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Article

Molecular Pairs and A Propeller Containing Quadruply Bonded Dimolybdenum Units Linked by Polyamidate Ligands

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Two molecular pairs $[Mo_2(DAniF)_3]_2$[*N*,*N*′-diethylterephthalamidate] (**1**) and $[Mo_2(DAniF)_3]_2\{1,3\text{-}C_6H_4[C(O)NPh]_2\}$ (**2**) where DAniF = *N*,*N*′-di-*p*-anisylformamidinate) and the propeller ($[Mo_2(DAniF)_3]_3\{1,3,5\text{-}C_6H_3[C(O)NPh]_3\}$ (**3**)) have been prepared in good yield and high purity by directly combining $Mo_2(DAniF)_3(O_2CCH_3)$ with the corresponding polyamidates. Electrochemical measurements of these complexes show unresolved redox waves, which indicate that the dimetal centers are only electronically weakly coupled. Compound **1** was chemically oxidized by ferrocenium tetrafluoroborate to the two-electron oxidation product **4**, where one electron was removed from each of the $[Mo_2]$ units. The hyperfine coupling in the EPR spectrum ($A = 22 \times 10^{-4}$ cm^{-1}) suggests that **4** is an electron-trapped species with one electron residing on each of the two dimolybdenum units, as suggested also by electrochemical measurements.

Introduction

In recent years, a large number of discrete, as well as extended, metal−organic architectural arrays have been made using building blocks with metal species joined by appropriate organic polydentate ligands.[1−4] 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,[5] sensors,[6] and catalysis.[7]

Selective use of the organic linkers is of particular importance in structural control because it is important to engender compounds with desirable functionalities. Commonly used linkers in metal-containing supramolecular arrays are the polycarboxylate anions. These linkers have generated a variety of metal−organic superstructures that vary from discrete molecular polygons to infinite networks with transition metal ions such as Zn^{2+}, Cu^{2+}, and Cr^{3+}.[3,4] In our laboratory,[8] polycarboxylate linkers have been employed to assemble covalently bonded dimetal units such as $[M_2(DAniF)_n]^{4-n}$ (M = Mo and Ru and Rh, where DAniF = *N*,*N*′-di-*p*-anisylformamidinate) to produce M_2-containing architectures that include pairs (dimers of dimers), loops, squares, triangles, complex polygons, and extended three-dimensional materials. These groups have also been used

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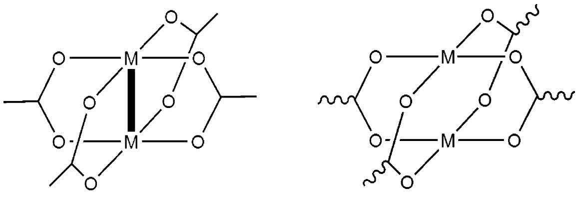
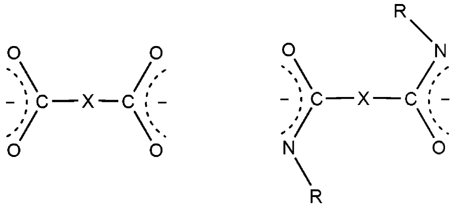
10.1021/ic0614723 CCC: $33.50

Scheme 1



I　　**II**

Scheme 2



III　　**IV**

elsewhere to bind other dimetal-containing units such as M_2^{n+} (M = W, Re).[9]

Unlike neutral organic ligands such as polyamine or polypyridyl compounds commonly used to build supramolecular compounds with single metal species and high ionic charges, the deprotonated polycarboxylate anions offset the positive charge, thereby producing neutral or low-charged complexes. In addition, the carboxylate group (O−C−O) offers various binding modes toward metal ions. It is capable of either bridging dimetal units with and without metal−metal bonds (**I** and **II**, respectively, in Scheme 1) or serving as a monodentate ligand to bind a mononuclear ion which enriches the chemistry and enhances structural diversity.

Compared to dicarboxylate anions (**III**), isoelectronic diamidate groups (**IV**) have drawn much less attention as linkers for supramolecular arrays. However, the amidate ligands possess attractive properties absent in the parent carboxylate species. Because amidate groups are much stronger Lewis bases than the corresponding carboxylate groups, it is anticipated that the resulting complexes would be thermodynamically more stable than the carboxylate prototypes. Furthermore, amidate ligands the R substituents on the N atoms, shown in **IV**, are synthetically adjustable in both steric and electronic properties and therefore can modify the molecular structure and tune the electronic properties of the complexes. Indeed, in prior work, when diaryloxamidate groups were used to link two dimolybdenum units, an interesting geometric isomer pair was isolated.[10] The two isomers differed in coordination modes and geometries and, more importantly, in their ability to facilitate electronic communication between the two dimolybdenum units. Recently, we also reported that spontaneous self-assembly of diamidate-linked molecular squares via C−H···F interactions may produce a one-dimensional network and a cage molecule, the synthesis of which can be controlled by introducing secondary functional groups, e.g., trifluoromethylphenyl, on the N atom of the amidate groups.[11]

