Neutral Dodecanuclear Supramolecular Complexes Containing Dimetal Units Linked by the Trimesate Anion

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Two compounds having six metal−metal bonded Mo_2^{4+} and Rh_2^{4+} units, the midpoints of which occupy the vertexes of an octahedron, are described here. Each of the M_2^{4+} units is also bridged by two mutually cis formamidinate groups of the type DAniF = *N,N*′-di-*p*-anisylformamidinate. These units are linked to each other by four tricarboxylate anions from trimesic acid, the centers of which form a tetrahedron that is encapsulated by the octahedron of dimetal units. Each of the neutral cages has a clathrated solvent molecule, CH_2Cl_2 when the metal M is Mo and CH_3CN when it is Rh. For the latter, there are CH_3CN molecules occupying $^2/_3$ of the axial sites on the Rh_2 units in a way that reduces the symmetry. These symmetrical structures appear to persist in solution as shown by the ^1H NMR spectra. The compounds $[M_2(cis\text{-DAniF})_2]_6[1,3,5\text{-}C_6H_3(CO_2)_3]_4$, **1** for M = Mo and **2** for M = Rh, were crystallized as **1**$\cdot 22.1CH_3CN\cdot 2.3CH_2Cl_2$ and **2**$\cdot 13.9CH_3CN$, respectively. In **1** there are four crystallographically independent quadruply bonded Mo−Mo distances in the narrow range 2.098−2.104 Å. For **2**, the six independent singly bonded Rh−Rh distances are in the range 2.428−2.438 Å.

Introduction

The field of supramolecular chemistry has been moving vigorously forward as the result of the creation of molecules having mononuclear units joined by polyfunctional linkers giving assemblies of varying geometries such as triangles, squares, and other polygons as well as complex polyhedra.[1−7] In most cases such compounds are ionic with the polynuclear cations having high charges (e.g., +8 and higher) which are almost always electrochemically inactive, and indeed unlikely to undergo any kind of redox chemistry without loss of structural integrity. However, a great many possible applications can be foreseen for such assemblies. For example, different sizes and shapes of the interstices could selectively trap specific molecules for separation, catalytic activation, or other purposes. If one could devise structurally similar materials which could also undergo changes in charge while retaining structural integrity, an entirely new dimension could be added. For example, the ability of such materials to bind anions could be modulated by switching them between neutral and positive states. Still another

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dimension could be added if paramagnetic materials could be made and their magnetic properties could be tuned by varying the interactions between the paramagnetic metal centers. It is obvious that neither of these two new dimensions are attainable if the assemblies are created by using only Pt^{2+}, Pd^{2+}, Cd^{2+}, or Zn^{2+}, which are at the heart of nearly all of the work published to date. That is why we have undertaken to develop a supramolecular chemistry that not only promises to rival the type created by others in the range and complexity of the structures obtainable but also allows for the fruitful study of electrochemistry, magnetism, and interesting spectroscopic properties.

In our laboratory, we have been synthesizing systematically a series of neutral complexes in which the corner units of the various polygons and polyhedra are metal−metal bonded units bridged by a variable number of formamidinate groups (typical is DAniF = *N,N′*-di-*p*-anisylformamidinate) and linked by dicarboxylate units,[8] and also EO_4^{2-}, E = S, Mo, W,[9] as well as carbonate anions.[10] In this way we have assembled essentially linear tetranuclear complexes of the type $[(DAniF)_3M_2](O_2C{-}\square{-}CO_2)[(DAniF)_3M_2]$,[8] as well as molecular loops of the type $[(DAniF)_2M_2]_2(O_2C{-}\square{-}CO_2)_2$.[11] Molecular triangles and squares having the formula $[(DAniF)_2M_2(O_2C{-}\square{-}CO_2)]_n$, where M = Mo, Rh and $n = 3$ for the triangle and 4 for the squares, are also obtainable.[12] These compounds crystallize so as to form interesting channels and interstices that are frequently filled with solvent molecules. They are neutral and have rich electrochemistry. Electrochemical studies have allowed us to probe the electronic communication between M_2 units, as well as the spectroscopic consequences of electronic coupling between the M_2 units.[13]

