

# Photoelectron Spectroscopy and DFT Calculations of Easily Ionized Quadruply Bonded Mo<sub>2</sub><sup>4+</sup> Compounds and Their Bicyclic Guanidinate Precursors<sup>†</sup>

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A series of five bicyclic guanidinate compounds containing various combinations of five- and six-membered rings and substituted alkyl groups have been shown by photoelectron spectroscopy to be easily ionized, with the one having two six-membered rings and four ethyl groups being the most easily ionized. The corresponding anions are capable of forming paddlewheel compounds having quadruply bonded Mo<sub>2</sub><sup>4+</sup> units which are also easy to ionize. The most easily ionized compound is the ethyl-substituted Mo<sub>2</sub>(TEhpp)<sub>4</sub> complex which has a broad first ionization band centered around 4.27 ± 0.03 eV and an ionization onset at the very low energy of 3.93 ± 0.03 eV. Even the compound with ligands containing two five-membered rings, which favors a long Mo–Mo separation because of the large ligand bite, has an ionization energy (4.78 eV) that is less than those of well-known organometallic reducing agents such as (η<sup>5</sup>-C<sub>9</sub>Me<sub>7</sub>)<sub>2</sub>Co and (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cr.

## Introduction

It has been established that guanidinate derivatives have an extraordinary ability to lower oxidation potentials and in turn stabilize higher oxidation numbers in compounds that feature quadruply bonded units such as Cr<sub>2</sub><sup>4+</sup>, Mo<sub>2</sub><sup>4+</sup>, and W<sub>2</sub><sup>4+</sup>.<sup>1</sup> This capacity is also manifested in the gas phase and indeed W<sub>2</sub>(hpp)<sub>4</sub><sup>2</sup> (hpp = the anion of the bicyclic guanidine 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2a]pyrimidine) is the most easily ionized molecule known. The onset ionization energy of W<sub>2</sub>(hpp)<sub>4</sub> (3.51 eV)<sup>2</sup> is even lower than that of the cesium atom (3.89 eV).<sup>3</sup> The dimolybdenum analogue, Mo<sub>2</sub>(hpp)<sub>4</sub>, has an onset ionization that is only slightly higher (4.01 eV) but still less than that of the francium and rubidium atoms.<sup>2</sup>

When the noncyclic triphenylguanidinate anion is used to bridge Mo<sub>2</sub><sup>4+</sup> units, stabilization of Mo<sub>2</sub><sup>5+</sup> and even Mo<sub>2</sub><sup>6+</sup> cores is observed.<sup>4</sup> However, this noncyclic ligand is far less efficient at stabilizing high oxidation states in dimetal units as shown by the fact that the potential for the Mo<sub>2</sub><sup>5+/4+</sup> process is about 1.2 V more positive than for the hpp compound.<sup>5</sup>

The reason for the ease of ionization of quadruply bonded M<sub>2</sub>(hpp)<sub>4</sub> compounds is that the π electrons of the highly basic guanidinate core strongly interact with the electrons in the M–M δ bond<sup>2a</sup> thereby destabilizing the M<sub>2</sub><sup>4+</sup> core and favoring oxidation to the relatively uncommon M<sub>2</sub><sup>5+</sup> and even rarer M<sub>2</sub><sup>6+</sup> species.

Because of such extraordinary properties of the M<sub>2</sub> compounds with these ligands and also because of the general interest in guanidinate ligands,<sup>6</sup> which have also been commonly used to stabilize mononuclear compounds<sup>7</sup> many of which are used in polymerization catalysis,<sup>8</sup> we decided to explore more

bicyclic guanidates to determine how changes in the geometry constraints of the fused-ring ligand system and/or addition of electron-donating substituents affect the ability of the anions to stabilize or destabilize charge in M<sub>2</sub> systems.