It should be noted that the large difference in acid−base properties between dicarboxylate and diamidate groups affects the reactivity toward metal ions. While carboxylate anions can be readily prepared and are easily handled, deprotonation of the amide ligands requires the use of strong bases and produces very basic and reactive anions that may complicate further reaction with certain starting materials. For example, the dimolybdenum complex $[Mo_2(DAniF)_3(NCCH_3)_2]^+$, an excellent starting material for the preparation of dicarboxylate-linked Mo_2 pairs,[12] cannot be used for the syntheses of diamidate analogues because there is nucleophilic attack by the diamidate anion on one of the coordinated acetonitrile molecules.[13] This difficulty can be overcome by use of the mixed-ligand compound $Mo_2(DAniF)_3(O_2CH_3)$ as starting material.[10]

Here we report several new polyamidate-linked dimolybdenum compounds, prepared in good yield and high purity by direct assembly of $Mo_2(DAniF)_3(O_2CCH_3)$ with polyamides in the presence of strong base (H^-). There are two molecular pairs with phthaloyldiamidate linkers, $[Mo_2(DAniF)_3]_2\{1,4\text{-}C_6H_4[C(O)NEt]_2\}$ (**1**) and $[Mo_2(DAniF)_3]_2\{1,3\text{-}C_6H_4[C(O)NPh]_2\}$ (**2**), and a molecular propeller having three dimolybdenum units linked by a triamidate ligand, $[Mo_2(DAniF)_3]_3\{1,3,5\text{-}C_6H_3[C(O)NPh]_3\}$ (**3**). To examine the electronic coupling interactions in the pairs, a compound with two Mo_2^{5+} units, $\{[Mo_2(DAniF)_3]_2[1,4\text{-}C_6H_4[C(O)NEt]_2]\}(BF_4)_2$ (**4**), has been prepared by oxidation of **1**. There is only weak electronic communication, as revealed by electrochemical measurements of the precursor (**1**), and magnetic studies of **4** that show that there is an unpaired electron localized on each of the $[Mo_2]$ units.

Results and Discussion

Syntheses. Compounds **1** and **2** were synthesized by mixing the dimolybdenum starting material $Mo_2(DAniF)_3(O_2CCH_3)$[10] with the corresponding diamides in the presence of the strong base $NaEt_3BH$.[14] As mentioned earlier, use of the mixed-ligand compound $Mo_2(DAniF)_3(O_2CCH_3)$, instead of $[Mo_2(DAniF)_3(NCCH_3)_2]^+$ to introduce the dimetal building blocks, precludes nucleophilic attacks of basic ligands onto coordinated acetonitrile molecules.[15] This procedure requires only short reaction times and produces significantly higher yields than those reported for the first dimolybdenum pairs linked by diamidate groups which were prepared by reaction of $Mo_2(DAniF)_3Cl_2$ with Zn in the presence of the linker.[13]

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Table 1. X-ray Crystallographic Data

	1·2.2CH_2Cl_2	**3**·4CH_2Cl_2	**4**·4CH_2Cl_2
empirical formula	$C_{104.2}H_{108.4}Cl_{4.4}Mo_4N_{14}O_14$	$C_{166}H_{161}Cl_8Mo_6N_{21}O_{19}$	$C_{106}H_{112}B_2Cl_8F_8Mo_4N_{14}O_{14}$
fw	2320.59	3613.40	2647.08
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	9.7891(9)	18.707(2)	13.694(2)
b, Å	14.024(1)	21.027(2)	14.231(2)
c, Å	20.359(1)	22.939(2)	17.720(3)
α, deg	96.806(2)	109.850(2)	106.745(2)
β, deg	99.006(2)	91.064(2)	93.660(3)
γ, deg	106.116(2)	98.470(2)	117.810(2)
V, Å^3	2613.1(4)	8372(2)	2843.7(7)
Z	1	2	1
T, K	213	213	213
λ, Å	0.71073	0.71073	0.71073
d_{calcd}, g/cm^3	1.475	1.433	1.546
μ, mm^{-1}	0.650	0.632	0.699
R1^a (wR2^b)	0.0797(0.1566)	0.1090(0.2319)	0.0659(0.1347)

