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The Extraordinary Ability of Guanidinate Derivatives to Stabilize Higher Oxidation Numbers in Dimetal Units by Modification of Redox Potentials: Structures of Mo_2^{5+} and Mo_2^{6+} Compounds

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Abstract: Full characterization of the first homologous series of dimolybdenum paddlewheel compounds having electronic configurations of the types $\sigma^2\pi^4\delta^x$, $x = 2, 1, 0$, and Mo−Mo bond orders of 4, 3.5, and 3, respectively, has been accomplished with the guanidinate-type ligand hpp (hpp = the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine). Essentially quantitative oxidation of $Mo_2(hpp)_4$, **1**, by CH_2Cl_2 gives $Mo_2(hpp)_4Cl$, **2**. The halide in **2** can be replaced by reaction with $TlBF_4$ to produce $Mo_2(hpp)_4(BF_4)$, **3**. Further oxidation of **2** by $AgBF_4$ produces $Mo_2(hpp)_4ClBF_4$, **4**. The change from bond order 4 (in **1**) to 3.5 in $Mo_2(hpp)_4Cl$ is accompanied by an increase in the Mo−Mo bond length of 0.061 to 2.1280(4) Å. A further increase of 0.044 Å in the Mo−Mo distance to 2.172(1) Å is observed as the bond order decreases to 3 in **4**. At the same time, the Mo−N distances decrease smoothly as the oxidation state of the Mo atoms increases. Electrochemical studies have shown two chemically reversible processes at very negative potentials, $E^1_{1/2} = -0.444$ V and $E^2_{1/2} = -1.271$ V versus Ag/AgCl. These correspond to the processes $Mo_2^{6+/5+}$ and $Mo_2^{5+/4+}$, respectively. The latter potential is displaced by over 1.5 V relative to those of the $Mo_2(formamidinate)_4$ compounds and the first one has never been observed in such complexes. Thus, in surprising contrast to previously observed behavior of the dimolybdenum unit, when it is surrounded by the very basic guanidinate ligand hpp, there is an extraordinary stabilization of the higher oxidation numbers of the molybdenum atoms.

Introduction

A wealth of knowledge[1] on multiple metal−metal bonded complexes has accumulated since the correct formulation of the first quadruply bonded species, $Re_2Cl_8^{2-}$, was published almost four decades ago.[2] Since then, other halide species $M_2X_8^{n-}$, **I**, having direct and unsupported metal−metal bonds have been made for four other metals, M = Mo, W, Tc, and Os, as shown in Figure 1.

Much of the progress in this field has come in quantum jumps closely associated with the development of new types of ligands. For example, substitution of the halide ions by carboxylate anions brought about an almost explosive growth. This allowed the preparation of hundreds of compounds having two metal atoms bridged by four monoanions, providing structures of type **II**, commonly known as paddlewheel or tetragonal lantern structures. As shown in Figure 1, metal atoms capable of forming such structural types include Cr, Ru, and Rh as well as those known to form $M_2X_8^{n-}$ species.

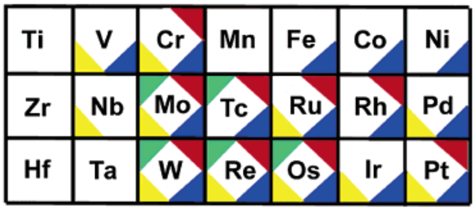

Figure 1. Portion of the periodic table depicting the groups 4 through 10 transition metals that form paddlewheel structures. Green represents halides, red represents carboxylates, blue represents formamidinates and related compounds, and yellow represents hpp compounds.

Further expansion of the number of elements capable of forming paddlewheel compounds had to wait until amidinate-type ligands, such as the formamidinates, **III**, were used.[1] These ushered in yet another stage of development, allowing isolation of the first Ni_2^{5+} complex having a bond order of 1/2,[3] as well as the first V_2^{4+},[4] $Fe_2^{3+,4+}$,[5] $Co_2^{3+,4+,5+}$,[6] Ir_2^{4+},[7] and $Pt_2^{4+,5+,6+}$

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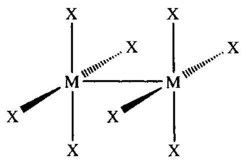
compounds[8] (see Figure 1), although for the latter, other types of Pt−Pt-bonded species were already known.[1]



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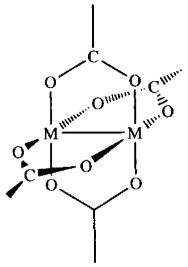

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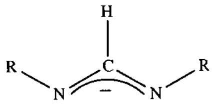
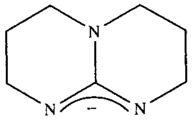


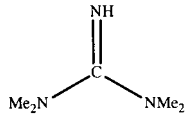
III



IV

Optimism about filling still more holes in the periodic table was tempered by the discovery that formamidinates are cleaved rather easily in the presence of certain low-valent metal species, for example those of Nb and Ta.[9] It was then necessary to find a more sturdy ligand that would not be cleaved as easily. One that seemed to have those desirable characteristics was the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, hpp (**IV**). The parent guanidinate-type compound had the advantage of being commercially available, and the anion had been shown to stabilize Ru_2^{6+} units.[10] Using this ligand, we were able to synthesize the first triply bonded Nb_2^{4+} complex.[11] As indicated in Figure 1, this anion can also form paddlewheel complexes with many other transition metal atoms.[12]

More importantly, it is now clear that not only is the hpp ligand more robust than the formamidinates but also that there are significant electronic differences. The hpp ligand has been considered a weak nucleophile, but studies of the electronic structure[13] have shown that it is a very strong Brønsted base. It has been estimated that it is nearly 100 times more basic than tetramethylguanidine,[14] **V**.