For compounds having dirhodium units, we have also been able to make equatorial and axial connections, thus producing sheetlike structures, assemblies having infinite tubes, and also interlocking lattices and double helixes.[14]

The choice of bridging ligands has an important role in the isolation of products. For example, the use of formamidinate groups to bridge the M_2 units has also been extremely beneficial because other ligands which are commonly used to form paddlewheel complexes such as ordinary carboxylates do not provide isolable crystalline materials,[15] although a special type has been used to form a few crystalline dirhodium compounds.[16]

When all ligands bridging the dinuclear units are dicarboxylates, one can form very insoluble materials which retain the M_2^{4+} units as shown in our laboratory in 1973 when we reported the preparation of the dimolybdenum oxalate.[17] More recently a large family of compounds of this type have been made and studies of their ability to absorb gases have been performed using dimolybdenum, diruthenium, and dicopper compounds.[18] These microporous materials are presumed to have structures consisting of grids of dimetal units linked by dicarboxylate anions, but no structural proofs have been provided yet.

Recently we also communicated the structure of a three-dimensional and neutral molecule synthesized by the designed self-assembly of six quadruply bonded Mo_2^{4+} units linked by four trimesate trianions (the anions of 1,3,5-tricarboxylatobenzene).[19] Here we report a full account of the structure and electrochemical behavior for this dodecanuclear molybdenum compound as well as its rhodium analogue.

Experimental Section

General Considerations. All the syntheses were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and then distilled under nitrogen following conventional methods. Chemicals were purchased from Aldrich and used as received. The tetrabutylammonium salt was prepared by neutralizing the tricarboxylic acid with 1.0 M $Bu^n{}_4NOH$ in MeOH solution, followed by vacuum drying at 40−50 °C for 24 h. The compounds $M_2(cis\text{-}DAniF)_2(CH_3CN)_4(BF_4)_2$ (where M = Mo,[20] Rh[21]) were prepared by following published procedures. Elemental analyses of samples that had been heated under vacuum were performed by Canadian Microanalytical Service, Delta, British Columbia, Canada. The cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer in 0.10 M $Bu^n{}_4NPF_6$ solution (CH_2Cl_2) with Pt working and auxiliary electrodes and a Ag/AgCl reference electrode, and scan rates of 100 mVs^{-1}. All the potential values are referred to the Ag/AgCl electrode, and under the present experimental conditions, the $E_{1/2}(Fc^+/Fc)$ was consistently measured at 440 mV. ^1H NMR spectra were recorded on a Varian XL-200E NMR spectrometer, with chemical shifts (δ) referenced to CD_2Cl_2.

Preparation of Complexes. $[Mo_2(cis\text{-}DAniF)_2]_6[1,3,5\text{-}C_6H_3(CO_2)_3]_4$ (1). To a stirred solution of $[Mo_2(cis\text{-}DAniF)_2(CH_3CN)_4](BF_4)_2$ (312 mg, 0.300 mmol) in 30 mL of CH_3CN was added $(Bu_4N)_3[1,3,5\text{-}C_6H_3(CO_2)_3]$ (187 mg, 0.200 mmol) in 20 mL of CH_3CN. An immediate reaction took place with the formation of a bright red precipitate, which was collected, washed several times with CH_3CN, and dried. The crude product was extracted with CH_2Cl_2 (3 × 5 mL). CH_3CN was then carefully layered on the top. Bright red crystals were collected after about 2 weeks. The yield was essentially quantitative. ^1H NMR δ (ppm, in CD_2Cl_2): 9.39 (s, 12H, aromatic protons of the trimesate groups), 8.52 (s, 12H, $-NCHN-$), 6.62 (q, 96H, aromatic protons of the formamidinate groups), 3.67 (s, 72H, $-OCH_3$). Anal. Calcd for $Mo_2C_{216}H_{192}N_{24}O_{48}$: 63.52% C, 4.74% H, 8.23% N. Found: 63.15% C, 4.49% H, 8.02% N.

