{OCH}_3$ ). Anal. Calcd for  $\text{C}_{90}\text{H}_{90}\text{Mo}_4\text{N}_{12}\text{O}_{16}\text{S}$ : C, 53.74; H, 4.51; N, 8.36; S, 1.59. Found: C, 53.21; H, 4.54; N, 8.15; S, 1.61.

**2:**  $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-MoO}_4)$ , 51% yield.  $^1\text{H}$  NMR  $\delta$  (ppm in  $\text{CD}_2\text{Cl}_2$ ): 8.69 (s, 4H,  $-\text{NCHN}-$ ), 8.11 (s, 2H,  $-\text{NCHN}-$ ), 6.63 (d, 16H, aromatic), 6.45 (d, 16H, aromatic), 6.35 (d, 8H, aromatic), 6.13 (d, 8H, aromatic), 3.65 (s, 24H,  $-\text{OCH}_3$ ), 3.59 (s, 12H,  $-\text{OCH}_3$ ). Anal. Calcd for  $\text{C}_{90}\text{H}_{90}\text{Mo}_5\text{N}_{12}\text{O}_{16}$ : C, 52.08; H, 4.37; N, 8.10. Found: C, 51.93; H, 4.35; N, 8.12.

**3:**  $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-WO}_4)$ , 54% yield.  $^1\text{H}$  NMR  $\delta$  (ppm in  $\text{CD}_2\text{Cl}_2$ ): 8.67 (s, 4H,  $-\text{NCHN}-$ ), 8.11 (s, 2H,  $-\text{NCHN}-$ ), 6.63 (d, 16H, aromatic), 6.45 (d, 16H, aromatic), 6.36 (d, 8H, aromatic), 6.15 (d, 8H, aromatic), 3.64 (s, 24H,  $-\text{OCH}_3$ ), 3.60 (s, 12H,  $-\text{OCH}_3$ ). Anal. Calcd for  $\text{C}_{90}\text{H}_{90}\text{Mo}_4\text{N}_{12}\text{O}_{16}\text{W}$ : C, 49.97; H, 4.19; N, 7.77. Found: C, 49.56; H, 4.17; N, 7.69.

## Results and Discussion

Compounds **1–3** are certainly the first examples of their class, that is, compounds with  $\text{EO}_4^{2-}$  ions bridging two dimetal moieties. As far as we know, these are the first compounds of any kind having this sort of  $\mu_2\text{-}\eta^2, \eta^2$  bridging by any  $\text{EO}_4^{2-}$  ion. The yields are relatively good, and the technique for making them is perfectly straightforward, as shown in eq 2. As shown



**Figure 2.** Cyclic voltammograms and differential pulse voltammograms of the three  $[\text{Mo}_2(\text{DAniF})_3]_2(\mu\text{-EO}_4)$  (E = S, Mo, W) compounds vs the Ag/AgCl reference electrode. All scans were run in  $\text{CH}_2\text{Cl}_2$  with  $\text{Bu}^n\text{NPF}_6$  as supporting electrolyte, a Pt disk working electrode, and a Pt wire auxiliary electrode.

in Figure 1, the structures of **1–3** are very similar to each other. The Mo–Mo distances of 2.09–2.12 Å are similar to those of many other quadruply bonded dimolybdenum complexes containing formamidinate ligands.<sup>15</sup> Other metrical parameters are summarized in Tables 2–4. The  $\text{Mo}_2$  units in each of the molecules are spanned by three bridging *N,N'*-di-*p*-anisylformamidinate ligands while the remaining cis equatorial positions are occupied by two oxygen atoms of the  $\text{EO}_4^{2-}$  ligand. These compounds may be viewed as examples of inorganic spiro molecules, the pivot atoms being S, Mo, and W. Neglecting the atoms beyond those shown in Figure 1, these molecules might have been expected to have idealized symmetry  $D_{2d}$ . It is very evident from Figure 1 that all three molecules deviate from this symmetry in the same way, namely, there is folding along the lines defined by each pair of two oxygen atoms coordinated to the same  $\text{Mo}_2$  unit. The dihedral angles listed in Table 4 describe these distortions quantitatively. They are greatest for the molybdate compound, slightly smaller for the tungstate compound, and only about two-thirds as great in the sulfate compound. The nature of the distortion, in each case, is such that one of the dihedral bends is 3–4 times greater than the other one. The reason for this difference is not obvious.



