be variously filled, or associated with, different alkali-metal ions, forming equilibrium mixtures between such adducts and true lacunary species. The preparations involved in the present work and in that reported earlier by Acerete et al.[6] have involved a variety of concentrations of K^+, Na^+, and Li^+ ions at various stages. There may be conditions where a V atom or a vanadate attaches to an alkali-metal-containing lacunary differently from the way it attaches to a true lacunary. We have not investigated possible effects of various concentrations of different alkali-metal ions during the preparation.

Acknowledgment. We are grateful to Dr. Christian Brevard, who ran the COSY spectrum for us on his Bruker WM 400 NMR spectrometer. This research was aided by NSF Grant CHE-8406088 and by an instrument grant from the W. M. Keck Foundation.

Registry No. ^{183}W, 14265-81-7; α_2-$[P_2W_{17}O_{61}]^{10-}$, 12412-89-4; α_2-$[P_2W_{17}VO_{62}]^{7-}$, 85585-35-9.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843-3255

Bond-Stretch Isomers of Transition-Metal Complexes. Do They Exist?

Jun Song and Michael B. Hall*

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The existence of bond-stretch isomers of transition-metal complexes and the electronic mechanisms explaining these isomers are investigated with ab initio calculations. For $(LWOCl_2)^+$ (L = *N,N',N''*-trimethyl-1,4,7-triazacyclononane) complexes, only the $^2A'$ state can be identified as a ground state. $^2A''$ is an excited state, and the orbital crossing mechanism cannot explain the occurrence of two stable isomers. For *cis-mer*-$MoOCl_2(PR_3)_3$ complexes, the second-order Jahn–Teller effect is too weak to cause the bond-stretch phenomenon. On both molecular systems, our calculations support the structure of the blue "isomer" as the stable compound and preclude the existence of any other isomer with a long M–O bond and similar energy.

Introduction

The term "bond-stretch isomerism" was proposed by Jean et al.[1] to describe complexes that have the same composition and geometry but differ only in the length of certain bonds. This phenomenon was first reported for the blue and green crystal structures of *cis-mer*-$MoOCl_2(PR_3)_3$.[2,3] The main differences between these two isomers are in the lengths of the Mo–O and $Mo–Cl_{(trans\text{-}to\text{-}O)}$ bonds (Figure 1). Since only the blue isomer was observed in solution, it appeared that the stability of the green one in the solid phase was simply caused by a packing effect. The recent discovery of the blue and green structures of $(LWOCl_2)^+$ complexes (L = *N,N',N''*-trimethyl-1,4,7-triazacyclononane),[4] where the W isomers differ most significantly in the W–O bond length (Figure 2), seems to belie these explanations. Both isomers appear to be stable in acetonitrile solution, as well as in the solid state.

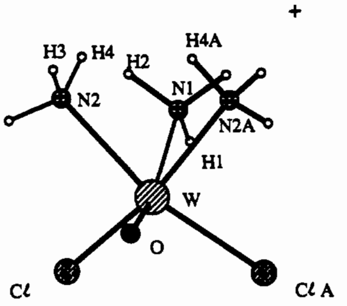
Two electronic mechanisms were proposed to explain these results.[1] "A real electronic crossing of filled and empty orbitals"[1] was used to explain the existence of the W isomers, which are d^1 transition-metal complexes. "The reorganization of the d–π bonding through a second-order Jahn–Teller effect"[1] was proposed to explain the structures of the Mo isomers, which are d^2 transition-metal complexes. These two explanations were supported by extended Hückel calculations.[1] This work promoted us to determine if these explanations could also be supported by ab initio calculations.

At first our inability to reproduce the experiment results with ab initio methods lead us to look for inadequacy in the method. Thus, we explored a variety of model ligands, since most of the experimental results have ligands which are too large for accurate calculations. We also explored partial vs full geometry optimizations, basis sets, and various levels of electron correlation. Finally, we began to question the experimental results.

