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The First Designed Syntheses of Bis-dimetal Molecules in Which the Bridges Are Diamidate Ligands

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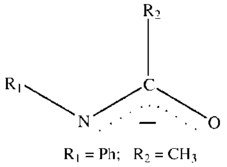
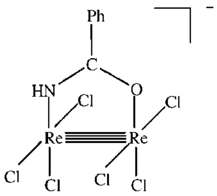
The first deliberate syntheses of molecules in which pairs of quadruply bonded Mo_2 units are bridged by *N*,*N*′-diarylterephthaloyldiamidate (aryl = Ph, *m*-CF_3Ph) ligands are described. The addition of neutral *N*,*N*′-diarylterephthaloyldiamide to 2 equiv of $[Mo_2(DAniF)_3(MeCN)_2]^+$ (DAniF = *N*,*N*′-di-*p*-anisylformamidinate) followed by the introduction of excess H_3CO^- in MeCN results in the formation of $(DAniF)_3Mo_2\{(C_6H_5)NC(O)C_6H_4(O)CN(C_6H_5)\}Mo_2(DAniF)_3$ (**1**) and $(DAniF)_3Mo_2\{[(m\text{-}CF_3)C_6H_5]NC(O)C_6H_4(O)CN[(m\text{-}CF_3)C_6H_5]\}Mo_2(DAniF)_3$ (**2**). The $\Delta E_{1/2}$ for the oxidation of each Mo_2 unit is greater for these terephthaloyldiamidate-bridged molecules (~100 mV) than for the analogous terephthalate-bridged compound (~60 mV). Variation in the nature of the substituents on the diamidate nitrogen atoms offers a means to fine-tune the oxidation potentials of the Mo_2 units.

The first examples of amidate ligands as μ_2,η^2 bridges across multiple metal–metal bonds were published in 1979,[1] in which **I** was used with Cr_2^{4+} and Mo_2^{4+} cores. These were made by designed syntheses. Numerous examples have followed, with many other amidates and many other dimetal units.[2] Importantly, catalytic[3] and medicinal[4] uses are now being proposed for some compounds of this type.



I



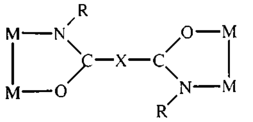
II

In addition to the designed syntheses there have been interesting examples of indirect (initially one might have called them *undesigned*) syntheses. The first of these was reaction 1, discovered in 1997,[5] but several others were soon reported.[6,7,8]

$$[Mo_2(CH_3CN)_{10}]^{4+} + 2H_2O \rightarrow cis\text{-}[Mo_2(\mu_2,\eta^2\text{-}CH_3CONH)_2(CH_3CN)_4]^{2+} \quad (1)$$

For example, Eglin and co-workers[6,7] prepared the anion **II** by the hydrolysis method. Eglin and co-workers also pointed out that the concept of accelerating the rate of hydrolysis of a nitrile to an amide by coordinating the nitrile to a metal ion was already known for single metal ions.[9]

In the past few years, we have published many examples of the use of dicarboxylic acids to bridge dimetal units (Mo_2, Rh_2, and Re_2), all of which have been made by carefully planned syntheses.[10] It was, therefore, natural for us to consider the use of diamidate ligands in an analogous way, and this type of work has been actively pursued here. In view of the recent report[11] of one such compound, **IIIa**,



III (a) R = H, M = Re
(b) R = Ph, M = Mo
(c) R = (*m*-CF_3)C_6H_4, M = Mo

entirely analogous to the recently reported $O_2CC_6F_4CO_2$-bridged compounds,[12] and made serendipitously by a method

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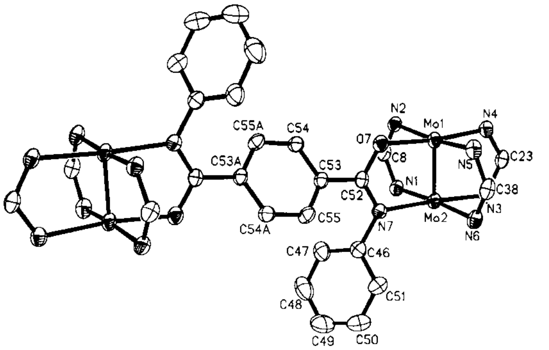

Figure 1. A view of the core atoms of complex **1** drawn with 40% probability ellipsoids. All *p*-anisyl groups have been omitted. Selected bond distances (Å): Mo1−Mo2, 2.0891(5); $Mo-N_{DAniF}$ (av), 2.15[2]; Mo1−O7, 2.106(3); Mo2−N7, 2.170(4).

entirely analogous to that used by Eglin to make anion **II**, we wish to report that diamidate compounds can be made by a very general method of designed synthesis. This point is important because it allows the deliberate introduction of virtually any R group in compounds of type **III**, where X is any suitable linker, e.g., p-C_6F_4 or p-C_6H_4, instead of having the limitation that R must be H.