V

From UV photoelectron spectroscopy, it has been established that the HOMO ionization of Hhpp corresponds to a nitrogen lone pair at the N(1) position (the N at the top in **IV**).[13] It has been argued that there are possible intramolecular interactions between orbitals localized on imine (η_{CN}, π_{CN}) and amine (η_N) moieties with the lone pairs from N(1) interacting more strongly with the π_{CN} orbital than with the lone pair orbital at the nonprotonated nitrogen atom. Thus, it is likely that such large electronic differences between hpp and formamidinate ligands are responsible for the stabilization of a series of highly oxidized M_2 species by hpp ligands. Because of the high basicity of bicyclic amines such as Hhpp, they have been used extensively as catalysts in many organic reactions such as nitroaldol (Henry) reactions, addition of dialkyl phosphates to a variety of carbonyl compounds and imines,[15] and transesterification reactions.[16] More recently, there has been great interest in the study of proton affinities of polyguanidines.[17] For those, their very large intrinsic basicity has been traced to a dramatic increase in the resonance stabilization of the conjugate bases. Also, an extensive review on the coordination chemistry of the simpler guanidines and guanidinates has appeared.[18]

In a preliminary communication, we reported the first triply bonded tetragonal lantern compounds having the Mo_2^{6+} units surrounded by nitrogen donor ligands.[19] Likewise, the first and only known singly bonded Pd_2^{6+} and doubly bonded Ir_2^{6+} tetragonal lantern compounds were prepared recently.[20,21] Unfortunately, $M_2(hpp)_4^{n+}$ species tend to have low solubility. Thus, reactions have been difficult to accomplish in a fully controlled manner. For example, when the oxidation of $Mo_2(hpp)_4$ with $AgBF_4$ was attempted for the first time, the doubly oxidized $[Mo_2(hpp)_4](BF_4)_2$ compound was the only product isolated, and the intermediate $[Mo_2(hpp)_4]^+$ species was not observed.[19] However, a few crystals of $Mo_2(hpp)_4Cl$ were isolated at a later stage.[22]

We have now overcome the synthetic problems encountered earlier after realizing that, contrary to what is commonly known for quadruply bonded Mo_2^{4+} species,[1] the Mo_2^{4+} unit is very easy to oxidize when it is embraced by hpp ligands. In fact, mere dissolution of $Mo_2(hpp)_4$ in CH_2Cl_2 causes formation of Mo_2^{5+} in essentially quantitative yield. In this solvent, addition of stronger oxidation agents such as $AgBF_4$ will proceed with further oxidation to Mo_2^{6+} and beyond. On the basis of the recognition of these facts, the series of $Mo_2(hpp)_4^{n+}$ species, for $n = 0$, 1, and 2 has been completed. This is the first truly homologous series having Mo_2^{n+} units with bond orders of 4,

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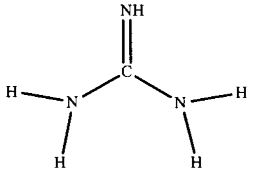
3.5, and 3 with an electronic configuration of the type $\sigma^2\pi^4\delta^x$, $x = 2, 1, 0$. Here we also report voltammetric studies on these molybdenum complexes and show the existence of an enormous difference in the oxidation potential of the Mo_2^{4+} unit of ~1.5 V for compounds with N-donor ligands of the formamidinate type and those with hpp. There exists a tremendous capability for tuning the oxidation potential of the Mo_2^{4+} unit by modifying the ligands, a situation that could be relevant in the creation of electrochemical sensors, an area of much current interest,[23] and other applications. Furthermore, it is important to recognize that the backbone of the hpp ligand is the guanidinate group, N_3C, derived from guanidine, **VI**. Guanidine has been recognized as an important biological molecule with many of its derivatives having important biological functions.[24]



VI

Experimental Section

General Procedures. All synthetic techniques were performed under a nitrogen atmosphere, and all glassware was oven-dried prior to use. Hexanes, toluene, THF, CH_2Cl_2, Bu_4NBF_4, and Hhpp were purchased from Aldrich. Butyllithium (1.6 M) in hexanes was purchased from Acros and used as received. The solvents THF, toluene, and hexanes were dried over Na/K alloy and CH_2Cl_2 over P_2O_5. All solvents were freshly distilled under nitrogen prior to use. Hhpp was sublimed, and Bu_4NBF_4 was oven-dried prior to use. $TlBF_4$ was prepared by titrating Tl_2CO_3 with $HBF_4{\cdot}2Et_2O$, both purchased from Strem and used as received. The oxidant $C_6H_5I{\cdot}Cl_2$ was prepared following a modification of published procedures by bubbling chlorine gas through iodobenzene.[25] After filtration, the yellow solid was washed with hexanes and stored at 5 °C. $Mo_2(hpp)_4$, **1**, was made using a modification of a previous synthesis[12a] where the solvent of reaction/crystallization was switched to THF.

Physical Measurements. Elemental analyses were performed by Canadian Microanalytical Service, Ltd., Delta, British Columbia, Canada. UV−vis spectra were recorded on a Cary 17D spectrophotometer for **4** and a Shimadzu UV-1601 PC spectrophotometer for **2** and **3**. ^1H NMR spectra were recorded on a Unity Plus 300 NMR spectrometer, using CH_2Cl_2 to reference chemical shifts (δ). Cyclic voltammetry was recorded using a BAS 100 electrochemical analyzer with a 2-mm diameter Pt disk working electrode, Ag/AgCl reference electrode, and Pt wire auxiliary electrode with $Bu_4NBF_4{\cdot}3$toluene as solvent.[26,27] The scan rate for the voltammograms was 200 mV/s. Potentials are reported versus Ag/AgCl.

Preparation of $Mo_2(hpp)_4Cl$, 2. Method A. $Mo_2(hpp)_4$ (0.20 g, 0.27 mmol) was dissolved in 20 mL of CH_2Cl_2. The deep red solution turned brown within 5 min, and was stirred for 1 h. The brown solution was transferred to a 50-mL Schlenk tube via cannula and layered with hexanes. Brown crystals (0.18 g) were collected after two weeks, giving a yield of 71%. X-ray studies confirmed the product as **2**·$2CH_2Cl_2$. Anal. Calcd for $C_{30}H_{52}Cl_5Mo_2N_{12}$: C, 37.93; H, 5.52; N, 17.69%. Found: C, 38.31; H, 5.77; N, 18.07%. Magnetism: 1.64 μ_B. EPR (CH_2Cl_2, 13 K) singlet, $g = 1.94$. Visible absorption spectrum (CH_2Cl_2): λ_{MAX}, nm; (ϵ_M, L/mol·cm) 770 (200), 500 (shoulder). IR (KBr, cm^{-1}): 2929(m), 2841(m), 2820(m), 1636(w), 1522(s), 1492(s), 1473(m), 1442(s), 1380(m), 1308(s), 1280(s), 1205(s), 1137(m), 1068(w), 1028(w), 739(m), 720(m), 414(w).

Method B. A red-orange solution of $Mo_2(hpp)_4$ (0.10 g, 0.13 mmol) in 10 mL of toluene was layered with a solution of $C_6H_5I{\cdot}Cl_2$ (0.018 g, 0.067 mmol) in 10 mL of acetonitrile. No solid precipitated as the layers diffused. After the diffusion was complete, the yellow-orange solution was layered with 10 mL of diethyl ether. A few yellow-orange crystals of **2** (free of interstitial solvent) grew within a few days. The yield was not optimized.