$[Rh_2(cis\text{-}DAniF)_2]_6[1,3,5\text{-}C_6H_3(CO_2)_3]_4(ax\text{-}CH_3CN)_{7.5}$ (2). To a stirred solution of $[Rh_2(cis\text{-}DAniF)_2(CH_3CN)_4](BF_4)_2$ (57 mg, 0.050 mmol) in CH_3CN (10 mL) was added $(Bu_4N)_3[1,3,5\text{-}C_6H_3(CO_2)_3]$ (50 mg, 0.050 mmol) in 5 mL of CH_3CN. The reaction mixture was stirred at ambient temperature for ca. 24 h. Self-assembly took place gradually with the formation of a greenish precipitate, which was collected by filtration and then washed several times with CH_3CN. The crude product was extracted with CH_2Cl_2 (2 × 3 mL) and layered with CH_3CN (10 mL). Then a very slow stream of N_2 was allowed to pass over the

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mixture. One week later, dark-green brick-shaped crystals of **2**·13.9CH_3CN suitable for X-ray structural analysis were collected by filtration. The yield was essentially quantitative. ^1H NMR δ (ppm, in CD_2Cl_2/CD_3CN): 8.58 (s, 12H, aromatic protons of the trimesate groups), 7.43 (b, 12H, −NC*H*N-), 7.09 (d, 48H, aromatic protons of the formamidinate groups), 6.69 (q, 48H, aromatic protons of the formamidinate groups), 3.72 (s, 72H, −OC*H*$_3$). Anal. Calcd for $Rh_2C_{216}H_{192}N_{24}O_{48}$: 63.31% C, 4.72% H, 8.20% N. Found: 63.02% C, 4.60% H, 8.05% N.

Crystallographic Procedures. Single-crystal X-ray work on compound **1** was performed on a Nonius FAST diffractometer utilizing the program MADNES.[22] 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 2θ range of 18.1−41.6°. Cell dimensions and Laue symmetry was confirmed with axial photographs. Data were corrected for Lorentz and polarization effects and processed using an ellipsoid-mask algorithm (program PROCOR).[23] The program SORTAV[24] was used to correct for absorption.

The data for **2** were collected on a Bruker SMART 2000 CCD detector system. Cell parameters were measured using the SMART[25] software. Data were corrected for Lorentz and polarization effects using the program SAINT.[26] Absorption corrections were applied using SADABS.[27] All other data collection procedures were similar to those used on the FAST diffractometer (vide supra).

For both structures, the positions of some or all of the non-hydrogen atoms were found via direct methods by way of the program package SHELXTL.[28] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. For compound **1**, the general structure of the complex is well-defined, but many of the *p*-anisyl groups of the ligands are disordered over two sites. One of the Mo_2 subunits resides on the crystallographic 2-fold axis, but the metal−metal vector is not exactly bisected by the 2-fold axis, so the metal atoms and formamidinate groups at this site are all disordered. Careful modeling and judicious use of restraints allowed successful refinement of the model. Disorder was also present at several of the 20 different sites containing interstitial acetonitrile and dichloromethane molecules. The most prominent is a "ball" of electron density due to a disordered molecule of CH_2Cl_2 located directly in the center of the metal-complex cage. Only the metal atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions on the metal cluster for structure factor calculations. For compound **2**, the core structure is well defined without any disorder. Each phenyl ring of the 12 *p*-anisyl groups was constrainted to be a regular hexagon having edge distances of 1.39 Å. Five of these phenyl rings were disordered and refined as two components. Only metal atoms were refined anisotropically. Hydrogen atoms were not included in the model. The existence of a substantial amount of interstitial solvent in both compounds was apparent before any diffraction data were collected; unprotected crystals lost solvent and turned powdery immediately upon removal from the mother liquor. Other details of data collection and refinement for all complexes are given in Table 1. Selected atomic distances and angles are provided in Table 2. Other crystallographic data are available as Supporting Information.