It should be noted that ligand tunability, the modification of electronic structure to achieve a desired property of the molecular system, has valuable applications in many areas of science. Specifically, the ability to control the ease with which an electron can be removed from a molecule is crucial for electron-transfer reactions, catalysis, and materials applications.<sup>9–13</sup>

We report here four bicyclic guanidinate ligands that have never been used before in coordination chemistry along with studies of some of their Mo<sub>2</sub><sup>4+</sup> species. In Figure 1, the ligand at the top is hpp, the benchmark for comparison of the modified ligands. The hpp anion has a 6,6 ring system with 12 hydrogen atoms on the 6 ancillary carbon atoms. In the middle of the figure are tbo and tbn. The first one, tbo, is the anion of 1,4,6-triazabicyclo(3.3.0)oct-4-ene. It has a 5,5 ring system containing 8 hydrogen atoms on the 4 ancillary carbon atoms. The second one, tbn, is the anion of 1,4,6-triazabicyclo(3.4.0)-non-4-ene, and it has a 5,6 ring system with 10 hydrogen atoms on the 5 ancillary carbon atoms. The bottom of the figure shows TMhpp and TEhpp. The former, TMhpp, is the anion of 3,3,9,9-tetramethyl-1,5,7-triazabicyclo[4.4.0]dec-4-ene and has a 6,6 ring system with the 4 hydrogen atoms on the carbon atom midway between the nitrogen atoms of each ring replaced with methyl groups. The latter, TEhpp, which is the anion of 3,3,9,9-tetraethyl-1,5,7-triazabicyclo[4.4.0]dec-4-ene, also has a 6,6 ring system but with the 4 hydrogen atoms on the corresponding carbon atoms replaced with ethyl groups.

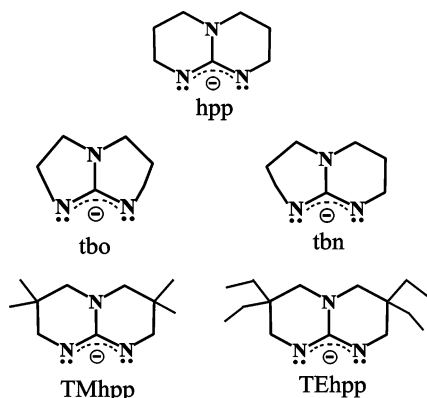
It should be noted that as a key feature for tbo and tbn there is a divergent angle between the bond directions from the ligating nitrogen atoms relative to hpp, while for TMhpp and TEhpp the alkyl groups have been inserted for the main purpose of enhancing solubility of the Mo<sub>2</sub>(bicyclic guanidinate)<sub>4</sub> compounds and have no first-order effect on the bite. This is

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**Figure 1.** Structures of the anions hpp, tbo, tbn, TMhpp, and TEhpp.

intended to be useful for their application as reducing agents. However, the alkyl groups may also affect the electron-donating properties relative to hpp.

We also report the ionization energies of Hhpp, Htbo, Htbn, HTMhpp, and HTEhpp ligands which have been determined using photoelectron spectroscopy and compare the ionization energies of  $\text{Mo}_2(\text{tbo})_4$  and  $\text{Mo}_2(\text{hpp})_4$ , and we provide preliminary spectra for the  $\text{Mo}_2(\text{tbn})_4$ ,  $\text{Mo}_2(\text{TMhpp})_4$ , and  $\text{Mo}_2(\text{TEhpp})_4$  molecules as well.

## Experimental Methods

**General Synthetic Methods.** All compounds were made under nitrogen. The ligand precursors Htbo, Htbn were prepared using slightly modified published procedures.<sup>14</sup> The alkyl-substituted compounds HTMhpp, HTEhpp were made according to Scheme 1 following slightly modified published procedures for the synthesis of bicyclic guanidinate.<sup>14,15</sup> The quadruply bonded compounds,  $\text{Mo}_2(\text{bicyclic guanidinate})_4$ , were made similarly to  $\text{Mo}_2(\text{hpp})_4$ .<sup>16</sup>

**Photoelectron Spectroscopy.** The photoelectron spectra were recorded using an instrument that features a 36 cm radius, 8 cm gap hemispherical analyzer,<sup>17</sup> and custom designed sample cells and detection and control electronics.<sup>18</sup> The argon  $2\text{P}_{3/2}$  ionization at 15.759 eV was used as an internal calibration lock of the absolute ionization energy. The difference between the argon  $2\text{P}_{3/2}$  and the methyl iodide  $2\text{E}_{1/2}$  ionization at 9.538 eV was used to calibrate the ionization energy scale. During data collection, the instrument resolution, measured using the full width at half-maximum of the argon  $2\text{P}_{3/2}$  ionization, was 0.020–0.038 eV. All data were intensity corrected with an experimentally determined instrument analyzer sensitivity function that assumes a linear dependence of analyzer transmission to the

kinetic energy of the electrons within the energy range of these experiments. The sublimation temperature was monitored using a “K” type thermocouple passed through a vacuum feedthrough and attached directly to the cell.