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**, **3**, and **4**

	1·2.2CH_2Cl_2	**3**·4CH_2Cl_2	**4**·4CH_2Cl_2
Mo(1)−Mo(2)	2.090(1)	2.091(2)	2.1237(6)
Mo(3)−Mo(4)		2.092(1)	
Mo(5)−Mo(6)		2.091(1)	
Mo(1)−O(1)	2.112(4)		2.082(3)
Mo(2)−O(1)		2.120(7)	
Mo(1)−N(2)	2.147(5)	2.162(9)	2.129(4)
Mo(1)−N(4)	2.162(5)	2.163(10)	2.093(4)
Mo(1)−N(6)	2.153(5)	2.176(10)	2.123(4)
Mo(1)−N(1)		2.187(9)	
Mo(2)−N(1)	2.177(5)		2.169(4)
Mo(2)−N(3)	2.172(5)	2.166(10)	2.104(4)
Mo(2)−N(5)	2.142(5)	2.136(10)	2.147(3)
Mo(2)−N(7)	2.190(5)	2.143(10)	2.135(4)

The molecular propeller **3** was synthesized similarly to **1** and **2**, but a longer reaction time and an excess of base were required to ensure the addition of an [Mo_2] unit to each of the three amidate groups of the linker. It should be noted that a carboxylate analogue using the anion of trimesic acid, $[Mo_2(DAniF)_3]_3[(1,3,5\text{-}C_6H_3)(CO_2)_3$, was previously synthesized by using a different and tedious method.[16] The synthesis of **3** also required a modification of the procedure developed earlier for the syntheses of pairs linked by oxamidates in which sodium methoxide reacts first with $Mo_2(DAniF)_3(O_2CCH_3)$ and then with the linker, a procedure that can also be used for the syntheses of **1** and **2**. However, when $NaOCH_3$ was used in an attempt to prepare **3**, an incomplete reaction was observed.[17] The preparative methodology for the three neutral compounds can be generally described by the general reaction:

$$n\mathrm{Mo_2(DAniF)_3(O_2CCH_3)} + \mathrm{H}_n[\mathrm{RN(O)C}]_n\mathrm{C_6H}_{6-n} + n\mathrm{H}^- \rightarrow [\mathrm{Mo_2(DAniF)_3}]_n[\mathrm{RN(O)C}]_n\mathrm{C_6H}_{6-n} + n\mathrm{H_2}\ (\mathrm{R} = \mathrm{Ph\ or\ Et})$$

It should also be noted that a synthesis employing sodium methoxide reported earlier[14] and the one reported here using $NaEt_3BH$ appear to be mechanistically different. When sodium methoxide is used, the reagent reacts with the dimolybdenum starting material upon mixing to form $Mo_2(DAniF)_3(OCH_3)(CH_3OH)$.[18] This highly reactive species then reacts with the diamide to form the target molecule. On the other hand, the $NaEt_3BH$ base appears to be strong enough to directly attack and deprotonate the diamide.

The ionic compound **4** was obtained by reaction at low temperature of the neutral compound **1** using 2 equiv of ferrocenium tetrafluoroborate as the oxidizing agent. Attempts to isolate the singly oxidized product by using only 1 equiv of the ferrocenium salt were unsuccessful. Failure to generate the monocation of **1** may be ascribed to the low thermodynamic stability of the mixed-valence complex, as indicated by the small comproportionation constant K_C (27) derived from $\Delta E_{1/2}$ (85 mV), as shown below.[19,20]

Solid State and Solution Structures. Crystallographic data for **1**·2.2CH_2Cl_2, **3**·4CH_2Cl_2, and **4**·4CH_2Cl_2 are given in Table 1, and selected bond distances are given in Table 2. Compound **1** crystallized in space group $P\bar{1}$ with $Z = 1$, which requires the molecule to reside on an inversion center. As shown in Figure 1, the core consists of two essentially parallel dimolybdenum units linked by the terephthaloyldiamidate ligand. This structure is closely related to those in compounds with a diarylterephthaloyldiamidate linker.[13] The Mo−Mo bond distance, 2.090(1) Å (Table 1), is characteristic for a quadruply bonded dimolybdenum unit supported by four three-atom bridging groups.[21] The separation between the midpoints of the metal−metal bonds is 11.4 Å. The bridging *p*-phenylene group shows appreciable deviation (48.3°) from the plane defined by the two Mo_2 units.

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(17) From a reactions using $NaOCH_3$ as the base, crystals of a compound with only two dimolybdenum units were isolated. Crystallographic data for $[Mo_2(DAniF)_3]_2\{PhNH(O)CC_6H_4[C(O)NPh]_2\}\cdot 2CH_2Cl_2$: space group $P\bar{1}$, $a = 10.561(2)$ Å, $b = 18.427(3)$ Å, $c = 33.767(6)$ Å, $\alpha = 81.092(3)°$, $\beta = 89.433(3)°$, $\gamma = 75.063(3)°$, $V = 6270(2)$ Å^3, $Z = 2$. The Mo−Mo distances are 2.093(3) and 2.092(3) Å. The core structure is given in Figure S1.