**Table 2.** Selected Interatomic Distances (Å) for Compounds **1–3** (E = S, Mo, W)

	( $\mu$ -SO <sub>4</sub> )	( $\mu$ -MoO <sub>4</sub> )	( $\mu$ -WO <sub>4</sub> )
<i>D</i> <sup>a</sup>	6.010	6.012	6.076
Mo(1)–Mo(2)	2.094(1)	2.119(1)	2.117(2)
Mo(3)–Mo(4)	2.089(1)	2.108(1)	2.110(2)
E–O(1)	1.492(6)	1.781(6)	1.782(9)
E–O(2)	1.487(6)	1.779(6)	1.775(9)
E–O(3)	1.494(6)	1.773(6)	1.783(9)
E–O(4)	1.475(6)	1.771(6)	1.767(9)
Mo(1)–O(1)	2.180(5)	2.130(6)	2.16(1)
Mo(1)–N(1)	2.148(6)	2.133(7)	2.13(1)
Mo(1)–N(3)	2.108(7)	2.114(7)	2.13(1)
Mo(1)–N(5)	2.143(3)	2.136(7)	2.15(1)
Mo(2)–O(2)	2.181(5)	2.125(6)	2.136(9)
Mo(2)–N(2)	2.128(6)	2.132(7)	2.13(1)
Mo(2)–N(4)	2.091(7)	2.083(7)	2.09(1)
Mo(2)–N(6)	2.153(6)	2.123(7)	2.15(1)
Mo(3)–O(3)	2.181(6)	2.168(6)	2.185(9)
Mo(3)–N(7)	2.121(7)	2.127(7)	2.13(1)
Mo(3)–N(9)	2.117(7)	2.112(7)	2.12(1)
Mo(3)–N(11)	2.110(7)	2.121(7)	2.15(1)
Mo(4)–O(4)	2.167(5)	2.134(6)	2.133(9)
Mo(4)–N(8)	2.159(7)	2.150(7)	2.13(1)
Mo(4)–N(10)	2.092(7)	2.110(7)	2.11(1)
Mo(4)–N(12)	2.136(7)	2.141(6)	2.14(1)

<sup>a</sup> Distance between centroids of Mo<sub>2</sub> units.**Table 3.** Selected Bond Angles (deg) for Compounds **1–3** (E = S, Mo, W)

	( $\mu$ -SO <sub>4</sub> )	( $\mu$ -MoO <sub>4</sub> )	( $\mu$ -WO <sub>4</sub> )
$\Phi$ <sup>a</sup>	89.0	90.4	90.3
O(1)–E–O(2)	109.5(3)	113.8(3)	113.6(4)
O(1)–E–O(3)	109.3(3)	109.4(3)	109.3(4)
O(1)–E–O(4)	108.5(3)	106.9(3)	107.0(4)
O(2)–E–O(3)	110.0(3)	106.9(3)	107.6(4)
O(2)–E–O(4)	110.0(3)	105.4(3)	106.6(4)
O(3)–E–O(4)	109.5(3)	114.6(3)	112.8(4)
N(1)–Mo(1)–O(1)	85.2(2)	89.1(3)	88.3(4)
N(1)–Mo(1)–N(3)	94.7(3)	91.0(3)	92.0(5)
N(1)–Mo(1)–N(5)	169.5(2)	172.1(3)	171.9(5)
N(3)–Mo(1)–O(1)	172.5(2)	166.6(3)	166.4(4)
N(3)–Mo(1)–N(5)	94.2(3)	94.7(3)	94.0(5)
N(5)–Mo(1)–O(1)	85.2(2)	84.0(3)	84.6(4)
N(2)–Mo(2)–O(2)	86.9(2)	90.8(3)	89.9(4)
N(2)–Mo(2)–N(4)	93.3(3)	92.5(3)	92.6(4)
N(2)–Mo(2)–N(6)	169.7(2)	172.6(3)	172.8(4)
N(4)–Mo(2)–O(2)	173.5(2)	164.9(3)	165.4(4)
N(4)–Mo(2)–N(6)	95.1(3)	93.3(3)	92.8(4)
N(6)–Mo(2)–O(2)	84.1(2)	82.5(3)	83.6(4)
N(7)–Mo(3)–O(3)	87.2(2)	86.3(2)	85.9(4)
N(7)–Mo(3)–N(9)	89.5(3)	95.7(3)	95.3(4)
N(7)–Mo(3)–N(11)	171.2(2)	170.1(3)	170.2(4)
N(9)–Mo(3)–O(3)	173.2(2)	167.7(3)	168.2(4)
N(9)–Mo(3)–N(11)	95.1(3)	91.6(3)	92.2(4)
N(11)–Mo(3)–O(3)	87.4(2)	85.1(2)	85.4(4)
N(8)–Mo(4)–O(4)	83.4(2)	85.8(2)	85.1(4)
N(8)–Mo(4)–N(10)	92.0(3)	94.9(3)	95.6(4)
N(8)–Mo(4)–N(12)	171.8(3)	169.4(3)	168.4(4)
N(10)–Mo(4)–O(4)	170.8(2)	163.4(2)	164.3(4)
N(10)–Mo(4)–N(12)	95.2(3)	94.9(3)	95.1(4)
N(12)–Mo(4)–O(4)	88.9(2)	83.6(2)	83.4(4)

<sup>a</sup> Twist angle between Mo<sub>2</sub> axes.