In the recently reported reexamination of the crystallography of the Mo isomers, Yoon, Parkin, and Rheingold found that the "bond-stretch" phenomenon in the Mo systems is due to a composition disorder.[5] Only the blue "isomer" corresponds to pure $Mo(PMe_2Ph)_3OCl_2$, while the green "isomer" is the compound contaminated with $Mo(PMe_2Ph)_3Cl_3$. Although most of our calculations were completed when we received a preprint of ref 5, the work gave us sufficient courage to describe briefly our most critical calculations. These calculations confirm the results of Yoon et al. on the d^2 Mo complexes[2] and suggested that a similar problem exists for the d^1 W complexes.[4]

Calculational Details

Three model compounds were used. For the tungsten isomers, the model compound is **1**, where three NH_3 groups were used to substitute *N,N',N''*-trimethyl-1,4,7-triazacyclononane. Model compounds **2** and **3** were used to examine the experimental structures of the molybdenum isomers and the second-order Jahn–Teller effect, respectively. PH_3 ligands were substituted for the PR_3 ligands found in the actual complexes. In the three models, the NH_3 and PH_3 groups were fixed by using



1 C_s

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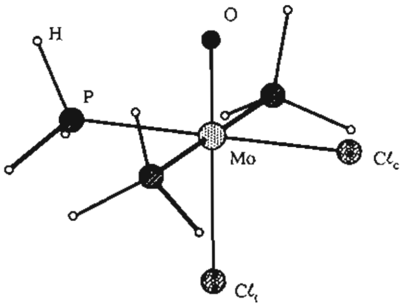
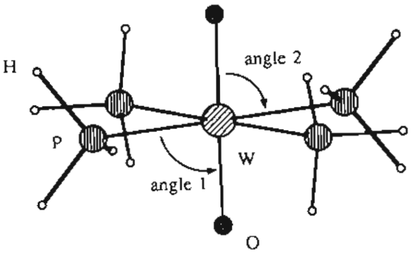


2 C_s



3

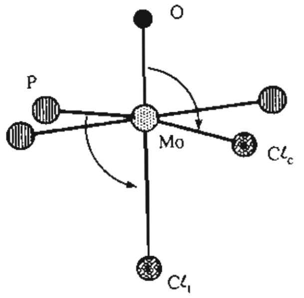
standard bond lengths and angles.[6]

In the calculations, the core electrons of W (Mo) were fit to an effective core potential (ECP 2) where the 5s and 5p (4s and 4p) electrons are treated explicitly as valence electrons of W (Mo). The valence electrons were described with a double-ζ basis [(10s5p3d/3s2p2d) for W and (10s5p4d/3s2p2d) for Mo] as described by Hay and Wadt.[7] For oxygen in **1** and **2**, chlorine, phosphorous, and nitrogen, effective core potentials and basis sets of Stevens, Basch, and Krauss[8] were used. The basis set for oxygen in **3** was represented (421/31/1), which is the split-valence form of Huzinaga's[9] (43/4) set with a d-polarization function. The basis set on hydrogen was a (21) contraction of an STO-3G representation.[10]

Ab initio MO calculations were performed via the restricted Hartree-Fock-Roothaan (HFR) methods.[11] Full-gradient techniques were utilized for geometry optimization calculations. Complete-active-space self-consistent-field (CASSCF)[12] calculations were also used to optimize the structures of **1**. The configuration interaction calculations with all single and double excitations (CISD) used the HFR result as the only reference configuration. All calculations were performed within the GAMESS[13] program package, at the Cornell National Supercomputer Facility on an IBM 3090-600VF computer and at the Supercomputer Center of Texas A&M University on a Cray Y-MP2/116 computer.