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(20) It should be noted that we have reported many single oxidations for complexes with two linked Mo_2^{4+} units to yield the corresponding mixed-valence compounds. See for example, (a) Cotton, F. A.; Dalal, N. S.; Liu, C. Y.; Murillo, C. A.; North, J. M.; Wang, X. *J. Am. Chem. Soc.* **2003**, *125*, 12945. (b) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Wang, X. *Chem. Commun.* **2003**, 2190. (c) Cotton, F. A.; Li, Z.; Liu, C. Y.; Murillo, C. A. *Inorg. Chem.* **2006**, *45*, 767.

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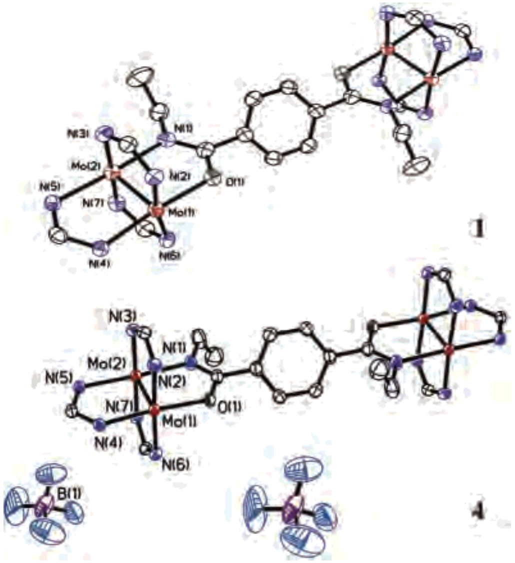

Figure 1. Core structures of **1** and **4** with displacement ellipsoids drawn at the 40% probability level. All *p*-anisyl groups and hydrogen atoms have been omitted for clarity.

Complex **2**, where the linker is 1,3-diphenylterephthaloyldiamidate is an isomer of a compound reported earlier having the 1,4-diphenylterephthaloyldiamidate linker.[13] Unfortunately, crystals of this complex do not diffract adequately for a full crystallographic characterization,[22] although the identity of the compound is unambiguous.

The ^{1}H NMR spectra of both **1** and **2** show that the compounds are diamagnetic, as expected for species containing quadruply bonded Mo_2^{4+} units. The spectra are also consistent with the molecules maintaining in solution the structures from their crystals. For example, the two signals for the methine protons appear as singlets in a ratio of 4:2, while there are four singlets for the methoxy groups of the anisyl groups that appear in a ratio of 12:12:6:6. Transitions in the electronic spectra at 442 and 436 nm for **1** and **2**, respectively, correspond to those found for the $\delta \rightarrow \delta^*$ transition in similar species with Mo−Mo quadruple bonds.[21b] For **3**, the ^{1}H NMR spectrum is again consistent with the presence of a symmetrical species with two singlets in a ratio of 2:1 (6:3) for the methine protons. The ratio of 1:18 (3:54) for the central C_6H_3 unit (7.49 ppm) in the linker to the total methoxy groups of the anisyl groups in the DAniF ligand is consistent with the presence of three Mo_2^{4+} units for each linker. These ratios are consistent with the X-ray structure that shows three $Mo_2(DAniF)_3$ units attached to a triamidate ligand giving the molecule a propeller shape, as shown in Figure 2. Because this compound crystallized in the space group $P\bar{1}$ with $Z = 2$, the two enantiomers are related by an inversion center. The three crystallographically independent Mo−Mo bonds are essentially equivalent and typical of quadruply bonded species (2.091(2), 2.092(1), and 2.091(1) Å) in a similar coordination environment.[21] The midpoints of the three Mo−Mo bonds define an essentially equilateral triangle with edges of 9.79 Å. The Mo−Mo axes are not in the same plane as the central aryl group of the linker nor are they perpendicular to it but all three [Mo_2] units are tilted in the same direction. So also are the three phenyl groups on the nitrogen atoms of the linker, which reside on the same side of the plane of the central aryl group, and the molecule possesses idealized C_3 symmetry. The overall structure of **3** resembles that of the carboxylate analogue $[Mo_2(DAniF)_3]_3\{1,3,5\text{-}C_6H_3(CO_2)_3\}$, with the important difference that the additional three phenyl groups in **3** create a cavity or pocket, as shown in Figure 2b.