The fact that such distortions occur at all may be attributable to the fact that they lead to decreases in the angles at the oxygen atoms, which would be about 125° in a structure with undistorted *D*<sub>2d</sub> symmetry. It is also likely that packing forces play some role.

The electrochemistry of **1–3** is interesting, especially when compared to that of the previously described compounds of type I. In this group of 12 compounds, the one with the greatest

**Table 4.** Selected Dihedral Angles (deg) between Mean Planes for Compounds **1–3** (E = S, Mo, W)

planes	( $\mu$ -SO <sub>4</sub> )	( $\mu$ -MoO <sub>4</sub> )	( $\mu$ -WO <sub>4</sub> )
Mo(1)–Mo(2)–O(1)–O(2) and O(1)–E–O(2)	14.5(3)	22.6(2)	22.2(4)
Mo(1)–Mo(2)–O(1)–O(2) and O(1)–E–O(2)–C(46)–C(61)–C(76)	14.4(2)	20.7(2)	20.5(3)
Mo(3)–Mo(4)–O(3)–O(4) and O(3)–E–O(4)	3.5(1)	8.7(3)	7.5(4)
Mo(3)–Mo(4)–O(3)–O(4) and O(3)–E–O(4)–C(1)–C(16)–C(31)	4.3(1)	6.8(2)	6.1(3)

**Table 5.** Electrochemical Data<sup>a</sup> for Compounds **1–3**

compound	<i>E</i> <sub>1/2</sub> (+/0), mV <sup>b</sup>	<i>E</i> <sub>1/2</sub> (2+/+), mV <sup>b</sup>	$\Delta E_{1/2}$ , mV	<i>K</i> <sub>c</sub> <sup>c</sup>
<b>1</b> , $\mu$ -SO <sub>4</sub>	+93	+321	+228	$7.2 \times 10^3$
<b>2</b> , $\mu$ -MoO <sub>4</sub>	+81	+392	+311	$1.8 \times 10^5$
<b>3</b> , $\mu$ -WO <sub>4</sub>	+102	+387	+285	$6.6 \times 10^4$

<sup>a</sup> The data were recorded on a BAS 100 electrochemical analyzer in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> solution (CH<sub>2</sub>Cl<sub>2</sub>) 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 potentials are referenced to Ag/AgCl, and under the present experimental conditions, the *E*<sub>1/2</sub>(Fc<sup>+</sup>/Fc) was consistently measured at 440 mV. <sup>b</sup> *E*<sub>1/2</sub> = *E*<sub>p</sub> + *E*<sub>pu</sub>/2, *E*<sub>pu</sub> = 50 mV for **1**; *E*<sub>1/2</sub> = (*E*<sub>pa</sub> + *E*<sub>pc</sub>)/2 for **2** and **3**. <sup>c</sup> *K*<sub>c</sub>, calculated from the formula *K*<sub>c</sub> = e <sup>$\Delta E_{1/2}$ /25.69</sup>. See ref 19.

coupling, as noted above, was the one with the oxalate bridge. All three of the compounds with EO<sub>4</sub><sup>2-</sup> bridges are more strongly coupled, as shown by the data in Figure 2 and Table 5. This is not surprising no matter what the exact nature of the coupling mechanism may be. In fact, the large values of the comproportionation constants, eq 1, may well (though not necessarily) imply that the +1 cations formed from **1–3**, and perhaps also the oxalate, are fully delocalized. Charge delocalization between two electroactive units is generally associated with  $\Delta E_{1/2}$  values of ca. 350 mV,<sup>16</sup> which suggests that **2** and **3** ( $\Delta E_{1/2}$  = 392 and 387 mV, respectively) may be described as Class III compounds according to the Robin–Day classification widely used by Creutz-Taube<sup>17</sup> and others.<sup>18</sup> Class I compounds are completely charge localized while Class III compounds have extensive delocalization and may be regarded as sharing half a positive charge equally between the metal units. Class II compounds are those intermediate between the other two with detectable electronic communication that partially mixes the character of oxidized and reduced metal units through interactions mediated by the orbitals of the linker. Attempts so far to isolate and obtain structures of the +1 ions have been unsuccessful, but efforts are continuing, and we plan to carry out other experimental work and also theoretical work to determine whether delocalization does occur.

- (15) Lin, C.; Protasiewicz, J. D.; Smith, E. T.; Ren, T. *Inorg. Chem.* **1996**, *35*, 6422.  
 (16) (a) Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 539. (b) Atwood, C. G.; Geiger, W. E. *J. Am. Chem. Soc.* **2000**, *122*, 5477.  
 (17) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.  
 (18) Cannon, R. D. *Electron-Transfer Reactions*; Butterworth: London, 1980.  
 (19) See, for example: (a) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248. (b) Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Kido, H.; Zavarine, I. S.; Richmond, T.; Washington, J.; Kubiak, C. P. *J. Am. Chem. Soc.* **1999**, *121*, 4625.

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**Supporting Information Available:** Three ORTEP drawings at 50% probability levels with complete atomic labeling, 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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