The new compounds that we report here correspond to **III**b and **III**c and will henceforth be designated **1** and **2**. The syntheses of these compounds were made possible by the availability of the necessary Mo_2 starting material, $[Mo_2(DAniF)_3Cl_2]$, a type of compound first reported in 1997, where DAniF represents the anion of *N*,*N*′-di-*p*-anisylformamidine.[13] Both diamide ligands are conveniently prepared in good yield from the corresponding diacyl chloride and 2 equiv of the desired aniline. Synthesis of the diamidate-bridged molecules **1** and **2** proceeds by a two-step, one-pot preparative reaction[14] in reasonable yield according to eq 2.

$$2Mo_2(DAniF)_3Cl_2 + Zn \xrightarrow{CH_3CN} 2Mo_2(DAniF)_3(CH_3CN)_2{}^+ + ZnCl_4{}^{2-} \quad (2a)$$

$$2Mo_2(DAniF)_3(CH_3CN)_2{}^+ + \text{diamide} + 2CH_3O^- \rightarrow Mo_2(DAniF)_3(\text{diamidate})Mo_2(DAniF)_3 + 2CH_3OH \quad (2b)$$

These reactions work optimally only by adding excess CH_3O^- to a mixture of $[Mo_2(DAniF)_3(MeCN)_2]^+$ (**3**) and the corresponding diamide rather than by first preparing the diamidate dianion in a prior step and introducing a solution of **3**. The latter approach, analogous to our assembly reactions with carboxylate linkers, results in the formation of significant amounts of $Mo_2(DAniF)_4$ and other unidentified species. It is important to note that substitution of CH_3O^- by the more standard and frequently used lithium alkyls produces only minute amounts of the target compounds in pure form. The mixture of products includes inter alia $Mo_2(DAniF)_4$.[15]

The structures of **1** and **2** are shown in Figures 1 and 2, respectively. They were determined[16] by conventional crystallographic methods. The structures closely resemble those of previously reported $O_2C-X-CO_2$ bridged compounds. The central bridging groups show appreciable deviation from overall planarity relative to the Mo_2 axes (34.2° for **1**, 32.9° for **2**), as was the case with various dicarboxylate analogues with aryl connectors, X.[12,17]

As would be expected[18] because of the electron-withdrawing CF_3 substituents on the *N*-aryl groups of the terephthaloyldiamidate bridge, the reduction potentials for the couples $Mo_2{}^{6+/5+}$ and $Mo_2{}^{5+/4+}$ for **2** occur at values ca. 45 mV more positive than those of **1**. Compounds **1** and **2** both display $\Delta E_{1/2}$ between successive one-electron oxidations of 100 mV, as determined from the differential pulse voltammograms by the width at half-height method described by Richardson

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(13) Cotton, F. A.; Jordan, G. T., IV; Murillo, C. A.; Su, J. *Polyhedron* **1997**, *16*, 1831.