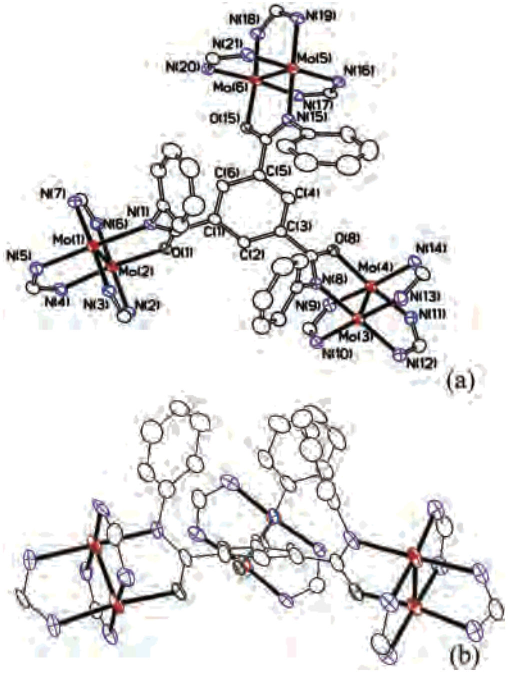

Figure 2. (a) Core of **3** with displacement ellipsoids drawn at the 40% probability level. (b) A side view of the core of the molecular propeller **3**. All *p*-anisyl groups and hydrogen atoms have been omitted for clarity.

Oxidation of **1** produces **4**. As shown in Figure 1, the overall cores of **1** and **4** are similar, with only one notable change in the structural parameters upon oxidation. The Mo−Mo distances are lengthened from 2.090(1) Å in **1** to 2.1237(6) Å in **4**, a change of 0.0337 Å that is caused by removing one electron from the δ orbital of a quadruply bonded Mo_2^{4+} unit, thus lowering the bond order from 4.0 to 3.5.[21a,23] The distance between linked [Mo_2] units, 11.3 Å, does not change relative to that in the neutral precursor, implying that the electrostatic interaction between the two positively charged Mo_2^{5+} units is weak. In the dication **4**, the torsion angle between the central benzene group and the plane containing the two Mo−Mo (55°) is about 7° larger than that in **1**.

Electrochemistry. The cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) for **1**−**3** are shown in Figure 3. The small $\Delta E_{1/2}$ values for the pairs (85 mV for **1** and 105 mV for **2**) indicate that the electronic coupling between the two dimetal centers is weak.

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(22) Multiple attempts to crystallize the compound from a variety of solvents yielded single crystals that had high mosaicity and diffracted only to low 2 Å angles. Dichloromethane/hexanes mixtures gave monoclinic crystals of $\mathbf{2}\cdot CH_2Cl_2$ (space group $C2/c$, $a = 19.117(5)$ Å, $b = 18.809(4)$ Å, $c = 34.996(8)$ Å, $\beta = 103.338(4)°$, $V = 12244(5)$ Å^3, $Z = 4$). A displacement ellipsoid plot is provided as Supporting Information in Figure S2.

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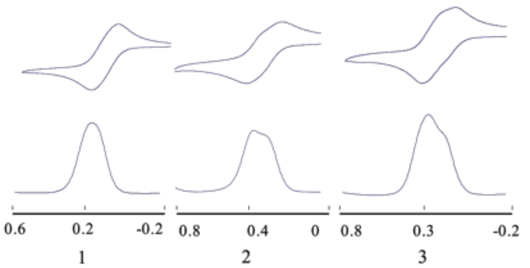

Figure 3. Cyclic voltammograms (with potentials in volts vs Ag/AgCl) and differential pulse voltammograms (DPV) for **1**, **2**, and **3** in CH_2Cl_2 solution.

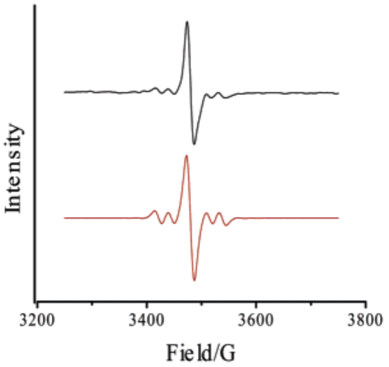

Figure 4. X-band EPR spectrum of **4** in CH_2Cl_2 solution at room temperature (top). The simulated spectrum is shown in red at the bottom.