$Mo_2(hpp)_4(BF_4)$, 3. $Mo_2(hpp)_4$ (0.20 g, 0.27 mmol) was dissolved in 20 mL of CH_2Cl_2. Once the red solution had turned brown, it was transferred via cannula to a flask with $TlBF_4$ (0.10 mg, 0.34 mmol) and stirred for 2 h. The brown solution was filtered into a 50-mL Schlenk tube and layered with hexanes. Brown crystals of **3**·$2CH_2Cl_2$ (0.15 g) were collected after 3 weeks, giving a 61% yield. Anal. Calcd for $C_{28}H_{48}BF_4Mo_2N_{12}$: C, 40.45; H, 5.82; N, 20.22. Found: C, 40.26; H, 6.12; N, 19.94. Visible absorption spectrum (CH_2Cl_2): λ_{MAX}, nm; (ϵ_M, L/mol·cm) 760 (200), 520 (shoulder). IR (KBr, cm^{-1}): 2934(m), 2847(m), 2821(m), 1629(w), 1522(s), 1490(s), 1467(s), 1445(s), 1382(s), 1308(s), 1281(m), 1207(s), 1139(m), 1054(s), 1026(s), 743(m), 720(w), 417(w).

$Mo_2(hpp)_4Cl(BF_4)$, 4. $Mo_2(hpp)_4$ (0.20 g, 0.27 mmol) was dissolved in 20 mL of CH_2Cl_2. Once the red solution had turned brown, it was transferred via cannula to a flask containing $AgBF_4$ (0.60 g, 0.31 mmol). The mixture was stirred for 2 h and then filtered into a 50-mL Schlenk tube and the solution layered with hexanes. Brown crystals (0.13 g) were obtained after two weeks, giving a 56% yield. Anal. Calcd for $C_{28}H_{48}BClF_4Mo_2N_{12}$: C, 38.79; H, 5.58; N, 19.39. Found: C, 38.98; H, 5.42; N, 19.61. ^1H NMR (CD_2Cl_2, ppm): 3.30 (t, $(CH_2)_2$), 2.01 (quin, CH_2). Visible absorption spectrum (CH_2Cl_2): λ_{MAX}, nm; (ϵ_M, L/mol·cm) 610 (270), 427 (15 000). IR (KBr, cm^{-1}): 2934(m), 2860(m), 1636(m), 1538(s), 1492(s), 1448(s), 1383(s), 1311(s), 1217(s), 1137(s), 1067(s), 1029(s), 880(w), 802(w), 751(s), 728(m), 518(w), 413(w).

X-ray Crystallography. Single crystals of **2**, **2**·$2CH_2Cl_2$, and **4**, were attached to quartz fibers with a minimum of silicone grease. Data were collected at 213 K on a Bruker SMART area detector using the SMART and SAINT programs[28,29] for **2**·$2CH_2Cl_2$ and **4**. For **2**, a Nonius FAST area detector was employed. The crystal structures were solved via direct methods and refined using SHELXL-97.[30] Hydrogen atoms were placed at calculated positions. Non-hydrogen atoms were refined with anisotropic displacement parameters. Cell parameters and refinement results for compounds **2**, **2**·$2CH_2Cl_2$, and **4** are summarized in Table 1.

Results and Discussion

Syntheses. The quadruply bonded starting material, $Mo_2(hpp)_4$, was prepared as before by reaction of $Mo_2(O_2CCF_3)_4$ and Lihpp.[12a] However, we made a simple but important modification by replacing toluene with THF as the solvent for the reaction. This switch from toluene to THF increased the yield of red crystalline material from 22% to 73%.

We had found earlier that this quadruply bonded compound could be oxidized, in low yield, to the triply bonded $Mo_2(hpp)_4(BF_4)_2$ species by reaction with $AgBF_4$ in CH_2Cl_2. Interestingly, the oxidation always resulted in the isolation of the Mo_2^{6+} species, even when the ratio of Mo_2^{4+} to Ag^+ was 1:1. An

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Table 1. Crystallographic Parameters for Compounds **2**, **2**·CH_2Cl_2 and **4**

cmpd	**2**	**2**·$2CH_2Cl_2$	**4**
formula	$C_{28}H_{48}ClMo_2N_{12}$	$C_{30}H_{52}Cl_5Mo_2N_{12}$	$C_{28}H_{48}BClF_4Mo_2N_{12}$
fw	780.11	949.97	866.92
space group	*P*4/*n* (No. 85)	*P*4/*nnc* (No. 126)	*P*4/*ncc* (No. 130)
a (Å)	13.561(11)	13.6912(8)	14.4878(8)
c (Å)	8.5330(3)	20.475(1)	16.3787(9)
V (Å^3)	1569(2)	3838.1(4)	3437.8(5)
Z	2	4	4
d_{calc} (g/cm^{-3})	1.651	1.644	1.675
μ (mm^{-1})	0.926	1.042	0.870
radiation		Mo Kα (λ_α = 0.71073 Å)	
T (K)		213(2) K	
R1,[a] wR2[b]	0.064, 0.113	0.027, 0.062	0.070, 0.135

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

attempt to oxidize a solution of **1** with $C_6H_5I{\cdot}Cl_2$ in CH_3CN finally provided the first few crystals of $Mo_2(hpp)_4Cl$, **2**, which allowed us to determine its structure.[22] While working to improve the yield, the reaction conditions were monitored in various ways. Whenever the ^1H NMR spectrum of $Mo_2(hpp)_4$ was checked, we noticed a change occurring as a function of time when the solvent was CD_2Cl_2 but not in other solvents such as CD_3CN. The longer the time after preparation of the samples, the broader the weak NMR signals became. There was also a noticeable darkening of the dilute solution. It soon became apparent that the broadening of the signals was due to the presence of the paramagnetic Mo_2^{5+} species, with CD_2Cl_2 unexpectedly acting as an oxidizing agent. Thus, bulk samples of the brown crystalline and paramagnetic material $Mo_2(hpp)_4Cl$ were prepared simply by dissolving $Mo_2(hpp)_4$ in CH_2Cl_2 and then stirring the solution at room temperature for an hour. After layering the solution with hexanes, crystals of **2**·$2CH_2Cl_2$ were isolated in about 71% yield. It is worth mentioning that although dichloromethane is seldom thought of as an oxidizing agent, it has been used in our laboratory for the oxidation of W_2^{4+} quadruple bonds,[31] and the reduction of alkyl halides has been a topic of much interest[32] and has been studied extensively (vide infra).

The chloride ion in **2** can be substituted by reaction with $TlBF_4$ whereby brown, paramagnetic $Mo_2(hpp)_4(BF_4)$, **3**, can be isolated.[33,34] Compounds **2** and **3** are slightly air-sensitive; crystals will decompose within 1 h when exposed to air. Like the parent $Mo_2(hpp)_4$ complex, **2** and **3** exhibit very limited solubility in most common laboratory solvents. They are, however, slightly more soluble in CH_2Cl_2, giving brown solutions.