Under the experimental conditions, the sublimation temperatures ( $^{\circ}\text{C}$ ) for these guanidinate compounds were Hhpp 25, Htbo 25, Htbn 30, HTMhpp 25, HTEhpp 80,  $\text{Mo}_2(\text{hpp})_4$  158,  $\text{Mo}_2(\text{tbo})_4$  227,  $\text{Mo}_2(\text{tbn})_4$  181,  $\text{Mo}_2(\text{hpp})_4$  225,  $\text{Mo}_2(\text{TMhpp})_4$  280, and  $\text{Mo}_2(\text{TEhpp})_4$  205.

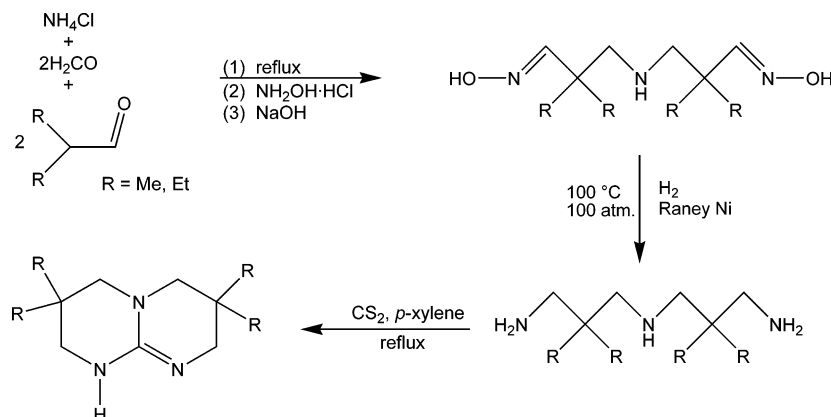
**Data Analysis.** The ionization bands in the photoelectron spectra are represented analytically with asymmetric Gaussian peaks, consistent with Poisson distributions of unresolved vibrational components.<sup>19</sup> Attention is focused on the first ionization band of these molecules. The first ionization band of the protonated ligands is modeled well with a single asymmetric Gaussian band. In the spectra of each of the  $\text{Mo}_2(\text{bicyclic guanidinate})_4$  molecules, the first ionization band is broad and gives evidence of two or more conformers (or possible isomers in the case of the  $\text{Mo}_2(\text{tbn})_4$  molecule) in the gas phase. The minimum number of Gaussian peaks with reasonable widths and shapes was used to represent the contours of the data. In the displays of the spectra, the experimental variances of the photoelectron counts are represented by the vertical length of each data mark and the overall fit of the contour is represented by the heavy solid line. The Gaussian peaks used to obtain the fit of the overall band contour are also shown, but the individual peaks should not be ascribed to any physical significance other than their statistical necessity for modeling the contour. A more detailed discussion of the fitting procedures has been given elsewhere.<sup>19</sup>

**Computational Studies.** Electronic structure calculations were carried out with the program ADF2002.02.<sup>20–23</sup> The PW91 density functional was used for all calculations.<sup>24,25</sup> The atomic orbitals on all centers were described by an uncontracted triple- $\zeta$  STO basis set with one polarization function (TZP) that is available with the ADF package. Relativistic effects were included in all calculations by the scalar ZORA formalism implemented as a part of the ADF2002 program.<sup>26–31</sup> All reported atomic charges are from Voronoi deformation densities.<sup>32</sup>

## Results and Discussion

**Electronic Structure of the Ligand Precursors.** By changing the geometry constraints due to ring fusion or the substituents on the guanidinate core, a change in the energy of the first ionization is seen in the He I valence photoelectron spectra of the protonated ligands shown in Figure 2. The low valence