Results and Discussion

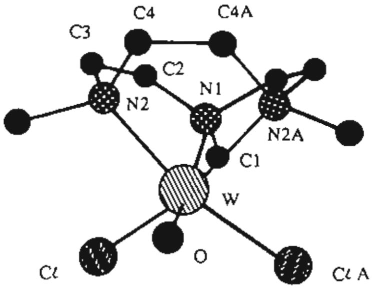
W Isomers. The molecular structures determined by X-ray crystallography have rigorous mirror symmetry about the O–W–N1–C1 plane, and both C2–C3 and C4–C4A (see Figure 2) are single bonds. There was no structural information about carbon atoms provided in the paper. To model the tridentate ligand, we took the N2–W–N2A and N1–W–N2 bond angles in **1** as their blue-green averages (i.e. the average of the corresponding crystallographic data in the blue and green isomers) and fixed the dihedral angle between H4–N2–W and N2–W–N2A planes to 20°, since, at this angle, the distance between H2 and H3 and the distance between H4 and H4A are about same (see **1**).



	blue	green	difference
Mo-O	1.676(7)	1.803(11) 1.80(2)*	0.127
Mo-$C\ell_t$	2.551(3)	2.426(6)	-0.125
Mo-$C\ell_c$	2.464(3)	2.479(5)	0.015
Mo-$P_{ave.}$	2.533(3)	2.553(6)	0.020

* Due to the instability of the green isomer of *cis-mer*-MoOCℓ_2(PMe$_2$Ph)$_3$, the blue isomer contains PMe$_2$Ph while the green one contains PEt$_2$Ph as reference 2(a). The green isomer of *cis-mer*-MoOCℓ_2(PMe$_2$Ph)$_3$ was characterized later (Mo-O = 1.80Å) as reference 3.

Figure 1. Structure of *cis-mer*-MoOCl$_2$(PR$_3$)$_3$. Selected bond distances[2a] (Å) are shown above.



	blue	green	difference
W-O	1.719(18)	1.893(20)	0.174
W-$C\ell$	2.322(5)	2.295(6)	-0.027
W-N1	2.370(17)	2.321(20)	-0.049
W-N2	2.239(13)	2.247(16)	0.008
$C\ell$-W-$C\ell$A	91.7(3)	93.5(4)	1.8
$C\ell$-W-O	102.8(8)	101.4(8)	-1.4
$C\ell$-W-N2	93.1(5)	93.3(7)	0.2
O-W-N2	91.1(8)	90.9(8)	-0.2
N1-W-N2	75.4(6)	75.8(8)	0.4
N2-W-N2A	78.3(6)	76.9(8)	-1.4

Figure 2. Structure of the cation [LWOCl$_2$]$^+$. Selected intramolecular distances (Å) and angles[4] (deg) are shown above.

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(13) Guest, M. F. SERC Daresbury Laboratory, Warrington WA4 4AD, U.K.

Table I. HFR Total Energies and Structures of $[WOCl_2(NH_3)_3]^+$

	1a′	1a″	diff
energy[a]	−146.267 94	−146.209 71	36.5
structure[b]			
W–O	1.660	1.708	0.048
W–Cl	2.362	2.317	−0.045
W–N1	2.548	2.444	−0.104
W–N2	2.279	2.375	0.096
Cl–W–ClA	98.5	105.0	6.5
Cl–W–O	106.5	109.7	3.2
Cl–W–N2	88.2	86.4	−1.8
O–W–N2	92.8	82.6	−10.2

[a] Energy in hartrees; energy difference in kcal/mol. [b] Bond distances in Å; bond angles in degrees.

With C_s symmetry, the d^1 complexes have two possible ground-state configurations $(a')^1$ and $(a'')^1$, which have state symmetries $^2A'$ and $^2A''$, respectively. Geometry optimizations were carried out for both of them. If an orbital crossing occurs as the W–O bond stretches, configurations $(a')^1$ and $(a'')^1$ should correspond to the ground state for each geometry, respectively. Therefore, the structures optimized for $(a')^1$ and $(a'')^1$ should have the following properties: (1) their geometric difference is mainly in the W–O bond length; (2) their total energy difference is small enough so that both isomers can be stable.