Further oxidation to the corresponding Mo_2^{6+} species was accomplished quite easily by allowing $Mo_2(hpp)_4$ to react with CH_2Cl_2 to give the corresponding Mo_2^{5+} complex and then adding one equivalent of $AgBF_4$. After workup of the reaction, the very dark brown and diamagnetic compound **4** was isolated in reasonably good yields (56%). Compound **4** also shows relatively low solubility in most common organic solvents. Thus the sequence of events leading from Mo_2^{4+} to Mo_2^{6+} via Mo_2^{5+} can be summarized as:

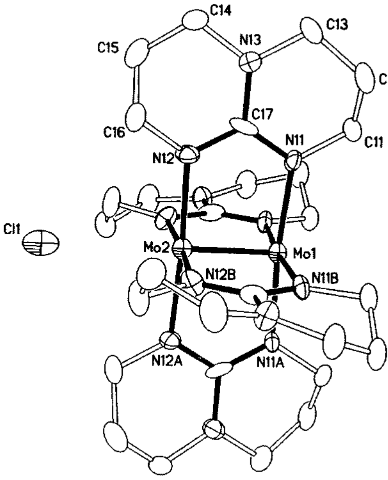


Figure 2. Thermal ellipsoid plot of $Mo_2(hpp)_4Cl$ in **2** with probability ellipsoids shown at the 50% level. The atoms Mo(1), Mo(2) and Cl(1) are on the four-fold axis. Selected interatomic distances (Å) are: Mo(1)−Mo(2) = 2.128(2), Mo(1)−N(11) = 2.122(6), Mo(2)−N(12) = 2.139(6), Mo(2)−Cl(1) = 3.091(6).

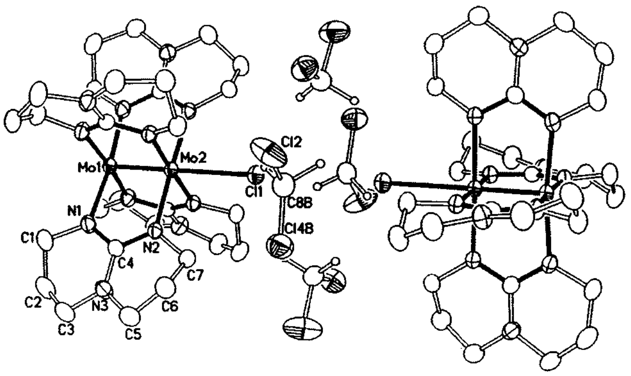
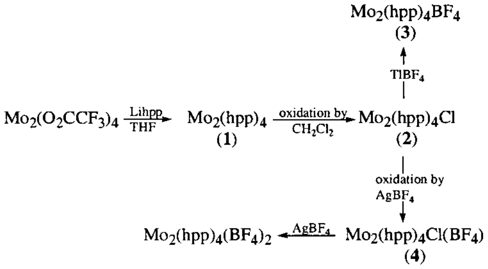


Figure 3. The crystal environment in **2**·$2CH_2Cl_2$. Labels are on the crystallographically independent hpp ligand, and probability ellipsoids are shown at the 50% level. Each CH_2Cl_2 has a 50% occupancy. Selected interatomic distances (Å) are: Mo(1)−Mo(2) = 2.1281(4), Mo(1)−N(1) = 2.102(2), Mo(2)−N(2) = 2.160(1), Mo(2)···Cl(1) = 2.838(1).



Structural Studies. All three complexes **2**, **2**·$2CH_2Cl_2$, and **4**, crystallized in a tetragonal space group, and their structures are shown in Figures 2, 3, and 4, respectively. For each of them, selected interatomic distances are given in the corresponding figure caption. There is a common structural motif whereby four guanidinate groups wrap the dimetal unit, giving a paddlewheel

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(31) Canich, J. A. M.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R. *Inorg. Chem.* **1988**, *27*, 804.

(32) See for example: (a) Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455. (b) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 9829. (c) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.

(33) If the stoichiometry was not carefully controlled during the preparation of **3** and less the 1 equiv of $TlBF_4$ was added to **2**, crystals of $Mo_2(hpp)_4Cl_{0.5}(BF_4)_{0.5}$ were obtained. These crystallized in the tetragonal space group *P*42$_1$2 with the following crystallographic parameters: *a* = 14.2091(8) Å, *c* = 16.415(1) Å, *V* = 3314.3(4) Å^3. The structure was highly disordered. The Mo−Mo distance was 2.1193(6) Å.

(34) Crystals of **3**·$2CH_2Cl_2$ have been obtained, and crystallographic characterization has revealed the presence of a highly disordered $Mo_2(hpp)_4^+$ cation and BF_4^- anion. Crystallographic data are: monoclinic space group *P*2$_1$/*c*, *a* = 9.820(3) Å, *b* = 20.859(5) Å, *c* = 19.797(3) Å, *β* = 96.44(1)°, *V* = 4029(2) Å^3. The Mo−Mo distance was 2.110(1) Å.

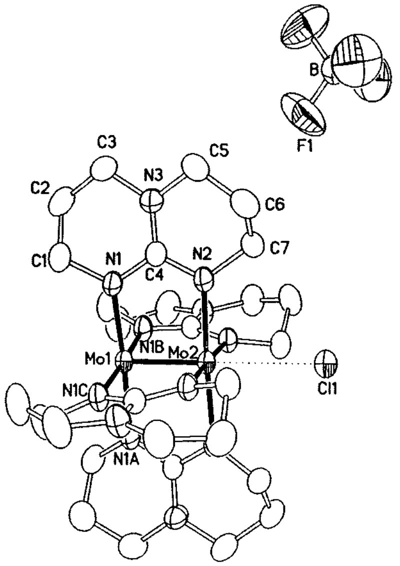

Figure 4. Thermal ellipsoid plot of the triply-bonded $Mo_2(hpp)_4Cl(BF_4)$ compound, **4**, showing displacement ellipsoids at the 50% probability level. Selected interatomic distances (Å) are: Mo(1)−Mo(2) = 2.1722(9), Mo(1)−N(1) = 2.092(4), Mo(2)−N(2) = 2.108(4), Mo(2)···Cl(1) = 2.983(2), Mo(1)···Cl(1) = 3.034(2).

or tetragonal lantern structure with the Mo_2^{n+} unit located along the four-fold axis, where the axial chloride ions are also found. These are at distances that are too long to be considered as making significant bonding contributions. The molecules are well-ordered with the hpp ligands being such that in one ring the central CH_2 group deviates in one direction and in the other ring the corresponding CH_2 group deviates in the opposite direction.