Table 1. Crystal and Structure Refinement Data for Compounds **1** and **2**

compound	**1**·22.1CH_3CN·2.3CH_2Cl_2	**2**·13.9CH_3CN
chem formula	$C_{262.5}H_{262.9}Cl_{4.6}$-$Mo_{12}N_{46.1}O_{48}$	$C_{243.8}H_{233.7}N_{37.9}$-$O_{48}Rh_{12}$
fw	6145.84	5697.51
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a, Å	29.825(3)	20.3608(8)
b, Å	27.377(2)	20.6954(9)
c, Å	38.248(3)	37.555(2)
α, deg		104.436(1)
β, deg	112.71(1)	104.354(1)
γ, deg		94.403(1)
V, Å^3	28809(4)	14684(1)
Z	4	2
T, K	173(2)	293(2)
λ, Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.417	1.289
μ, mm^{-1}	0.622	0.724
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.098, 0.217	0.089, 0.238

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

Table 2. Selected Bond Distances (Å) for Compounds **1** and **2**

	Compound **1**		
Mo(1)−Mo(2)	2.099(2)	Mo(5)−Mo(6)	2.098[4]
Mo(3)−Mo(3A)	2.098(2)	Mo−N (av)	2.10[1]
Mo(4)−Mo(4A)	2.104(5)	Mo−O (av)	2.20[2]
	Compound **2**		
Rh(1)−Rh(2)	2.432(2)	Rh(11)−Rh(12)	2.435(2)
Rh(3)−Rh(4)	2.428(2)	Rh−N_{eq} (av)	2.018[3]
Rh(5)−Rh(6)	2.433(1)	Rh−N_{ax} (av)	2.20[10]
Rh(7)−Rh(8)	2.432(1)	Rh−O (av)	2.068[3]
Rh(9)−Rh(10)	2.438(2)		

Results and Discussion

Syntheses. The complexes were readily prepared by treating $[M_2(cis\text{-DAniF})_2(CH_3CN)_4](BF_4)_2$ (M = Mo, Rh) with the trimesate anion in CH_3CN according to the following reaction:

$$6[M_2(cis\text{-DAniF})_2(CH_3CN)_4](BF_4)_2 + 4(Bu_4N)_3[1,3,5\text{-}C_6H_3(CO_2)_3] \xrightarrow{CH_3CN} [M_2(cis\text{-DAniF})_2]_6[C_6H_3(CO_2)_3]_4 + 12NBu^n{}_4BF_4 \quad (1)$$

The formation of the molybdenum adduct **1** is almost instantaneous, while that of the rhodium analogue **2** requires about 1 day. The yields are essentially quantitative. The compounds are very soluble in CH_2Cl_2 and moderately soluble in many common organic solvents. The ^1H NMR spectra are consistent with the presence of highly symmetrical species in solution. They show the expected singlets for the aromatic protons of the trimesate anions, the methine protons of the formamidinate bridges, and the methoxy groups in the corresponding ratios of 1:1:6 (12:12:72). Anisyl protons appear in each case as the quartets expected for an AA′BB′ set of hydrogen atoms.

Both **1** and **2** proved very difficult to crystallize as each crystal contains a large number of interstitial solvent molecules. However, single crystals suitable for X-ray analysis were reproducibly obtained under the conditions described in the Experimental Section. Unprotected crystals lost solvent and turned powdery immediately upon removal from the mother liquor.