In general, the main contributions to electronic coupling between two linked metal centers are electrostatic interactions and electron delocalization.[24] While the former depends heavily on the length of the linker, the later depends greatly on orbital interactions of the metal units and the linker. Because the two [Mo_2] units are separated by about 11 Å in **1**, weak electronic interactions might be expected. Additionally, since the central aryl group from the linker is not coplanar with the Mo−Mo vectors, and there is a torsion angle of 48°, the possibility of $\delta-\pi$ conjugation is significantly diminished. Therefore, one [Mo_2] unit hardly "senses" the presence of the other unit. This contrasts with the strong electronic communication in the β form of the *N*,*N*′-dimethyloxamidate-linked compound, where the [Mo_2]···[Mo_2] separation is only 6.25 Å and there is good $\delta-\pi$ conjugation that leads to the formation of a heteronaphthalene.[14] For **2**, the $\Delta E_{1/2}$ of 105 mV is slightly larger than that of **1** because of the shorter [Mo_2]···[Mo_2] separation (about 10 Å) relative to that in **1**. For the molecular propeller **3**, the redox waves for the three one-electron oxidations strongly overlap, indicating that the three dimolybdenum centers are weakly coupled, and in this respect, it resembles the tricarboxylate analogue.[16]

Magnetism of 4. Compound **4** is paramagnetic, and its X-band EPR spectrum was measured at room temperature in CH_2Cl_2 solution. The spectrum, top image in Figure 4, shows a prominent symmetric peak at g = 1.94 that corresponds to the metal-based unit (^{96}Mo (I = 0)). The smaller peaks on both sides of the strong signal are the hyperfine structure from the ^{95,97}Mo (I = 5/2) isotopes.[25,26] A simulation of the spectrum with one odd electron residing on each of the two Mo_2 units and using the parameters g = 1.94 and $A = 22 \times 10^{-4}$ cm^{-1} shows satisfactory agreement with the experimental data. These magnetic parameters are very similar to those in the parent paddlewheel cation $[Mo_2(DAniF)_4]^+$.[27] Previous work has also shown that hyperfine coupling constant for [Mo_2]-linked compounds provide reliable information on the nature of the electronic interactions. For example, small hyperfine coupling constants are characteristic of highly delocalized systems, e.g., 11.5×10^{-4} cm^{-1} for $\{[Mo_2(DAniF)_3](\mu\text{-}H)_2[Mo_2(DAniF)_3]\}^{+}$[27] and 12.2×10^{-4} cm^{-1} for the oxidized species of $\{[Mo_2(DAniF)_3](C_6H_2O_4)[Mo_2(DAniF)_3]\}$,[28] while larger hyperfine coupling constants are typical in localized systems, e.g., $A_{\|}$ of 37.7 G and $A_{\perp}$ of 15.6 G were observed for the compounds $\{[Mo_2(DAniF)_3]_2[M(OCH_3)_4]\}^+$ (M = Zn and Co).[20a] Similar results were also observed by Chisholm and co-workers in their work on dimolybdenum pairs linked by oxalate (A = 14.8 G) and perfluoroterephthalate (A = 27.2 G).[29]

The variable-temperature magnetic measurements of **4** (Figure S3) show a χT (emu K mol^{-1}) of 0.75 at 300 K, a value corresponding to two noninteracting unpaired electrons (g = 2.0 and S = 1/2).[30] The χT value decreases very slowly with the lowering of temperature but much more rapidly below 20 K. This sharper decrease, which extrapolates to $\chi T = 0$ at 0 K, is indicative of either weak antiferromagnetic interactions or weak intermolecular interactions. Therefore, the doubly oxidized **4** is an electron-trapped species with one unpaired electron residing on each of the two Mo_2^{5+} units, as suggested also by electrochemical measurements.

Conclusions. A good, general, and convenient synthetic method for the preparation of polyamidate-linked dimolybdenum compounds is described. It is shown that the separation between [Mo_2] units has a significant effect in the electronic communication. When compounds **1**−**3**, which are linked with polyamidate groups separated by an aryl group, are compared to analogues with short linkers such as *N*,*N*′-dimethyloxamidate in the β form,[10] a significant decrease in the electronic communication is observed.

Experimental Section

Materials and Methods. All manipulations were performed under a nitrogen atmosphere, using either a drybox or standard Schlenk line techniques. Solvents were purified under argon using a Glass Contour solvent purification system or distilled over appropriate drying agents under nitrogen. The starting material $Mo_2(DAniF)_3(O_2CCH_3)$ was synthesized following a reported procedure,[10] and commercially available chemicals were used as

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(30) According to Curie's law, $\chi_m = Ng^2\beta^2/3\kappa T\cdot S(S+1)$, $\chi_m T = Ng^2\beta^2/3\kappa\cdot S(S+1) = 1/8\cdot g^2 S(S+1)$.

received. The polyamide linkers were conveniently prepared by reaction of the polycarboxylic chlorides with the corresponding amines by analogy to a procedure reported for other polyamides.[13]

Physical Measurements. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ. Electronic spectra were measured at room temperature on a Shimadzu UV-2501PC spectrometer in CH_2Cl_2 solution. ^1H NMR spectra were recorded on a Inova-300 or Mercury NMR spectrometer with chemical shifts (δ, ppm) referenced to $CDCl_3$. Cyclic voltammogram and differential pulse voltammogram were collected on a BAS 100 electrochemical analyzer with Pt working and auxiliary electrodes, Ag/AgCl reference electrode, scan rate (for CVs) of 100 mV/s, and 0.10 M Bu_4NPF_6 (in CH_2Cl_2) as electrolyte. EPR spectra were recorded on a Bruker ESP300 spectrometer, and magnetic susceptibility measurements were performed on a Quantum Design SQUID MPMS-XL magnetometer.