(14) Preparation of the ligands and complexes: ***N*,*N*′-Diphenylterephthaloyldiamide.** A solution of terephthaloyl chloride (8.10 g, 40.0 mmol) in 25 mL of THF was added dropwise to a stirred solution containing 9.31 g (100 mmol) of aniline in 100 mL of THF in the presence of 30.0 g of anhydrous K_2CO_3. A white solid formed immediately. After the addition, the mixture was stirred for an additional 30 min; the THF was then removed under reduced pressure. To the remaining solid, 200 mL of water was added with vigorous stirring. The white solid product was separated by filtration, washed with water until pH = 7, and dried in air first, then under vacuum, yielding 12.0 g of diamide as a white powder, 95%. ^1H NMR (δ in DMSO-d_6): 8.09 (s, 4H, $-C_6H_4-$), 7.80 (d, 4H, aromatic C−H), 7.36 (t, 4H, aromatic C−H), 7.16 (t, 2H, aromatic C−H). This compound was used in the synthesis of complex **1** without further purification. ***N*,*N*′-Di(*m*-trifluoromethyl)phenylterephthaloyldiamide.** This was prepared by a similar procedure. ^1H NMR (δ in DMSO-d_6): 8.28 (s, 2H, *m*-CF_3-phenyl group), 8.14 (s, 4H, $-C_6H_4-$), 8.08 (d, 2H, *m*-CF_3-phenyl group), 7.65 (t, 2H, *m*-CF_3-phenyl group), 7.48 (d, 2H, *m*-CF_3-phenyl group). **$1 \cdot 2CH_2Cl_2$.** $Mo_2(DAniF)_3Cl_2$, 0.400 g (0.389 mmol), was reduced by stirring with 5.0 g (76 mmol) of Zn dust in 40 mL of acetonitrile for 1.5 h. The resultant yellow mixture was filtered through a Celite-packed column and added to a solution having 0.0615 g (0.194 mmol) of *N*,*N*′-diphenylterephthaloyldiamide in 15 mL of THF. With stirring, 2 mL of a $NaOCH_3$ solution (0.5 M in CH_3OH) was added dropwise. A yellow solid formed after a few minutes. The mixture was stirred for 24 h at room temperature. The color of the yellow solid changed to orange-red. The solvents were removed in vacuo; the resulting solid residue was washed, extracted with 2 × 20 mL of CH_2Cl_2, and filtered through packed Celite to remove insoluble materials. The filtrate was evaporated to dryness, and the crude red product was extracted with 3 × 5 mL of CH_2Cl_2. The extracts were filtered and layered with 4 mL of Et_2O followed by 50 mL of hexanes; 0.176 g (37.8%) of red crystalline needles was obtained in two crops. ^1H NMR (δ in CD_2Cl_2): 8.57 (s, 4H, $-NCHN-$), 8.38 (s, 2H, $-NCHN-$), 7.29 (s, 4H, $-C_6H_4-$ bridging), 6.77 (q, 6H, aromatic C−H), 6.67 (d, 8H, aromatic C−H), 6.59 (d, 8H, aromatic C−H), 6.37−6.52 (m, 16H, aromatic C−H), 6.14−6.28 (m, 12H, aromatic C−H), 5.93 (d, 8H, aromatic C−H), 3.72 (s, 12H, $-OCH_3$), 3.68 (s, 12H, $-OCH_3$), 3.65 (s, 6H, $-OCH_3$), 3.63 (s, 6H, $-OCH_3$). Absorption spectrum (CH_2Cl_2) λ_{nm} (ϵ_M): 241 (102000), 279 (sh, 103000), 293 (106000), 462 (12500). Anal. Calcd for $C_{110}H_{104}Mo_4N_{14}O_{14}$: C, 59.25; H, 4.70; N, 8.79. Found: C, 58.85; H, 4.56; N, 8.76. **$2 \cdot 1.58CH_2Cl_2$.** This compound was synthesized as bright red needles in 41.8% yield by a procedure similar to that described for **1**. ^1H NMR (δ in CD_2Cl_2): 8.61 (s, 4H, $-NCHN-$), 8.39 (s, 2H, $-NCHN-$), 7.29 (s, 4H, $-C_6H_4-$ bridging), 7.05 (d, 2H, aromatic C−H), 6.84 (t, 2H, aromatic C−H), 6.67 (d, 8H, aromatic C−H), 6.61 (d, 8H, aromatic C−H), 6.38−6.51 (m, 20H, aromatic C−H), 6.28 (d, 4H, aromatic C−H), 6.16 (d, 4H, aromatic C−H), 5.91 (d, 8H, aromatic C−H), 3.72 (s, 12H, $-OCH_3$), 3.675 (s, 12H, $-OCH_3$), 3.665 (s, 6H, $-OCH_3$), 3.62 (s, 6H, $-OCH_3$). Absorption spectrum (CH_2Cl_2) λ_{nm} (ϵ_M): 251 (129100), 268 (129200), 297 (123000), 473 (16500). Anal. Calcd for $C_{112}H_{102}F_6Mo_4N_{14}O_{14} \cdot {}^1/_2CH_2Cl_2$: C, 56.11; H, 4.31; N, 8.14. Found: C, 56.36; H, 4.47; N, 8.26.