Structural Results. The X-ray structures of **1** and **2** with all formamidinate ligands removed are depicted in Figures 1 and

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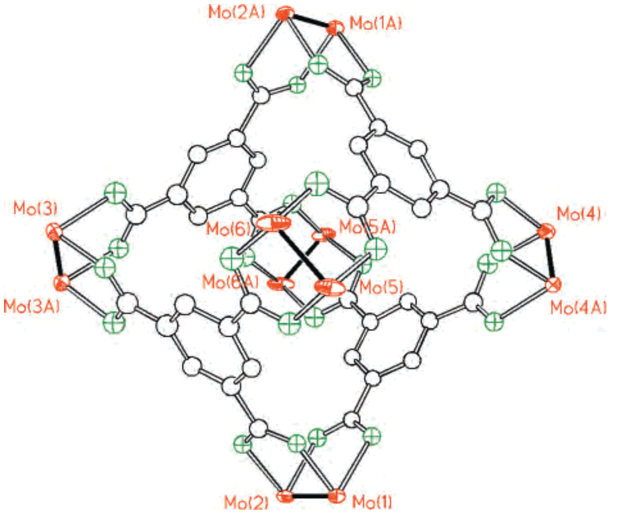

Figure 1. Molecular core structure of $[Mo_2(DAniF)_2]_6[\mu_3\text{-}C_6H_3(CO_2)_3]_4$ in **1**$\cdot 22.1CH_3CN\cdot 2.3CH_2Cl_2$ with displacement ellipsoids drawn at the 30% probability level. The two DAniF anions attached to each quadruply bonded Mo_2^{4+} unit, all hydrogen atoms, and the encapsulated CH_2Cl_2 molecule have been omitted for clarity.

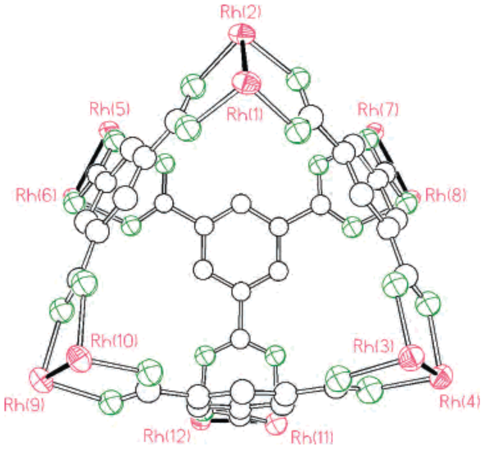

Figure 2. Molecular core structure of $[Rh_2(DAniF)_2]_6[\mu_3\text{-}C_6H_3(CO_2)_3]_4$ in **2**$\cdot 13.9CH_3CN$ with displacement ellipsoids drawn at the 40% probability level. The two DAniF anions attached to each singly bonded Rh_2^{4+} unit, all hydrogen atoms, the CH_3CN molecules attached to some of the axial positions, and the encapsulated solvent molecules have been omitted for clarity.

2, respectively. Compound **1** crystallizes in the monoclinic space group $C2/c$ with $Z = 4$. Each dimolybdenum unit consists of an eclipsed paddlewheel arrangement, with two cis formamidinate and two carboxylate paddles. As shown in Figure 1, the centroids of the six Mo_2^{4+} units define an octahedron and the centroids of the four trimesate six-membered rings define a tetrahedron. The overall idealized symmetry is T_d, but crystallographically there is only a single 2-fold axis that bisects the bonds between the atoms Mo(4), Mo(4A) and Mo(3), Mo(3A). The crystallographically independent Mo−Mo distances, 2.099(2), 2.098(2), 2.104(5), and 2.098(4) Å, are equal within 3σ and are typical quadruply bonded Mo_2 distances. Other bond distances and bond angles are similar to those found in other dimolybdenum paddlewheel complexes and require no further comment. One disordered CH_2Cl_2 molecule is located in the center of the cage, while at least two other CH_2Cl_2 molecules and 22 CH_3CN molecules fill intermolecular interstices.