At the HFR level, our initial calculation optimized all the bond distances and angles in **1** and gave two converged structures **1a′** and **1a″** (see Table I) corresponding to the configurations $(a')^1$ and $(a'')^1$, respectively. In contrast to the experiment, the two optimized structures obviously differ in W–N1 bond length (0.104 Å) and O–W–N2 angle (10.2°). The W–O bond-length difference 0.048 Å is only 28% of the experiment difference, 0.174 Å. Moreover, the energy difference, 36.5 kcal/mol, is too large for the existence of two stable isomers.

Since the tridentate ligand is more rigid than our $(NH_3)_3$ model, we performed a second pair of calculations in which we fixed the model compound's W–N1 and W–N2 bond lengths to the lengths of the blue-green average values. Although the difference in the O–W–N2 angle decreased to 7.4°, the two states still show a small difference in W–O bond length (0.061 Å) and a large energy difference (37.2 kcal/mol). To emphasize the change of W–O bond lengths, the third pair of calculations only optimized the W–O bond distances, while other bond lengths and angles were set to their blue-green averages. Even here, the results only showed a difference of 0.064 Å in the W–O bond length with an energy difference of 39.1 kcal/mol.

Furthermore, if the optimized geometry for the $^2A''$ state is used to calculate the energy for the $^2A'$ state, the $^2A'$ energy is still 36.1 kcal/mol lower. Thus, the $^2A''$ state is not the ground state even for the distorted geometry; only the $^2A'$ state corresponds to the ground state. Apparently, the bond-stretch phenomenon in these d^1 W complexes cannot be predicted at the HFR level.

To explore the bond-stretch phenomenon at a higher theoretical level, we attempted several complete-active-space self-consistent-field (CASSCF) calculations. However, as we have seen before in other systems,[14] the CASSCF calculations for the two states converged to solutions with very different active spaces. Thus, they could not be used for a comparison of these states. Larger CASSCF calculations were not merited, and we turned to direct CI calculations with single and double excitations (CISD).

In the CISD calculations, only the W–O bond length was varied; the other parameters were fixed at their blue-green average values. Since the CI calculation will lengthen the W–O bonds (more configurations with occupied W–O antibonding orbitals), the CI potential energy curves were determined by beginning at the previously optimized W–O distances and increasing the distances by 0.050 and 0.100 Å. The results of the 25 e^-/71 MO CISD calculations are shown in Figure 3. The W–O bond-length difference remains 0.068 Å with an energy difference of 38.3 kcal/mol. Thus, correlation energy does not seem to modify our conclusions.

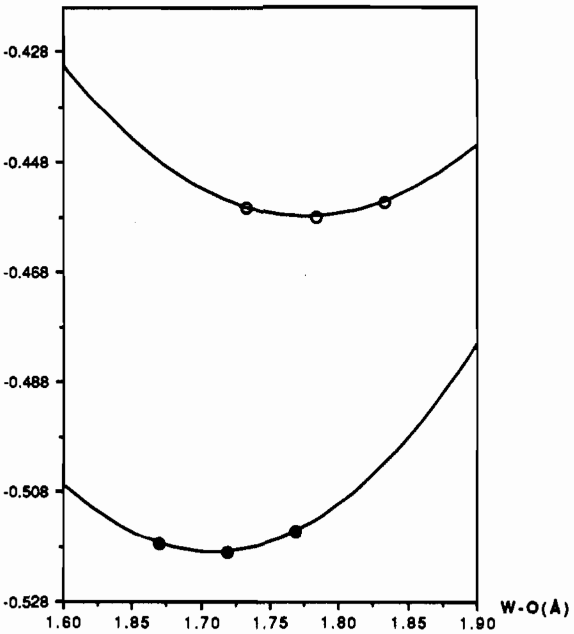

Figure 3. CISD energies of the W isomer model with configurations $(a')^1$ (●) and $(a'')^1$ (○) as functions of W–O bond length. The large energy difference and the similarity of W–O bond lengths suggest that the ground state is $^2A'$ and that $^2A''$ is an excited state and not an isomer.