For all three complexes the distances within the hpp ligands are very similar. Outside the guanidine core, CN_3, the C−N and C−C distances are ~1.45 and ~1.50 Å, respectively. For the core, the two chemically equivalent C−N distances in each of the hpp ligands are significantly shorter and fall in the range 1.33−1.35 Å while those C−N distances between the atoms shared by the two rings of the hpp ligands are just slightly longer and in the range between 1.35 and 1.39 Å. This is consistent with the four atoms of the guanidinate core being regarded as sp^2 hybridized with some of their electrons occupying $p\pi$ molecular orbitals, leading to near planarity of the CN_3 unit.

Structural Trends among the Dimetal Cores. With this report concerning the first two $Mo_2(hpp)_4^+$ species, we can now for the first time track accurately how the Mo−Mo distances vary as the charge of the Mo_2^{n+} unit changes from 4 to 5 and 6 on a series of homologous compounds. The data are presented in Table 2 which also includes the results of a parallel study on $W_2(hpp)_4^{n+}$ analogues.[35] When the average Mo−N distances are compared, the general trend is for a small but significant decrease as the oxidation state increases. This is consistent with the generally observed shrinking of the atomic radii as the charge increases. The overall change in going from Mo_2^{4+} to Mo_2^{6+} is 0.08−0.10 Å with the difference roughly split for the Mo_2^{5+} species. Slightly smaller differences have been observed for the only other Mo_2^{4+}/Mo_2^{5+} couples surrounded by nitrogen ligands, also shown in Table 2.

What is more remarkable is the magnitude of the difference for comparable oxidation numbers in changing the ligand from the formamidinate DTolF[36] to the guanidinate-type μ_2-η^2-$(NPh)_2$-CNHPh[37] and hpp. It appears that the shorter Mo−N distances for the latter are a reflection of stronger binding that is likely to be due to the higher basicity of the hpp ligand, a derivative of the extremely basic prototype guanidine, $(H_2N)_2C{=}NH$.

The Mo−Mo distances in Table 2 also show a marked variation as the oxidation state increases. However, the variation is the opposite of that for the Mo−N distances. Clearly, there is an even, stepwise increase of the metal−metal distance in going from Mo_2^{4+} to Mo_2^{5+} and Mo_2^{6+}. This is consistent with the decrease in bond order combined with the increase in charge. In the parent compound **1** the electronic configuration of the Mo_2^{4+} is that of a typical quadruply bonded unit where the eight bonding electrons give a $\sigma^2\pi^4\delta^2$ configuration. The removal of an electron reduces the bond order to 3.5, and the Mo−Mo separation increases by 0.06 Å. Removal of another electron from the δ orbital brings the bond order to 3, and the Mo−Mo distance increases by 0.01−0.04 Å for $Mo_2(hpp)_4(BF_4)_2$ and **4**, respectively.

The relatively small magnitudes of the changes are likely due to the fact that the electrons are being removed from δ orbitals which do not make a major contribution to the total Mo−Mo bond strength. Nevertheless, the trend clearly supports the change in electronic configuration from $\sigma^2\pi^4\delta^2$ to $\sigma^2\pi^4\delta$ and $\sigma^2\pi^4$ as the value of n in the Mo_2^{n+} species changes from 4 to 5 and 6, respectively.

Variations in the same direction are also observed for the other two Mo_2^{4+}/Mo_2^{5+} couples shown in Table 2. For another pair, namely that of $Mo_2(SO_4)_4^{4-}$[38]and $Mo_2(SO_4)_4^{3-}$,[39] the metal−metal distances show a similar increase as they vary from 2.110(3) to 2.164(3) Å. It is important to note that entirely analogous trends are to be found[35] for the $W_2(hpp)_4$, $W_2(hpp)_4^+$, and $W_2(hpp)_4^{2+}$ series with the metal−metal distances increasing by ~0.04 Å and the average W−N distances decreasing by a similar amount. Again, this is consistent with the corresponding configurations of $\sigma^2\pi^4\delta^2$, $\sigma^2\pi^4\delta$, and $\sigma^2\pi^4$.

Although there are a large number of structures of quadruply bonded $Mo_2(carboxylate)_4$ compounds known having Mo−Mo distances of ~2.07−2.10 Å,[1] the actual isolation of oxidized Mo_2^{5+} species has been challenging and it was not until very recently that structures of the first three compounds having $Mo_2(carboxylate)_4^+$ monocations were reported.[40] Once again a small lengthening of metal-to-metal distances of ~0.06 Å with respect to that of the corresponding parent compound was observed. As expected, the increase in the charge on the Mo_2 core from the loss of one electron caused the Mo−O bonds in the cations to shrink by ~0.025 Å. Unfortunately, the only previously reported $Mo_2(carboxylate)_4^{2+}$ species cannot be included in the comparison for the following reasons. This is a tetraacetate

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(35) Cotton, F. A.; Huang, P.; Murillo, C. A.; Timmons, D. J. *Inorg. Chem. Commun.* **2002**, *5*, 501.

(36) Cotton, F. A.; Feng, X.; Matusz, M. *Inorg. Chem.* **1989**, *28*, 594.

(37) (a) Bailey, P. J.; Bone, S. F.; Mitchell, L. A.; Parsons, S.; Taylor, K. J.; Yellowlees, L. J. *Inorg. Chem.* **1997**, *36*, 867. (b) Bailey, P. J.; Bone, S. F.; Mitchell, L. A.; Parsons, S.; Taylor, K. J.; Yellowlees, L. J. *Inorg. Chem.* **1997**, *36*, 5420.

(38) Angell, C. L.; Cotton, F. A.; Frenz, B. A.; Webb, T. R. *J. Chem. Soc., Chem. Commun* **1973**, 399.

(39) Cotton, F. A.; Frenz, B. A.; Webb, T. R. *J. Am. Chem. Soc.* **1973**, *95*, 4431.