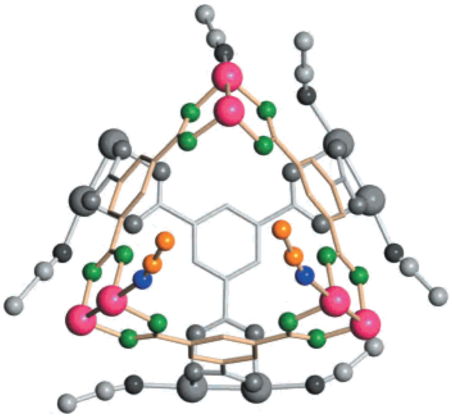

Figure 3. Simplified diagram of **2** showing that only two axially coordinated CH_3CN molecules can fit on each face of the octahedron defined by the midpoints of the Rh−Rh bonds.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. As in **1**, six Rh_2^{4+} units and four trimesate linkers assemble into a discrete molecular cage. The six crystallographically independent Rh−Rh distances are 2.432(2), 2.428(2), 2.433(1), 2.432(1), 2.438(2), and 2.435(2) Å. The molecular cages in **2** are fractionally occupied by acetonitrile molecules, which, like the CH_2Cl_2 molecules in **1**, are disordered. Interestingly, crystals having well-ordered, clathrated CH_2Cl_2 can also be obtained by diffusion of ether into a CH_2Cl_2/CH_3CN solution of **2**. However, full refinement of this structure could not be completed due to the poor crystal quality.[29] Nevertheless it was clear that the core of the structure is essentially the same as that of **2**$\cdot 13.9CH_3CN$.

In compound **2**$\cdot 13.9CH_3CN$ there are 7.5 coordinated CH_3CN molecules distributed over the 12 available axial coordination sites of the Rh_2 cores. This is unusual since dirhodium centers normally have all axial sites occupied by donor ligands. This unique feature appears to result from the steric crowding experienced by the ligands as they are distributed on the outside of the cage as shown in Figure 3. Here it can be seen that it is not possible to accommodate three acetonitrile molecules on a triangular face of the octahedron defined by the midpoints of three adjacent Rh−Rh bonds. Thus, each of the faces has, as an upper limit, two axial ligands. These ligands also show distortions from linearity which are most likely also due to the crowding.

The partial occupancy of the 12 potentially available sites for axial ligands merits more detailed discussion. Given that, as just noted, only two of the three sites directed at each of the four tetrahedral faces that are defined by the $C_6H_3(CO_2)_3$ ligands can be occupied, the maximum possible number of axial ligands is eight. This means that two of the six Rh_2 units must have two axial ligands and the other four only one each. There are only two ways to satisfy this requirement. If we imagine that the six lines defined by the Rh−Rh bonds are each extended until they meet two others at each end, a tetrahedron whose vertexes lie directly above the C_6 rings will be defined. The two doubly liganded Rh_2 groups may be (1) two that do not share a vertex or (2) two that do converge at a common vertex. The first arrangement of the eight axial ligands would allow the structure to retain S_4 symmetry, while the second would leave no symmetry element at all. Nature, contrary to what some might suppose, does not choose the symmetric alternative. In addition, there is a slight underpopulation of the eight sites so that the total number of axial CH_3CN ligands is about 7.5.

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(29) Crystal data for $[Rh_2(DAniF)_2]_6[\text{trimesate}]_4\cdot x CH_3CN\cdot y CH_2Cl_2$: triclinic, space group $P1$, $a = 20.619(3)$ Å, $b = 20.379(3)$ Å, $c = 37.683(6)$ Å, $\alpha = 103.912(4)°$, $\beta = 105.109(3)°$, $\gamma = 95.376(3)°$, $V = 14631(7)$ Å^3, $Z = 2$. Data were collected at 293(2) K.

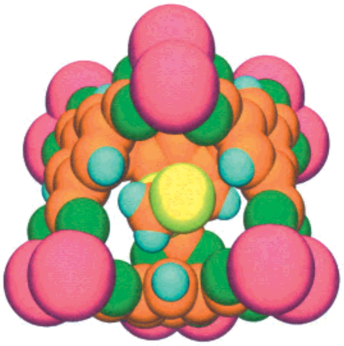

Figure 4. A space-filling representation of molecule **2**, which also shows the ordered CH_2Cl_2 molecule located inside.