Table II. HFR Total Energies and Structures of *cis-mer*-$MoOCl_2(PH_3)_3$

	2a′	2a″	diff
energy[a]	−136.043 35	−135.908 59	84.5
structure[b]			
Mo–O	1.669	1.837	0.168
$Mo–Cl_t$	2.566	2.633	0.067
$Mo–Cl_c$	2.538	2.405	−0.133
Mo–P	2.686	2.708	0.022

[a] Energy in hartrees; energy difference in kcal/mol. [b] Bond distances in Å.

From Figure 3, the optimized W–O bond length for $^2A'$ is 1.709 Å, which is close to the experiment value, 1.719 Å, in the blue isomer. Therefore, the geometry of the blue isomer can be reproduced by a CI calculation on the $^2A'$ state. However, the optimized W–O bond length for $^2A''$ is 1.777 Å, which is much shorter than the experiment value of 1.893 Å for the green isomer. The difference between the two energy minima (38.3 kcal/mol) again suggests that the $^2A''$ state is simply an excited state of the blue isomer.

Although two optimized molecular structures have been obtained for the two configurations $(a')^1$ and $(a'')^1$, which correspond to the postulated orbital crossing,[1] only the former ($^2A'$) can be identified as the ground state for the blue isomer. The existence of the green isomer and the orbital crossing mechanism cannot be confirmed by our calculations.

Mo Isomers. Although we now know the origin of the apparent isomerization,[5] at the time these calculations were performed we were attempting to find an electronic origin for this phenomenon. Initially we restricted our model, **2**, to an ideal pseudooctahedral geometry with C_s symmetry. Although the symmetry of the HOMO of such a d^2 system can be different, either a′ or a″, the derived ground states with configurations $(a')^2$ or $(a'')^2$ have the same symmetry, $^1A'$. At the HFR level, we first optimized all bond distances in **2** and obtained two molecule structures **2a′** [corresponding to $(a')^2$] and **2a″** [corresponding to $(a'')^2$] (see Table II). Compared with those in **2a′**, both Mo–O and $Mo–Cl_t$ bond distances are lengthened in **2a″**, a result in contrast to the experiment, where the changes in Mo–O and $Mo–Cl_t$ bond lengths from the blue to the green isomers appear to be in opposite directions. The energy difference between **2a′** and **2a″** is 84.5

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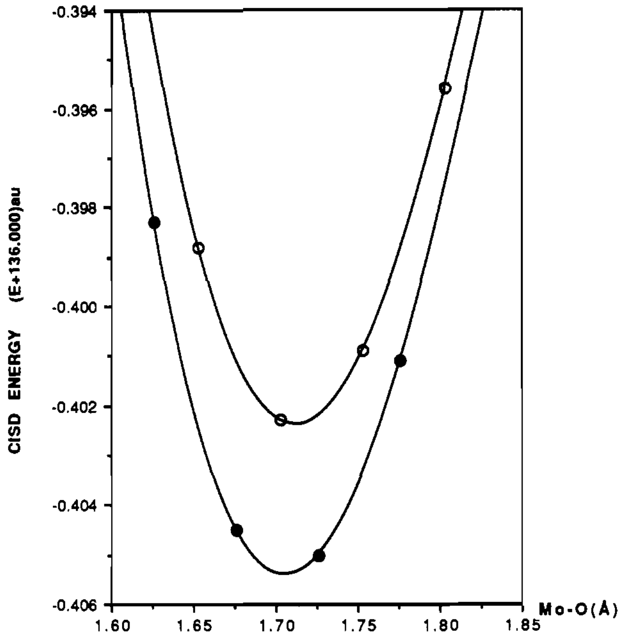