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Table 2. Variations of the M−M and M−N and Selected M···Cl Distances (Å) for Paddlewheel Families (M = Mo, W) and Differences in the Metal−Metal Distance between the Corresponding Cationic and Neutral Species

cmpd	M–M	Δ(M–M) species M_2^{5+}–M_2^{4+}	 M_2^{5+}–M_2^{6+}	M–N (av)	M···Cl	charge of M_2^{n+} unit	ref
$Mo_2(DTolF)_4$[a]	2.085(4)	0.037		2.17		4	36, 46
$[Mo_2(DTolF)_4]PF_6$[a]	2.122(3)			2.15		5	36
$Mo_2\{\mu\text{-}\eta^2\text{-}(NPh)_2CNHPh\}_4$	2.0839(9)	0.035		2.17		4	37
$[Mo_2\{\mu\text{-}\eta^2\text{-}(NPh)_2CNHPh\}_4]BF_4$	2.119(1)			2.14		5	37
$Mo_2(hpp)_4$	2.067(1)	0.061		2.16		4	12a
$Mo_2(hpp)_4Cl$	2.128(2)	0.061	0.044 (0.014)[b]	2.13	3.091(6)	5	this work
$Mo_2(hpp)_4Cl\cdot 2CH_2Cl_2$	2.1280(4)		0.044 (0.014)[b]	2.13	2.838(1)	5	this work
$Mo_2(hpp)_4Cl(BF_4)$	2.1722(9)			2.10	2.983(2)	6	this work
$Mo_2(hpp)_4(BF_4)_2$	2.142(2)			2.08		6	19
$W_2(hpp)_4\cdot 2NaHBEt_3$	2.1607(4)			2.15		4	35
$W_2(hpp)_4Cl_{0.5}Cl_{0.5}$[c]	2.209(1)	0.048	0.041	2.12	2.8425(9)	5	35
$W_2(hpp)_4Cl$	2.2131(8)	0.052	0.037	2.12	2.938(4)	5	35
$W_2(hpp)_4Cl_2$	2.250(2)			2.08	3.064(9)	6	12b

[a] DTolF = *N*,*N*′-di-*p*-tolylformamidinate anion. [b] The numbers outside parentheses are relative to **4**; those within the parentheses are compared to $Mo_2(hpp)_4(BF_4)_2$. [c] The net stoichiometry is $W_2(hpp)_4Cl$. Each axial position is half occupied by a chlorine atom.

derivative having a neopentyl (np) group at each of the axial sites.[41] Here the Mo−Mo distance is 2.1302(6) Å, and the average Mo−O distance is 2.103(1) Å. For comparison, the Mo−Mo bond length in Mo_2(2,4,6,-triisopropylphenylcarboxylate)$_4PF_6$, Mo_2(2,4,6,-triisopropylphenylcarboxylate)$_4BF_4$, and $Mo_2(pivalate)_4PF_6$ are 2.1364(8), 2.1441(5), and 2.1512(5) Å, respectively, and the corresponding average Mo−O distances are 2.066, 2.067, and 2.077 Å. Thus the Mo−Mo bond distance in the Mo_2^{6+} species is slightly shorter than those in Mo_2^{5+} compounds, and the corresponding average Mo−O distances are longer. It is important to note, however, that in the triply bonded Mo_2^{6+} species the axially coordinated neopentyl groups are presumably covalently bonded to the Mo atoms (M−C = 2.103(1) Å) while the anions in the Mo_2^{5+} carboxylates do not interact strongly with axial ligands. It does not seem reasonable to compare a compound of the $Mo_2(O_2CR)_4R'_2$-type with the $Mo_2(O_2CR)_4^+$ or $Mo_2(hpp)_4^{n+}$ (n = 1, 2) types. The bonding in the $Mo_2(O_2CR)_4R'_2$ type molecule, along with several analogous W_2^{6+} complexes was described as $\pi^4\delta^2$. However, this does not appear to be an entirely satisfactory explanation, since it seems very peculiar that removal of a σ bond from the M_2 manifold would strengthen the M_2 bond enough to break the trend of increasing M−M distances as the oxidation of Mo_2^{4+} species takes place. More work will be needed to reconcile this apparent discrepancy.

Magnetic Behavior. ^{1}H NMR data clearly show that **4**, having the Mo_2^{6+} core, is diamagnetic as is **1**, the parent Mo_2^{4+} complex. For **4** there are a sharp triplet and quintet centered at 3.30 and 2.01 ppm, respectively, that integrate in the expected ratio of 2:1. For all of the Mo_2^{5+} compounds the ^{1}H NMR gives only very broad signals which are typical of paramagnetic substances. The presence of the expected unpaired electron was confirmed by variable-temperature magnetic measurements (see Supporting Information) and the EPR spectrum of **2** in CH_2Cl_2 glass at 13 K which shows a metal-centered free radical signal with values of $g_\perp = g_\| = 1.94$ similar to those found in $Mo_2(carboxylate)_4^+$ species.[40] In a tetraguanidinato complex of Cr_2^{5+}, namely $Cr_2[(PhN)_2CN(CH_2)_4]_4PF_6$, the g value was 1.973.[42]

Electrochemistry. The recent creation of extended structures with multiple Mo_2^{4+} units, for example, pairs, loops, triangles, squares, cages, and more complex architectures has allowed further electrochemical study of Mo_2^{4+} units.[43] In these a range of electronic interactions between Mo_2 units occur through the linker ligands as oxidation of the entire supramolecule proceeds.[44] In this class of compounds the maximum extent of electrochemical oxidation thus far observed leads to four Mo_2^{5+} units in one molecule and never to an Mo_2^{6+} species.[45] Thus, to gain insight into the apparent ability of hpp to stabilize higher oxidation numbers in dimetal units we decided to study the electrochemistry of the $Mo_2(hpp)_4$ system. Solubility problems precluded the use of the traditional conditions in obtaining a cyclic voltammogram (CV) or a differential pulse voltammogram (DPV). However, a search of less common electrochemical media revealed $Bu_4NBF_4\cdot 3$toluene, first described by Pickett[26] and further characterized by Fry and Touster,[27] to be suitable for this purpose. The CV and DPV of $Mo_2(hpp)_4$ show two waves corresponding to reversible one-electron processes at $E_1 = -0.444$ V and $E_2 = -1.271$ V versus Ag/AgCl (Figure 5). Under these conditions, the ferrocene/ferrocenium couple is found at +0.524 V, and the $Mo_2(DTolF)_4/Mo_2(DTolF)_4^+$ couple is at +0.417 V. For comparison, the latter was reported at +0.333 V for a measurement carried out in CH_2Cl_2 with Bu_4NBF_4 as the supporting electrolyte.[46]

For these values to be compatible with the chemistry described above, the dominant species at the resting point must be the doubly oxidized Mo_2^{6+} species. Thus, the $E^1_{1/2}$ must correspond to the reduction to Mo_2^{5+}, and the $E^2_{1/2}$ at −1.271 V must be associated with the second reduction to the neutral $Mo_2(hpp)_4$ complex.

The number of reports on electrochemical behavior of M_2 (Mo and W) formamidinates, carboxylates, and related ligands is rather limited. Some have already been mentioned above,[40,41,43−46] but others are also relevant.[47] Some data are summarized in Figure 6. It is important to note that potentials are relative to Ag/AgCl and that the data have been collected

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(41) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Van Der Sluys, W. G.; Kober, E. M.; Lichtenberger, D. L.; Bursten, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 6796.