Preparation of $[Mo_2(DAniF)_3]_2\{1,4\text{-}C_6H_4[C(O)NEt]_2\}$, 1. To a solution of $Mo_2(DAniF)_3(O_2CCH_3)$ (610 mg, 0.600 mmol) and *N,N′*-diethylterephthamide (66 mg, 0.30 mmol) in 30 mL of THF was added with stirring 0.60 mL of a 1.0 M solution of $NaBEt_3H$ in THF. The color of the mixture changed from yellow to brown. The reaction mixture was stirred at room temperature for 6 h, and then the solvent was removed under vacuum. The remaining solid was extracted with 3 × 5 mL of dichloromethane and filtered through a filter frit packed with Celite. The volume of the filtrate was reduced to about 2 mL under vacuum, and then 50 mL of ethanol was added, producing a yellow solid and a brown supernatant solution. After the solution was decanted, the solid was washed with ethanol (2 × 15 mL) followed by hexanes (2 × 15 mL) and then dried under vacuum. The crude product was dissolved in 15 mL of dichloromethane and layered with hexanes. An orange-yellow crystalline solid formed within 2 days. The solid was collected by filtration and briefly placed under vacuum. Yield: 0.525 g (82%). ^1H NMR (δ, ppm in $CDCl_3$): 8.46 (s, 4H, $-NCHN-$), 8.42 (s, 2H, $-NCHN-$), 7.57 (s, 4H, aromatic C$-H$ in linker), 6.62 (d, 4H, aromatic *H*), 6.57 (m, 24H, aromatic *H*), 6.38 (m, 16H, aromatic *H*), 6.14 (d, 4H, aromatic *H*), 3.71 (s, 6H, $-OCH_3$), 3.70 (s, 12H, $-OCH_3$), 3.67 (s, 12H, $-OCH_3$), 3.61 (s, 6H, $-OCH_3$), 3.42 (q, 4H, CH_2), 0.25 (t, 6H, CH_3). UV$-$vis, λ_{max} (nm) (ϵ, M^{-1} cm^{-1}): 442 (3.2×10^3). Anal. Calcd for $C_{105.5}H_{111}Cl_6N_{14}O_{14}Mo_4$ ($1{\cdot}3.5CH_2Cl_2$): C, 52.01; H, 4.56; N, 8.05. Found: C, 51.79; H, 4.86; N, 8.18.

Preparation of $[Mo_2(DAniF)_3]_2\{1,3\text{-}C_6H_4[C(O)NPh]_2\}$, 2. This yellow compound was made similarly to **1**. Yield: 340 mg (76%). ^1H NMR (δ, ppm in $CDCl_3$): 8.56(s, 4H, $-NCHN-$), 8.38(s, 2H, $-NCHN-$), 7.67 (s, 1H, aromatic C$-H$ in linker), 7.01 (t, 1H, aromatic C$-H$ in linker), 6.71 (d, 2H, aromatic *H*), 6.68 (m, 8H, aromatic *H*), 6.64 (d, 12H, aromatic *H*), 6.60 (d, 2H, aromatic *H*), 6.49 (d, 8H, aromatic *H*), 6.42 (m, 8H, aromatic *H*), 6.32 (m, 4H, aromatic *H*), 6.20 (d, 4H, aromatic *H*), 6.12 (d, 4H, aromatic *H*), 5.96 (d, 8H, aromatic *H*), 3.72 (s, 12H, $-OCH_3$), 3.69 (s, 12H, $-OCH_3$), 3.68 (s, 6H, $-OCH_3$), 3.67 (s, 6H, $-OCH_3$). UV$-$vis, λ_{max} nm (ϵ, M^{-1} mol^{-1}): 436 (3.0×10^3). Anal. Calcd for $2{\cdot}2.5CH_2Cl_2$ ($C_{112.5}H_{109}Cl_5Mo_4N_{14}O_{14}$): C, 55.33; H, 4.50; N, 8.03. Found: C, 55.22; H, 4.69; N, 8.16.