Figure 4. CISD energies of the "blue" Mo isomer model (●) and the "green" Mo isomer model (○) with ground-state configuration $(a')^2$ as functions of Mo–O bond length. The similarities in the Mo–O bond lengths and energies suggest that only one isomer exists for the $(a')^2$ configuration and that the structure for the blue isomer is the correct one.

kcal/mol, an indication that **2a″** is very disfavored energetically. The structure and high energy of **2a″** are a result of an a″ HOMO that has strong antibonding character for both the Mo–O and the Mo–Cl_t bonds. Obviously, molecular structure **2a″** as well as the configuration $(a'')^2$ can be excluded as a possible candidate to account for either the blue or green isomer. The result is consistent with previous conclusions that an orbital crossing need not be invoked to explain the existence of the Mo isomers.[1]

Although only one optimized molecule structure **2a′** was produced on the basis of the $(a')^2$ configuration, we attempted to determine whether another stable molecular structure can be produced through the d–π reorganization by forcing the apparent distortions on **2a′**. The apparent difference in the Mo–Cl_t bond length between the blue and green isomers is −0.125 Å, while the corresponding difference in the Mo–Cl_c bond length is 0.015 Å.[2a] First, assuming **2a′** was the blue isomer, we shortened Mo–Cl_t by 0.125 Å, lengthened Mo–Cl_c by 0.015 Å, and reoptimized the Mo–O bond length. Then, assuming **2a′** was the green isomer, we lengthened Mo–Cl_t by 0.125 Å, shortened Mo–Cl_c by 0.015 Å, and reoptimized the Mo–O bond length. In spite of the changes to the Mo–Cl_t and Mo–Cl_c bonds, the Mo–O bond only deviates from its value in **2a′** by 0.006 and −0.005 Å for the two distortions, respectively. No obvious d–π reorganization can be observed. Consequently, the bond-stretch isomerism for the Mo compound cannot be reproduced at the HFR level.

Beginning with the HFR solutions of $(a')^2$, we performed 38 e^-/77 MO CISD calculations on the apparent structures for the blue and green isomers. The Mo–P bond lengths were fixed at their blue-green average value, and Mo–Cl_t and Mo–Cl_c bond distances were fixed to their apparent values[2a] in the blue and green isomers, respectively. Optimizing the Mo–O bond distance, we found two energy minima at Mo–O bond lengths of 1.706 Å for the "blue" and 1.712 Å for the "green" structures (see Figure 4). The difference between the two Mo–O bond lengths (0.006 Å) is much smaller than the apparent experiment difference (0.127 Å). Consistent with the HFR results, the Mo–O bond length seems to be independent of the stretch of the Mo–Cl_t bond. At both HFR and CISD levels, the optimized Mo–O bond lengths are in the range of a normal Mo–O bond length,[15] which corresponds to the experimental datum for the blue isomer. Thus, as for the tungsten d^1 systems, only the blue isomer can be predicted for the molybdenum d^2 systems.

Table III. HFR Total Energies and Structures of *trans*-$WO_2(PH_3)_4$

	C_{4h}	C_4	C_s1	C_s2
energy[a]	−248.775 35	−248.775 35	−248.775 35	−248.775 35
structure[b]				
W–O1	1.784	1.784	1.784	1.784
W–O2	1.784	1.784	1.784	1.785
W–P	2.648	2.648	2.648	2.649
angle 1	90.0	90.0	89.9	90.0
angle 2	90.0	90.0	89.9	89.9

[a] Energy in hartrees; energy difference in kcal/mol. [b] Bond distances in Å; bond angles in degrees.