It is also worth noting that these molecules are able to encapsulate the CH_2Cl_2 and CH_3CN molecules as shown in Figure 4. Thus, it may be possible to crystallize them from a solvent whose molecules are too large to fit inside but in the presence of small gas molecules (e.g., N_2, He, Ne, Ar) so that these will occupy the cavities. Efforts to do this are to be made.

Shortly after the submission of our preliminary communication on compound **1**, a report on the structure of $[Cu_3(C_6H_3(CO_2)_3)_2(H_2O)_3]_n$ appeared.[5g] Here there are $Cu_2(O_2CR)_4(H_2O)_2$ units, R = the aromatic portion of trimesate, with the carboxylate ligands arranged as a paddlewheel and the H_2O molecules located along the Cu−Cu axis. The structure is three-dimensional giving a nanoporous material with a basic building block consisting of six dicopper units linked by four trimesate anions. This building block is structurally analogous to that found in **1** and **2**. In our compounds, polymer formation is prevented by the formamidinate groups.

The design principle upon which the present work is based is that a large closed structure can be obtained by employing large triangular tridentate connecting groups and metal corners each having two available sites for ligation which are at about 90° to each other in a ratio of 4:6. This was first done by Fujita and co-workers[30] in 1995, who used linkers of the type **I** and $enPd^{2+}$ for the six corners.

In 1997, Stang et al. used the tridentate linker **II** and Pd(diphos) and Pt(diphos) corners,[31] to form a similar molecule. Also in 1997 a similar molecule in which the linker **III** was used and the octahedral apexes were formed by *trans*-$PdCl_2$ units was reported.[32] The molecules reported here show that the same concept, *mutatus mutandis*, can be effective in the syntheses of molecules with redox-active dimetal corners.

Electrochemistry. Compounds **1** and **2** have been examined by both cyclic voltammetry and differential pulse voltammetry; the results are displayed in Figure 5. In **1**, three distinct reversible oxidation steps occur at $E_{1/2}$ of 268, 330, and 370 mV vs the Ag/AgCl couple. On the basis of DPV, the ratio of the number of electrons involved in these steps is 1:1:1. Using $Mo_2[(m\text{-}CF_3C_6H_4N)_2CH]_4$ as a standard,[33] these have been assigned as one-electron-oxidation steps. The peak separations of 62 and 40 mV indicate that the electronic communication between the six Mo_2^{4+} units is moderately good, according to the concepts discussed earlier.[12b] In **2**, there are 2 reversible waves, each corresponding to 6*e* oxidations, according to the same calibration procedure. The first broad wave is centered at 300 mV, with a small shoulder at 145 mV, indicative of a very small degree of electronic communication. The second wave is sharp and centered at 1084 mV. The unsplit signal and its sharpness are an indication of the lack of electronic coupling.[8b]

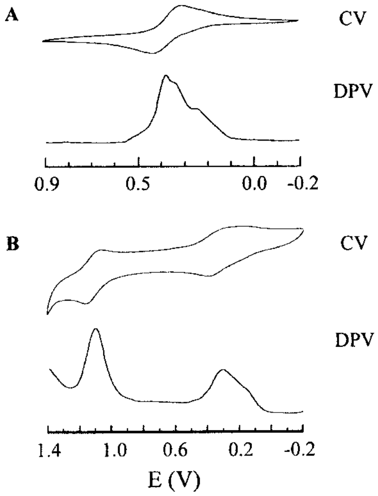

Figure 5. Cyclic voltammograms, CV, and differential pulse voltammograms, DPV, of compounds **1** (A) and **2** (B).

Concluding Remarks

The two compounds reported here are the first two examples of polyhedral molecules assembled from dimetal corner pieces and linkers that are more than bifunctional. Clearly these are, metaphorically, just the tip of the iceberg. The preparation and characterization of others are underway in this laboratory.

Acknowledgment. We are grateful to the National Science Foundation for support, to Dr. Lee M. Daniels for helpful crystallographic advice, and to Johnson Matthey for a generous loan of $RhCl_3$.

Supporting Information Available: An X-ray crystallographic file for compounds **1** and **2**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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