## SCHEME 1



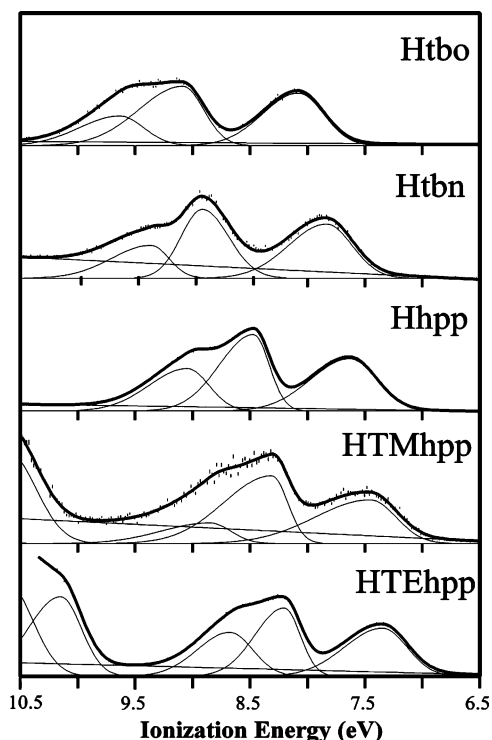


Figure 2. Photoelectron spectra of the bicyclic guanidinate derivatives.

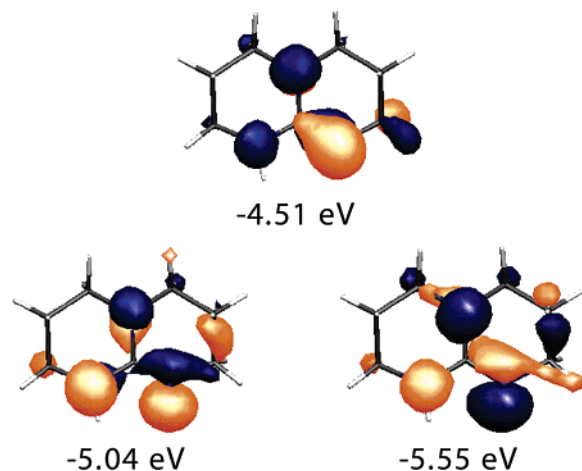


Figure 3. Highest occupied orbitals of Hhpp.

photoelectron spectrum of the Hhpp molecule has been reported previously and, other than the lower signal-to-noise ratio in the previous spectrum, displays the same ionization features and energies within the uncertainty of the experiment.<sup>33</sup> All ligand precursors have a broad single peak as their first feature which is modeled well with a single asymmetric Gaussian peak. The next profile arises from two overlapping ionizations. The top three occupied molecular orbitals as obtained from the electronic structure calculations are shown in Figure 3. The highest occupied molecular orbital (HOMO) is predominantly the N=C  $\pi$  bond mixed in an antisymmetric fashion with the out-of-plane p orbital lone pairs of both the protonated nitrogen and the nitrogen shared between the fused rings. The next two orbitals are combinations of the in-plane lone pair of the unprotonated nitrogen with the out-of-plane p orbitals of the other two nitrogen atoms. The mixing of the in-plane lone pair with the out-of-plane p orbitals is allowed because of the nonplanarity of Hhpp (discussed later), but the two combinations are not expected to be widely different in energy.

TABLE 1: Experimental Ionization Features of the Protonated Guanidinate Ligands

ligand	peak position (eV)	width-high <sup>a</sup> (eV)	width-low <sup>a</sup> (eV)	rel. area
Htbo	8.08	0.73	0.51	100
	9.08	0.90	0.43	121
	9.64	0.82	0.49	60
Htbn	7.83	0.77	0.53	100
	8.91	0.44	0.53	95
	9.36	0.81	0.37	55
Hhpp	7.63	0.80	0.54	100
	8.47	0.70	0.32	111
	9.05	0.78	0.44	74
HTMhpp	7.45	1.13	0.52	100
	8.31	0.98	0.32	123
	8.85	0.99	0.42	41
HTEhpp	7.35	0.78	0.50	100
	8.20	0.60	0.33	103
	8.68	0.67	0.47	81

<sup>a</sup> Width-high and width-low are the half-widths for the asymmetric Gaussian peak on the high binding energy side and low binding energy side of the peak, respectively, which along with the position and the intensity define the model Gaussian band shape. See ref 19.