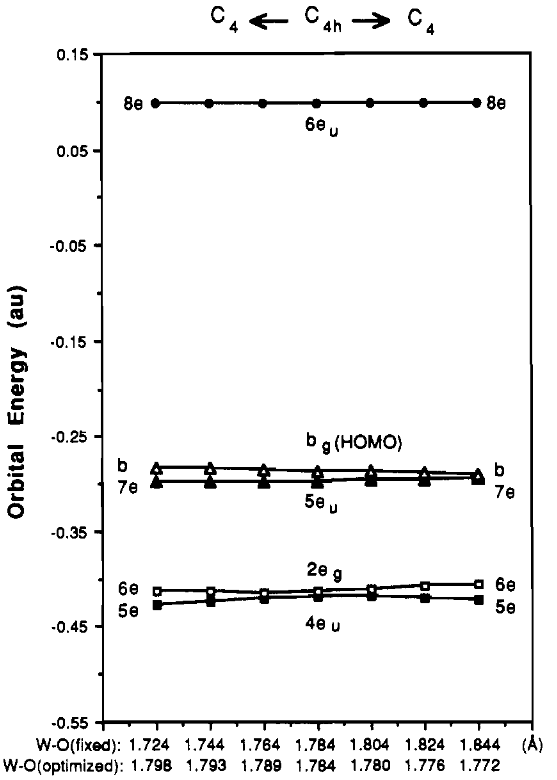

Figure 5. Orbital energy diagram of the asymmetric distortion of the two W–O bonds in model compound *trans*-$WO_2(PH_3)_4$. b_g is the metal d_{xy} orbital. O p_π pairs transform as e_g and e_u. $2e_g$ is (d_{xz}, d_{yz}) and O p_π bonding, while $3e_g$ is (d_{xz}, d_{yz}) and O p_π antibonding. $5e_u$ and $4e_u$ contain O p_π but are nearly nonbonding with respect to W because the W p orbitals are mainly involved in σ bonding. These orbitals are similar to those depicted in Figure 12 of ref 1a.

Second-Order Jahn–Teller Effect. A second-order Jahn–Teller effect was postulated as the origin of the isomerism in the Mo d^2 systems.[1] This distortion should be largest and most easily calculated for a symmetric system with strong π bonding. Thus, we attempted to find this second-order Jahn–Teller effect in the model compound *trans*-$WO_2(PH_3)_4$ (**3**), where the small first-row O combined with the 5d metal should show the strongest possible π bonding. To further enhance π bonding, d-polarization functions were included in the basis sets for oxygens. The orientations of the PH_3 ligand were such that **3** has C_{4h} symmetry when two W–O bonds have equal length and C_4 symmetry when the two W–O bonds have different lengths.

We first optimized all the bond lengths in **3** beginning with a C_{4h} structure and a distorted C_4 structure. The two calculations converged to the C_{4h} structure (see Table III). Thus, only the C_{4h} structure corresponds to the energy minimum. Beginning at the geometry of the optimized C_{4h} structure, we progressively changed the length of one of W–O bonds and optimized the other one. The W–O bond lengths and several metal–oxygen π molecular orbital levels are shown in Figure 5. A second-order Jahn–Teller effect can be seen in the stabilization of the 5e orbital,

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but the energy involved is far too little to cause a geometric distortion of the two W–O bonds. The relative independence of the two W–O bonds is revealed by the small response of the optimized bond to changes in the distorted one (see abscissa of Figure 5). The extended Hückel calculations do not reveal this independence because they are dominated by overlap effects which cause the stretching of one bond to be followed closely by the compression of the other.

In the early experimental results, distortions of the two isomers from ideal octahedral angles were most noticeable in the O–Mo–Cl_c and P–Mo–Cl_t angles (see Figure 1).[2a] To examine the role of these angles in the d–π reorganization, we did two additional calculations, C_s1 and C_s2, in which the angles 1 and 2 as well as all the bond lengths in **3** were optimized. For C_s1 the two W–O bonds were constrained to be the same, while for C_s2 they were allowed to be different. Again these geometry optimizations returned the molecule to the C_{4h} structure (see Table III).