Preparation of $[Mo_2(DAniF)_3]_3\{1,3,5\text{-}C_6H_3[C(O)NPh]_3\}$, 3. To a mixture of $Mo_2(DAniF)_3(O_2CCH_3)$ (610 mg, 0.600 mmol) and 1,3,5-benzenetricarboxanilide (87.2 mg, 0.200 mmol) was added 30 mL of THF, producing a yellow solution. With stirring, 1.8 mL of a 1.0 M solution of $NaEt_3BH$ in THF was then added to the yellow solution which quickly turned brown. Following a crystallization procedure similar to that for **1**, orange crystals were obtained. Yield: 0.458 g (69.3%). ^1H NMR (δ, ppm in $CDCl_3$): 8.57 (s, 6H, $-NCHN-$), 8.32 (s, 3H, $-NCHN-$), 7.49 (s, 3H, aromatic C$-H$), 6.69 (d, 12H, aromatic *H*), 6.56 (m, 24H, aromatic *H*), 6.43 (d, 12H, aromatic *H*), 6.36 (m, 12H, aromatic *H*), 6.26 (m, 6H, aromatic *H*), 6.16 (d, 6H, aromatic *H*), 6.01 (d, 6H, aromatic *H*), 5.87 (d, 12H, aromatic *H*), 3.71 (s, 18H, $-OCH_3$), 3.65 (s, 9H, $-OCH_3$), 3.64 (s, 9H, $-OCH_3$), 3.60 (s, 18H, $-OCH_3$). UV$-$vis, λ_{max} (nm) (ϵ, M^{-1} cm^{-1}): 447 (9.4×10^3). Anal. Calcd for $4{\cdot}3.5CH_2Cl_2$ ($C_{165.5}H_{160}N_{21}O_{21}Mo_6$): C, 55.16; H, 4.44; N, 8.17. Found: C, 54.85; H, 4.66; N, 8.18.

Preparation of $[Mo_2(DAniF)_3]_2\{1,4\text{-}C_6H_4[C(O)NEt]_2\}(BF_4)_2$, 4. Solutions of **1** (106 mg, 0.050 mmol) in 10 mL of CH_2Cl_2 and ferrocenium tetrafluoroborate (Cp_2FeBF_4, 30 mg, 0.11 mmol) in 10 mL of CH_2Cl_2 were prepared separately and cooled to −78 °C. The solution of Cp_2FeBF_4 was transferred to the solution of **1**, and the color changed immediately from yellow-orange to dark brown. The mixture was stirred at low temperature for 30 min, and then an isomeric mixture containing 40 mL of precooled hexanes was added to precipitate a brown solid. A yellow supernatant solution was decanted, and the remaining solid was washed with cooled hexanes (2 × 15 mL) and dried under vacuum. The dry solid was dissolved in 15 mL of dichloromethane in a Schlenk tube, and the solution was layered with hexanes. The Schlenk tube was kept in a freezer at −50 °C. Very dark (almost black) crystals formed within 2 weeks. Yield: 86 mg (75%). UV$-$vis, λ_{max} nm (ϵ, M^{-1} mol^{-1}): 458 (3.3×10^3). Anal. Calcd for $4{\cdot}CH_2Cl_2$ ($C_{103}H_{106}B_2Cl_2F_8Mo_4N_{14}O_{14}$): C, 51.33; H, 4.52; N, 8.14. Found: C, 51.22; H, 4.32; N, 7.99.

X-ray Structure Determinations. Single crystals suitable for X-ray diffraction analysis of all compounds were obtained by diffusion of hexanes into a CH_2Cl_2 solution of corresponding product. Each crystal was mounted and centered in the goniometer of a Bruker SMART 1000 CCD area detector diffractometer and cooled to −60 °C. Cell parameters were determined using the program SMART.[31] Data reduction and integration were performed with the software package SAINT,[32] and absorption corrections were applied using the program SADABS.[33] In all structures, the positions of the heavy atoms were found via direct methods using the program SHELXTL.[34] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were added in idealized positions. Non-hydrogen atoms were refined with anisotropic displacement parameters. Some of the anisyl group in the DAniF ligands and interstitial CH_2Cl_2 molecules were found disordered, and they were refined with soft constraints.

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Supporting Information Available: X-ray crystallographic data for $1{\cdot}2.2CH_2Cl_2$, $3{\cdot}4CH_2Cl_2$, and $4{\cdot}4CH_2Cl_2$ in CIF format, a drawing of the core structure of $[Mo_2(DAniF)_3]_2\{PhNH(O)CC_6H_4\text{-}[C(O)NPh]_2\}$ (Figure S1) and **2** (Figure S2) and variable-temperature magnetic susceptibility data (a plot of χT vs T in Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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