TABLE 2: Photoelectron Spectroscopic and Computationally Determined First Ionization Energies for Protonated Guanidinate Ligands (eV)

ligand	HOMO	experimental	$\Delta E_{\text{SCF}}$	experimental - $\Delta E_{\text{SCF}}$
Htbo	-4.72	8.08	7.77	0.31
Htbn	-4.62	7.83	7.53	0.30
Hhpp	-4.51	7.63	7.37	0.26
HTMhpp	-4.45	7.45	7.20	0.25
HTEhpp	-4.44	7.35	7.08	0.27

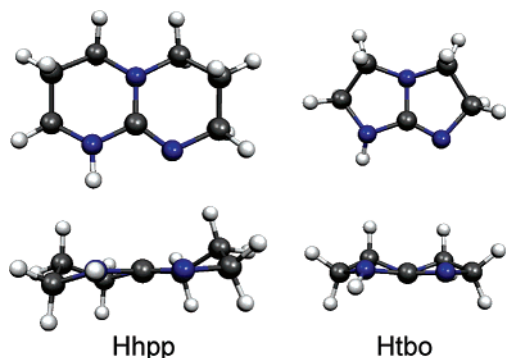
The low ionization energy peak positions, relative areas, and half-widths for all the ligand precursors are given in Table 1. The alkylated Hhpp derivatives (HTEhpp and HTMhpp) have first ionization energies lower than that of Hhpp, but those containing five-membered rings (Htbn and Htbo) have energies that are higher than that of Hhpp. The ionization energies of this series of molecules follow a general trend of decreasing ionization energy with increasing number of ancillary carbon atoms in the molecule. The Htbo molecule has four ancillary carbon atoms, Htbn has 5, Hhpp has 6, HTMhpp has 8, and HTEhpp has 10 ancillary carbon atoms.

The experimental and calculated first ionization energies for the five protonated precursors are compared in Table 2. Although the ionization energies calculated by the  $\Delta E_{\text{SCF}}$  method are consistently lower than the experimental values, the difference of ca. 0.3 eV is rather constant. Furthermore, in all cases, the trend follows the correct order, namely, that the compounds with low experimental values are calculated with low values and similarly for those with high values. Thus, the shifts in the first ionization energies are accounted for reasonably well by the  $\Delta E_{\text{SCF}}$  computations. The decreasing ionization energies in this series with increasing numbers of ancillary carbon atoms may be interpreted as an inductive effect that either destabilizes the energy of the HOMO in the neutral molecule or stabilizes the positive charge in the cation. Comparison of the shifts in the HOMO energies with the  $\Delta E_{\text{SCF}}$  ionization energies in Table 2 shows that both mechanisms are operable but the latter is the dominant factor. For example, the calculated shift in the HOMO energy between HTEhpp and HTMhpp is only 0.01 eV, but the shift in calculated ionization energy taking into account electron relaxation in the positive ion is 0.12 eV. The greater electron relaxation energies of the larger molecules are most important in this series.

**TABLE 3: Charges on the Nitrogen Atoms of Guanidinate Ligand Anions and Relative HOMO Energies**

ligand	HOMO (eV)	N' charges <sup>a</sup>	N'' charge <sup>b</sup>
tbo	1.08	−0.391	−0.157
tbn	1.06	−0.381	−0.145
hpp	1.22	−0.369	−0.131
TMhpp	1.01	−0.368	−0.124
TEhpp	0.88	−0.367	−0.123

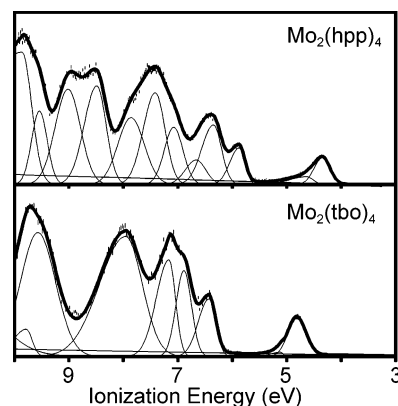
<sup>a</sup> N' are the two nitrogen atoms that coordinate to the metal. <sup>b</sup> N'' is the nitrogen atom shared between the fused rings.

**Figure 4.** Geometry-optimized structures of Hhpp and Htbo. The bottom view shows the puckering of the rings.

**Ligand Factors Determining Low Ionization Energies of  $M_2(L\wedge L)_4$  Paddlewheel Molecules.** Although the experimental valence ionizations and density functional calculations of the protonated ligands give an understanding of the basic ligand electronic structures, several factors must be considered in regard to how these electronic structures contribute to low ionization energies in  $M_2(L\wedge L)_4$  paddlewheel molecules. First is the overall electron distribution in the ligands and orbital energies, and next is orbital overlap interaction between the ligands and the metals and between the metal atoms themselves.