(15) The reason for the dramatic difference between using $NaOCH_3$ and an alkyl lithium is the formation of an insoluble yellow intermediate, which is $[Mo_2(DAniF)_3]_2Zn(OMe)_4$. This has been characterized crystallographically (Cotton, F. A.; Liu, C. Y.; Murillo, C. A. Unpublished results). We believe that replacement of the bound CH_3CN ligands by $Zn(OMe)_4{}^{2-}$ units is crucial for reactions using very basic ligands such as the amidates reported here, since it is known that strong nucleophiles can attack metal-bound CH_3CN groups. Indeed this is how amidates of type **II** and others have been made.[5−9]

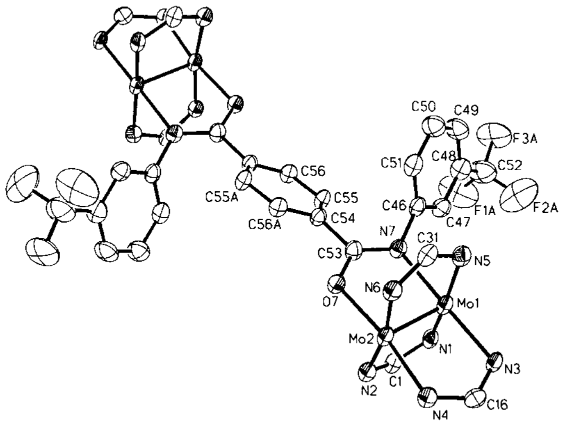

Figure 2. The core structure of **2** showing thermal ellipsoids at the 30% probability level. All of the *p*-anisyl groups on the ligands have been omitted for clarity. Selected bond distances (Å): Mo1−Mo2, 2.0885(8); Mo−N_{DAniF} (av), 2.15[1]; Mo1−N7, 2.199(5); Mo2−O7, 2.105(4).

and Taube.[19] These $\Delta E_{1/2}$ values are appreciably greater than that for the analogous terephthalate-bridged compound (60 mV) and suggest that the greater basicity and hence tighter binding of the diamide bridge may permit measurably better electrochemical communication between Mo_2^{4+} units.

We recognize that other properties of **1** and **2** (as well as di- and triamidate compounds) besides their preparations, structures, and electrochemistry are of interest, and there will be full reports on such studies forthcoming.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1**·$2CH_2Cl_2$ and **2**·$1.58CH_2Cl_2$. This material is available free of charge at http://pubs.acs.org.

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(16) X-ray crystallography: Single-crystal X-ray data for **1**·$2CH_2Cl_2$ and **2**·$1.58CH_2Cl_2$ were collected on a Bruker-SMART 1000 CCD area detector system. Data were collected at 213(2) K. Structure determination and refinement were carried out using the SHELXS-97 and SHELXL-97 programs. Crystal data for **1**·$2CH_2Cl_2$: $C_{112}H_{108}Cl_4Mo_4N_{14}O_{14}$, $M = 2399.68$, triclinic space group $P\bar{1}$, $a = 10.0257(7)$ Å, $b = 14.798(1)$ Å, $c = 20.293(1)$ Å, $\alpha = 71.031(1)°$, $\beta = 84.761(1)°$, $\gamma = 78.980(1)°$, $Z = 1$, $V = 2793.4(3)$ Å^3. The structure was refined on F^2 and converged for 9684 unique reflections and 740 parameters to give R1 = 0.072 and wR2 = 0.143 and a goodness-of-fit = 1.047. Crystal data for **2**·$1.58CH_2Cl_2$: $C_{113.58}H_{105.16}Cl_{3.16}F_6Mo_4N_{14}O_{14}$, $M = 2500.02$, triclinic, space group $P\bar{1}$, $a = 10.954(1)$ Å, $b = 16.445(1)$ Å, $c = 16.497(1)$ Å, $\alpha = 109.566(2)°$, $\beta = 90.092(2)°$, $\gamma = 92.186(2)°$, $Z = 1$, $V = 2798.0(4)$ Å^3. The structure was refined on F^2 and converged for 9685 unique reflections and 731 parameters to give R1 = 0.116 and wR2 = 0.154 and a goodness-of-fit = 1.006.

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