(42) Cotton, F. A.; Daniels, L. M.; Huang, P.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 317.

(43) (a) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759. (b) Cotton, F. A.; Lin, C.; Murillo, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4810.

(44) See for example: Cotton, F. A.; Donahue, J. P.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 1234.

(45) Cotton, F. A.; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **2001**, *123*, 2670.

(46) Lin, C.; Protasiewicz, J. D.; Smith, E. T.; Ren, T. *Inorg. Chem.* **1996**, *35*, 6422.

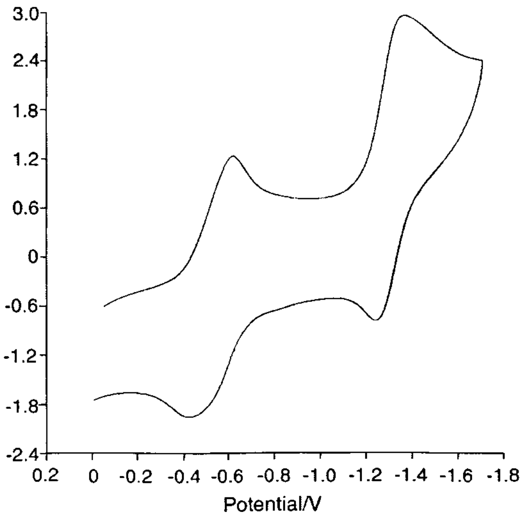

Figure 5. Cyclic voltammogram of $Mo_2(hpp)_4$, **1**, in $Bu_4NBF4 \cdot 3$toluene with potentials referenced vs Ag/AGCl showing two reversible one-electron events at $E^1_{1/2} = -0.444$ V and $E^2_{1/2} = -1.271$ V. Under these conditions, the ferrocene/ferrocenium couple appeared at +0.524 V.

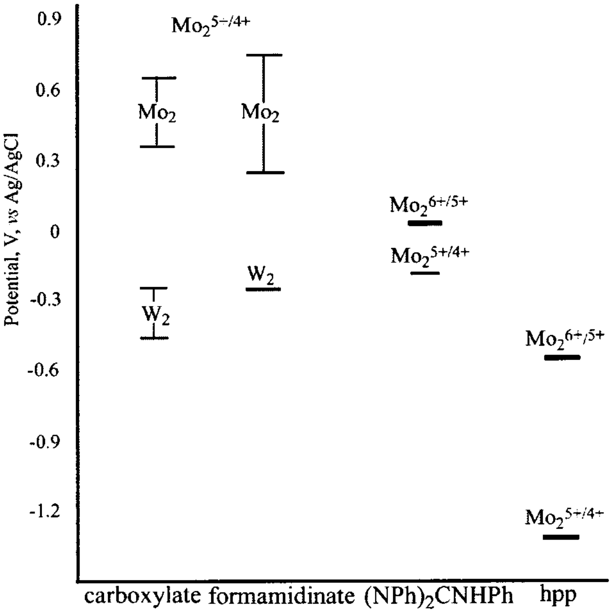

Figure 6. Variation in potentials as a function of ligand for paddlewheel complexes of the type M_2L_4, M = Mo, W. The data were compiled as follows: for carboxylates from reference 40, for formamidinates from reference 46, for $(HPh)_2CNHPh$ from reference 37, and for hpp the data are from this work.

in a variety of conditions that might be expected to change the potentials by a few millivolts. Nevertheless, some of the trends observed are overwhelmingly clear. For example, oxidation of comparable quadruply bonded W_2^{4+} species is significantly easier (by >0.5 V) than those having Mo_2^{4+} units. It is also apparent that oxidation of formamidinates is not significantly different than that of carboxylates, although variation of substituents in the aryl groups provides considerable tunability of the potentials.[46] However, the most amazing observation is the very large magnitude of the change of the potential as the ligands are modified to include the guanidinate core, CN_3, especially for those of the hpp ligand. Here the $E_{1/2}$ for the process:

$$Mo_2(hpp)_4^+ + 1e \rightarrow Mo_2(hpp)_4$$

is ~1.5 V apart from that of the corresponding process for the tetraformamidinate having anisyl groups (p-C_6H_4OMe) and almost 2.0 V from that of p-$C_6H_4CF_3$. Thus, such an enormous shift in the electrode potential is what allows the observation of an electrochemical wave for the process corresponding to:

$$Mo_2^{5+} \rightarrow Mo_2^{6+} + 1e$$

The reduction potential at −0.444 V (Figure 5) indicates that even the oxidation of $Mo_2(hpp)_4^+$ is far easier than that of any of the neutral tetraformamidinate or tetracarboxylate species, M_2L_4. This great ability of the guanidinate-type ligands to stabilize higher oxidation numbers places them in a unique new category among the ligands that have revolutionalized the chemistry of metal−metal compounds. These allow another quantum jump and the creation of a category of highly oxidized paddlewheel dimetal units.

The increased stability of higher oxidation number given to dimetal units by hpp is further supported by the isolation of other M_2^{6+} compounds, for example, M = W,[12b] Re,[48] Ru[10], Os,[12b] Ir,[21] Pd,[20] and Pt.[12b] There are other signs that this generality does exist. It has also been reported[10] that $Ru_2(hpp)_4^{2+}$ can be reversibly oxidized to $Ru_2(hpp)_4^{3+}$, the only known case of Ru_2^{6+} to Ru_2^{7+}. In addition, we have recently prepared and characterized the first Os_2^{7+} species, $Os_2(hpp)_4(BF_4)_3$.[49]

It appears that one of the reasons for this behavior is the presence of the guanidinate skeleton with the partial C−N double bond character of each of the three bonds as shown by the short distances (vide supra). However, important differences between hpp and $(NPh_2)_2CNHPh$ also indicate that it is likely that electronic effects from substituents must play a role (e.g., changes in basicity). The rigidity imposed by the fusion of the two rings in the hpp ligand could also be important.

To evaluate the relative importance of various factors it will be necessary to create new ligands of the guanidinate type; those having additional arms will be particularly appealing because they should also increase solubility of the dinuclear units. Efforts to develop the necessary synthetic chemistry are currently underway in our laboratory.

Comparison with $Mo_2[Mo(CO)_4(PhPO_2)_2]_2^{4-}$. At the same time we were studying the $Mo_2(hpp)_4^{n+}$ system, we were reinvestigating a compound reported earlier[50] as $(Bu_4nN)_2H_2$-$\{Mo_2[Mo(CO)_4(PhPO_2)_2]\}_2$. We have determined that the two hydrogen atoms in the originally proposed formula are not present, and thus the Mo_2 unit contains a triple, not a quadruple, bond and should be regarded as an Mo_2^{6+} unit.[51] Interestingly, electrochemical study shows that for such a system there is one (not two) chemically reversible one-electron wave at the very

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(47) See for example: (a) Cotton, F. A. Pederson, E. *Inorg. Chem.* **1975**, *14*, 399. (b) Santure, D. J.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1985**, *24*, 371. (c) Cotton, F. A.; Ren, T. *J. Am. Chem. Soc.* **1992**, *114*, 2237.