Table 3 gives the calculated atomic charges of the nitrogen atoms and the relative HOMO energies of the free guanidinate ligand anions. The trend is an increase in negative charge on the nitrogen atoms from TEhpp to tbo, which is counterintuitive from the trend of increasing ionization energies of the protonated molecules in this series from HTEhpp to Htbo. Increasing negative charge generally is associated with lower ionization energies. The explanation is that in the case of the ionization energies of the protonated ligands, the larger molecules with the greater number of ancillary carbon atoms have a greater ability to stabilize the cations resulting from ionization by relaxation of the electron density toward the positive hole. Similarly, in the series of ligand anions, the larger molecules have a greater ability to stabilize the negative charge by delocalization of electron density in the opposite direction.

Equally interesting are the relative HOMO energies. According to these calculations, hpp has the least stable HOMO. Both TEhpp and TMhpp give rise to more stable anions, partly due to the stabilization of negative charge in the larger molecules as mentioned above. The tbn and tbo anions also have more stable HOMO energies than hpp, suggesting that the charge effects in the negative ions are overcome by the decreasing 6,5 and 5,5 ring sizes in tbn and tbo, respectively. The decreasing ring sizes of tbn and tbo also have an effect on the ligand orbital interactions with the metals. Figure 4 shows the geometry-optimized structures of Hhpp and Htbo. It may be noted that these molecules have the possibility of different conformers according to the puckering of the saturated carbon atoms in the rings. The conformers shown have the related carbon atoms on

**Figure 5.** Photoelectron spectra of  $Mo_2(tbo)_4$  and  $Mo_2(hpp)_4$ .

each half of the molecules either both above or both below the mean plane of the guanidinate core, such that the fused bond is in an approximate plane of symmetry between the two halves of the molecules. In an alternative conformation, each related pair of carbon atoms on the two halves of the molecule are on opposite sides of the mean plane, such that the fused bond is an approximate  $C_2$  symmetry axis. Regardless of the conformations, the calculations show two significant differences between Hhpp and Htbo which are consequences of the constraints imposed by the smaller ring sizes in Htbo. First, the direction of the N–H bond of Hhpp is tilted toward the other nitrogen atom that will be bound to the  $Mo_2$  unit, whereas in Htbo the N–H bond is tilted away from the other nitrogen atom. Because the same is expected for the lone pairs in hpp and tbo, metal–metal distances when tbo is used may be larger than that for hpp and the ligand donation interactions may be weaker due to poorer overlap. Second, the distance between the nitrogen atoms that are used to bind dimetal units in hpp is calculated to be 2.29 Å compared with 2.45 Å for Htbo. This geometry change contributes to the greater stability of the HOMO of tbo compared with hpp mentioned above because of the decreased antibonding interaction between these two nitrogen atoms, and this consequently decreases the donation of electron density from this orbital to the metals. The smaller bite angle for the hpp ligand indicates that it should favor shorter Mo–Mo distances without distortion of the ligand.<sup>34</sup>

**Dimolybdenum Compounds.** The He I photoelectron spectra of  $Mo_2(hpp)_4$  and  $Mo_2(tbo)_4$  are compared in Figure 5. As with the  $M_2(hpp)_4$  molecules, the first ionization feature of  $Mo_2(tbo)_4$  shows a shoulder on the high binding energy side. The first ionization band corresponds to the metal–metal  $\delta$  bond ionization, and the shoulder may be due to the presence of a minor conformer in the gas phase, as described below. The ligand-based ionizations begin in the vicinity of 6 eV. The analytical representation of the ionization features of  $Mo_2(tbo)_4$  is given in Table 4. The  $\delta$  bond ionization of  $Mo_2(tbo)_4$  occurs at about 0.4 eV greater ionization energy than that of  $Mo_2(hpp)_4$ . This shift is similar to that seen for the first ionization of Hhpp to Htbo.