All the results on **3** support our previous conclusions on **2**. Our ab initio calculations reveal that the second-order Jahn–Teller effect, whose magnitude is overemphasized by the extended Hückel method, cannot explain the existence of the bond-stretch isomers in d^2 Mo complexes.

Conclusion

The work described here illustrates the advantages of ab initio methods when one attempts to predict experimental results which are, in the final analysis, flawed. Since the ab initio methods contain all the essential physics, one does not have parameters to adjust in order to reproduce the experimental observations. In this work we attempted to "set up" the problem so that if the phenomenon existed, we would predict it. Thus, when the physics fails to produce the expected result, even after being "set up" to do so, one must conclude that one's expectations were false.

Here, we have shown that the second-order Jahn–Teller effect is not nearly strong enough to cause bond-length distortions in closed-shell molecules similar to the Mo complexes of Chatt et al.,[2] confirming the recent experimental work of Yoon, Parkin, and Rheingold.[5] Furthermore, we have shown that the bond-stretch phenomenon is also unlikely to be occurring in the d^1 W complexes of Wieghardt et al.[4] Our results and those of Yoon et al. would lead one to suggest that these W structures suffer from a similar impurity problem. On both systems the calculations support the structure of the blue "isomer" as the stable compound. They preclude the existence of any other isomer with a long M–O bond and similar energy.

We have not answered the general question on the existence of any bond-stretch isomers in other (yet undiscovered) transition-metal complexes. It is well-known that many porphyrin complexes undergo geometric changes when the spin state changes.[16] However, the geometric change occurs along one of the softer normal coordinates. Distortion along one of the complex's strongest bonds during a change in the equilibrium of a system with two spin states is unlikely, since other softer modes of distortion should accomplish the same result.

Note Added in Proof. Recently, the green "isomer" of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ was spectroscopically and chromatographically characterized as a mixture of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *mer*-$MoCl_3(PMe_2Ph)_3$.[17] Experimental studies of the W system are currently in progress (Enemark, J. H.; Wieghardt, K. Personal communications).

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Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Chemical Applications of Topology and Group Theory. 25. Electron Delocalization in Early-Transition-Metal Heteropoly- and Isopolyoxometalates[1]

R. B. King

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The d^0 early-transition-metal polyoxometalates which are reversibly reducible are constructed from octahedra having only one terminal oxygen atom. Such MO_6 octahedra each contain a single nonbonding d orbital. Overlap of these d orbitals results in delocalization, which may be regarded as binodal aromaticity and which is much weaker but topologically related to the aromaticity from overlap of the anodal sp hybrids of the boron atoms in the $B_nH_n^{2-}$ anions ($6 \le n \le 12$) or the uninodal carbon p orbitals in benzene. The improper 4-fold symmetry of these d orbitals leads to polyhedra of O_h symmetry and all vertices of degree 4 for the basic building blocks of binodal orbital aromatic systems corresponding to the octahedra found in polyoxometalates of the type $M_6O_{19}^{n-}$ (n = 8, M = Nb, Ta; n = 2, M = Mo) and the cuboctahedra found in Keggin ions of the type $XM_{12}O_{40}^{n-}$ (n = 3–7; M = Mo, W; X = B, Si, Ge, P, Fe^{III}, Co^{II}, Cu^{II}, etc.).

Introduction

The heteropoly- and isopolyoxometalates of early transition metals[2,3] have been known for well over a century and have become of increasing interest in recent years. Their structures are characterized by networks of MO_6 octahedra in which the early transition metals M (typically V, Nb, Mo, and W) are typically in their highest (d^0) oxidation states. A characteristic of many, but not all, of such structures is their reducibility to highly colored mixed oxidation state derivatives, e.g., "molybdenum blues"[2,4] and "tungsten blues".[2] The redox properties of these polyoxometalates make them important as catalysts for a number of oxidation and dehydrogenation reactions of organic substrates.[5,6]

Several efforts have been made to relate the redox properties of early-transition-metal polyoxometalates to their structures.

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