(48) Cotton, F. A.; Gu, J.; Murillo, C. A.; Timmons, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 3741.

(49) Cotton, F. A.; Huang, P.; Murillo, C. A. Unpublished results.

(50) Wong, E. H.; Valdez, C.; Gabe, E. V.; Lee, F. L. *Polyhedron* **1989**, *8*, 2339.

(51) Cotton, F. A.; Daniels, L. M.; Liu, C. Y.; Murillo, C. A.; Schultz, A. J.; Wang, X. *Inorg. Chem.* **2002**. In press.

negative potential of −1.54 V versus Ag/AgCl that corresponds to the process $Mo_2^{6+} + e \rightarrow Mo_2^{5+}$.

Thus, the stabilization of the Mo_2^{5+} and Mo_2^{6+} cores is effected by two very different types of ligand: the hpp anion and the *cis*-$[Mo(CO)_4(PhPO_2)_2]^{4-}$ tetraanion. The key to the action of the hpp ligand is its extremely high basicity coupled with its ability to interact with the Mo_2^{n+} cores via its delocalized π orbitals. For the *cis*-$[Mo(CO)_4(PhPO_2)_2]^{4-}$ ion, the key feature is the large amount of negative charge, 8−, distributed over eight oxygen atoms.

Comproportionation Constant, K_C. From the electrochemical data provided above, and using the $\Delta E_{1/2}$ values, measured by the method of Richardson and Taube,[52] it is possible to calculate the comproportionation constant for the process

$$Mo_2(hpp)_4 + Mo_2(hpp)_4^{2+} \rightleftharpoons 2Mo_2(hpp)_4^{+}$$

The equilibrium constant at 298 K, K_C, is given by the expression[53] $K_C = \exp(\Delta E_{1/2}/25.69)$ where $\Delta E_{1/2}$ is the separation for successive one-electron processes in millivolts.

Thus, for $E^1_{1/2}$ of −0.444 V and $E^2_{1/2}$ of −1.271 V, the $\Delta E_{1/2}$ is 827 mV, and K_C is 9.56×10^{13}, indicating that the equilibrium strongly favors the monooxidized species. This is not due to the lack of stability of the $Mo_2(hpp)_4^{2+}$ species but to the apparently disfavored $Mo_2(hpp)_4$ complex, a phenomenon observed now for the first time in quadruply bonded Mo_2^{4+} species.

Because of the large value of K_C, it should be no surprise that the cation $Mo_2(hpp)_4^{+}$ forms even by reaction of $Mo_2(hpp)_4$ with CH_2Cl_2 at room temperature. A cyclovoltammogram of the solvent CH_2Cl_2 (1 mM in Bu_4NBF_4·3toluene) shows a chemically and electrochemically irreversible reduction wave at −1.114 V. At this potential, CH_2Cl_2 is able to oxidize $Mo_2(hpp)_4$ to the corresponding monocation.

Some Additional Thoughts. At least two aspects of the present work provoke some thoughts on biological systems. One is the known toxicity of CH_2Cl_2 and the reduction via production of free radicals.[54] The other aspect is the importance of guanidinate groups in living processes.[55]

It has been proposed that possible mechanisms that lead to reduction of alkyl halides, for example, CH_2Cl_2, are the following types:[32]

$$R{-}X + e \rightarrow R^{\bullet} + X^{-} \text{ (electrochemical)}$$

$$R{-}X + A^{\bullet -} \rightarrow R^{\bullet} + X^{-} + A \text{ (homogeneous)}$$

where $A/A^{\bullet -}$ is a chemically stable redox couple reacting in an outer-sphere manner. Such single-electron-transfer reactions have been shown to play an important role in homogeneous chemistry and also in photochemistry. Interestingly, the action of free radicals has long been implicated in cancers and many degenerative diseases.[56] Thus, it is not surprising to see a very large number of studies on the toxicity of CH_2Cl_2.[57]

It is noteworthy that the reaction of $Mo_2(hpp)_4$ with CH_2Cl_2 leads to the reduction of the dihalomethane and concomitant formation of metal-based radicals as shown by the EPR spectra (vide supra). This reaction is occurring because of the high stabilization of the oxidized dimetal units by the hpp ligands which are guanidine derivatives.

This might be relevant to biological systems as it is known that many enzymes containing dimetal units with bridging ligands do participate in many redox processes.[58] From what we have shown in this work, it is clear that very large changes in potentials can be created by the nature of the ligands.

The capacity of changes in ligands (or in any other, or additional, component of the environment) surrounding a metal atom, or group of metal atoms, to modify the oxidation potential of the metal atom (or group) is as fundamental a question as any in chemistry. With the evolution of our knowledge of bioinorganic chemistry, the question has taken on still wider interest and significance.[59] We have shown here a dramatic example of how to change the redox potential of a metal unit simply by modifying the ligands.[60]

Concluding Remarks

We have completed the series $Mo_2(hpp)_4^{n+}$ for $n = 0$, 1, and 2. We have now also shown that the electrode potentials of bonded dimolybdenum units are extraordinarily sensitive to variations resulting from ligand changes. Variations of more than 1.5 V in the potentials of such Mo_2 units open up the possibility, inter alia, of using them as sensors that could be fine-tuned by small variations in the substituents.

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Supporting Information Available: PDF plots of χT, $1/\chi$, and χ vs temperature for **2** and X-ray crystallographic files in CIF format for compounds **2**, **2**·$2CH_2Cl_2$, and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(60) In making this statement we set several defining conditions to avoid ambiguity: (1) only ligands, not any aspect of the redox center itself, are changed; (2) the redox reaction occurs at the metal atom (or cluster of metal atoms) as demonstrated by EPR spectroscopy; (3) in each couple, the redox reaction entails no change in the ligands other than small ones that are unavoidable in view of the alteration of the charge on the redox center; (4) spin states on corresponding sides of the couples being compared are the same; thus, for example, we exclude comparing $Fe(H_2O)_6^{2+}/Fe(H_2O)_6^{3+}$ (both high-spin) with $Fe(CN)_6^{2-}/Fe(CN)_6^{3-}$ (both low-spin), or $Co(NH_3)_6^{2+}/Co(NH_3)_6^{3+}$ (high- to low-spin) with $Co(H_2O)_6^{2+}/Co(H_2O)_6^{3+}$ (high-spin to high-spin).