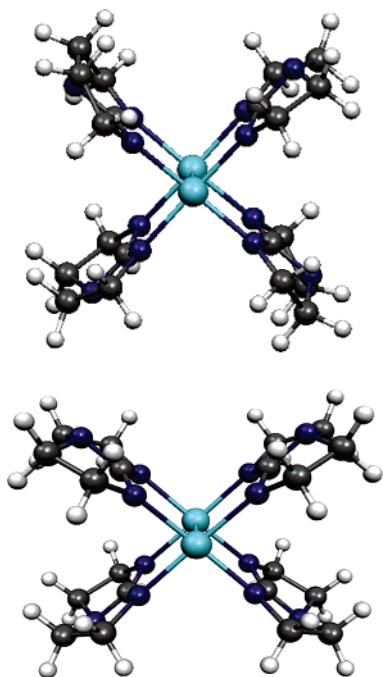
Two geometry-optimized conformations of  $Mo_2(tbo)_4$  (Figure 6) were calculated. In each structure, all of the tbo ligands are in the conformation depicted in Figure 4 and described earlier. In the  $C_{4h}$  structure of the dimetal complex, the 4-fold axis is along the metal–metal bond. In the  $D_{2h}$  structure, the 2-fold axis is orthogonal to the metal–metal bond and lies between the tbo ligands. The structure with  $C_{4h}$  symmetry is the more stable of the two by 0.8 eV. A similar result was obtained for  $Mo_2(hpp)_4$ . Other lower symmetry structures are possible but were not investigated. The experimental difference in the first



**TABLE 4: Experimental Ionization Energy Features of  $\text{Mo}_2(\text{tbo})_4$** 

peak position (eV)	width-high <sup>a</sup> (eV)	width-low <sup>a</sup> (eV)	area
4.78	0.39	0.39	100
5.11	0.42	0.10	8
6.43	0.46	0.28	146
6.89	0.34	0.32	196
7.16	0.55	0.28	273
7.96	1.13	0.72	756
9.57	0.76	0.76	640
9.79	0.56	0.26	76

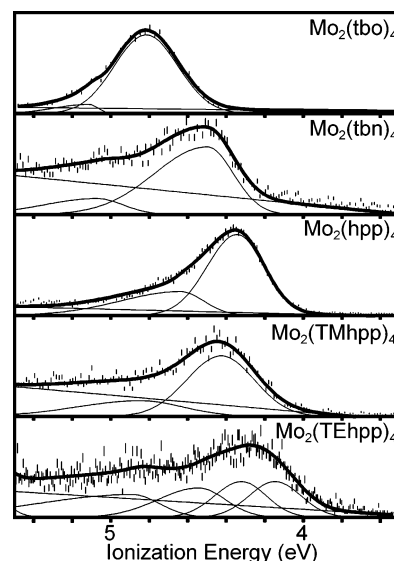
<sup>a</sup> For a definition of width-high and width-low, see the footnote to Table 1.

**Figure 6.** Structures of  $\text{Mo}_2(\text{tbo})_4$  from theoretical calculations:  $C_{4h}$  (top) and  $D_{2h}$  (bottom). The structure with  $C_{4h}$  symmetry is the most stable.

ionization energy between  $\text{Mo}_2(\text{hpp})_4$  and  $\text{Mo}_2(\text{tbo})_4$  is 0.38 eV, and the calculated  $\Delta E_{\text{SCF}}$  ionization energies are different by 0.31 eV.

The Mo–Mo distance for  $\text{Mo}_2(\text{tbo})_4$  is calculated to be 2.18 Å.<sup>35</sup> This is 0.10 Å longer than the Mo–Mo distance calculated for  $\text{Mo}_2(\text{hpp})_4$ .<sup>36</sup> The Mo–N distances are 2.16 Å and essentially unchanged from the calculated distances for  $\text{Mo}_2(\text{hpp})_4$ . The Mo–Mo–N angles are 92.5° and also essentially unchanged from the calculated angles for  $\text{Mo}_2(\text{hpp})_4$ . The distances between nitrogen atoms of the tbo ligand that are used to bind to dimetal units have shortened to 2.38 Å from the distances calculated for Htbo molecules (2.45 Å), while the distances between the metal-bound nitrogen atoms of the hpp ligand (2.30 Å) remain essentially the same as the calculated distance for the protonated Hhpp molecule. It appears that the Mo–N bonds are optimized by adjusting the geometries of the tbo ligands and lengthening the Mo–Mo distance in  $\text{Mo}_2(\text{tbo})_4$  compared with  $\text{Mo}_2(\text{hpp})_4$ . The geometry of the hpp ligand appears to be ideal for both the Mo–Mo bonding and the Mo–N bonding.

The first ionization bands of the  $\text{Mo}_2(\text{L}\wedge\text{L})_4$  molecules are compared for each of the bicyclic guanidinate ligands in this study in Figure 7. The most broad and complex profiles for the first ionization bands are found for the  $\text{Mo}_2(\text{tbn})_4$  and  $\text{Mo}_2(\text{TEhpp})_4$  molecules. In addition to the conformational possibilities already discussed for the  $\text{Mo}_2(\text{tbo})_4$  and  $\text{Mo}_2(\text{hpp})_4$

**Figure 7.** Photoelectron spectra of  $\text{Mo}_2(\text{bicyclic guanidinate})_4$  compounds.**TABLE 5: Energies (eV) of the First Ionization Bands**

molecule	band maximum	band onset
$\text{Mo}_2(\text{tbo})_4$	4.82	4.4
$\text{Mo}_2(\text{tbn})_4$	4.50	4.2
$\text{Mo}_2(\text{hpp})_4$	4.34	4.01
$\text{Mo}_2(\text{TMhpp})_4$	4.43	4.0
$\text{Mo}_2(\text{TEhpp})_4$	4.31	3.93

molecules, the  $\text{Mo}_2(\text{tbn})_4$  molecule has the additional degree of freedom of isomers of head-to-head and head-to-tail orientations of the 5,6 fused rings around the  $\text{Mo}_2$  core. The first ionization of the  $\text{Mo}_2(\text{TEhpp})_4$  molecule has a very broad profile for which the orientations of the ethyl groups may play a role. The only significance to the Gaussian peaks used to fit the bands is that, unlike the first ionizations of the protonated ligands, it takes more than one Gaussian peak to reasonably model the first ionization profile of the  $\text{Mo}_2$  complexes.

The energies of the first ionization bands of these complexes are collected in Table 5. The first ionization band of  $\text{Mo}_2(\text{tbn})_4$  is intermediate to the first ionization bands of  $\text{Mo}_2(\text{tbo})_4$  and  $\text{Mo}_2(\text{hpp})_4$ . The first ionization energy of  $\text{Mo}_2(\text{TMhpp})_4$  is about 0.1 eV greater than the first ionization energy of  $\text{Mo}_2(\text{hpp})_4$ , and the first ionization energy of  $\text{Mo}_2(\text{TEhpp})_4$  is about 0.07 eV less than the first ionization energy of  $\text{Mo}_2(\text{hpp})_4$ . This shows the difficulty of predicting the ionization energy trends of the dimetal complexes based on the trends of the free ligands because of the several competing factors that are involved.

## Conclusions

The photoelectron spectra of a series of bicyclic guanidates (Htbo, Htbn, Hhpp, HTMhpp, and HTEhpp) have shown that these compounds are highly basic and ionize readily. However, those with five-membered rings are less basic than those with two six-membered rings. Alkylated compounds such as HTMhpp and HTEhpp are even more easily ionized than the parent Hhpp.

When the corresponding anions form compounds with quadruply bonded  $\text{Mo}_2^{4+}$  units, the ionization energies are very low, with the lowest due to  $\text{Mo}_2(\text{TEhpp})_4$  (centered near 4.27 eV). The ionization onset of the  $\text{Mo}_2(\text{TEhpp})_4$  molecule is about 0.08 eV less than the ionization onset of the  $\text{Mo}_2(\text{hpp})_4$  molecule. On the basis of previous comparisons of the ionization energies of  $\text{Mo}_2$  and  $\text{W}_2$  complexes with the same ligand sets

and the very low ionization energy of  $W_2(hpp)_4$ ,<sup>2a</sup> the  $W_2-(TEhp)_4$  molecule is a candidate for a new lowest ionization energy of any neutral molecule or atom.<sup>37</sup> However, it should be noted that even the worst performer,  $Mo_2(tbo)_4$ , which has an elongated Mo–Mo bond because of the unfavorable geometry of the ligand, has an ionization energy of 4.78 eV, and this is lower than that of the well-known reducing agents ( $\eta^5-C_9-Me_7$ )<sub>2</sub>Co (4.89 eV)<sup>38</sup> and ( $\eta^5-C_5Me_5$ )<sub>2</sub>Cr (4.93 eV).<sup>39</sup>

It is important to note that the ionization energies of the protonated ligand precursors are not the sole determining factor for the ionization energies of the dimetal compounds because two major factors are decisive in determining the ionization energies of the  $M_2(L\wedge L)_4$  molecules, namely, orbital overlap interactions and the ability of the ligands to stabilize charge. The different geometries of the ligands alter the relevant  $\pi$  orbitals in the guanidinate core (N–C(N)–N) and change the overlap of these orbitals with the metal–metal  $\delta$  orbital which in turn may either strengthen or weaken metal–metal  $\delta$  overlap and bonding.

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