

# Nonoctahedral Structures

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## ABSTRACT

There is always a special reason when six-coordinate molecules or complexes are nonoctahedral. The Jahn–Teller distortion is the longest known example. Also well understood now is the steric activity or nonactivity of a nonbonding electron pair, for example  $\text{XeF}_6$ . In the past few years, it became obvious that six-coordinate  $d^0$  and  $d^1$  complexes with  $\sigma$  only ligands such as  $\text{Mo}(\text{CH}_3)_6$  are far from octahedral; rather, they are trigonal prismatic or even  $C_{3v}$  distorted trigonal prismatic. This phenomenon can be explained with simple molecular orbital or valence bond models.

## Introduction

Since the establishment of the octahedron as the fundamental geometry in six-coordinate structures in inorganic chemistry about a century ago, such structures are ubiquitous in coordination and organometallic chemistry. The total number of compounds with an octahedral structure is certainly more than  $10^4$ . Only the tetrahedron as a structural principle in four-coordinate compounds has more examples, which of course include organic molecules. The human demand for simplicity, symmetry, and beauty is pleased by the octahedron even more than the tetrahedron. As always in science, once a rule is established, the search for exceptions is started. The necessity to test structural postulates helps to further strengthen the rule or to show its limitations.

Before we embark on a discussion of nonoctahedral structures, it should be clearly stated that the majority of structures are certainly octahedral. If the molecule has a closed-shell configuration, e.g., obeying the 18 valence electron count for transition metal compounds, then there is no reason to assume nonoctahedral behavior if secondary effects, e.g., steric properties of ligands, are not considered. The reader more distant to inorganic chemistry who does not want to have his world view of simple structural chemistry disturbed can stop reading at this point. But even six-coordinate compounds whose structures deviate from octahedral have a long history; the oldest examples are associated with the Jahn–Teller distortion. This phenomenon will be only briefly mentioned. More recently, it has been observed that certain main group compounds are octahedral and others are not, for example  $\text{SF}_6$  vs  $\text{XeF}_6$ . This phenomenon has been explained by the “nonbonding electron pair” effect, and

we will show that, with fairly simple models, one can still predict the structure accurately.

The main focus of this Account is solely  $\sigma$ -bonded organometallic compounds, such as  $\text{W}(\text{CH}_3)_6$ , in which deviations from an octahedral structure are largest. This phenomenon was discovered about 15 years, and only recently have more examples been discovered which yield more insight into the true reasons for these deviations.

It is immediately obvious that all three types of non-octahedral structures are based on the same reason: the electron configuration of the compounds, or more simply, the electron configuration of the central atom.

## Jahn–Teller Distortion

This phenomenon is explained in detail in all modern textbooks of inorganic chemistry, so only a brief description is necessary here. However, we want to point out one remaining problem. The theorem was stated in 1937: “A non linear molecular system in a degenerate electronic state is unstable and splits the degenerate state energetically by lowering the symmetry.”<sup>1</sup> Six-coordinate complexes with high-spin  $d^4$  ( $\text{Mn}^{3+}$ ), low-spin  $d^7$  ( $\text{Ni}^{3+}$ ), and particularly  $d^9$  ( $\text{Cu}^{2+}$ ) electron configuration show the Jahn–Teller distortion by lifting the degeneracy of the  $e_g$  orbitals. One question is whether the anticipated smaller Jahn–Teller effect for  $t_{2g}$  electronic systems can be structurally observed. Ideal candidates are the hexafluorides  $\text{MoF}_6$ ,  $\text{WF}_6(d^0)$ ,  $\text{TeF}_6$ ,  $\text{ReF}_6(d^1)$ ,  $\text{RuF}_6$ ,  $\text{OsF}_6(d^2)$ ,  $\text{RhF}_6$ ,  $\text{IrF}_6(d^3)$ , and  $\text{PtF}_6(d^4)$ . All these are octahedral in the gaseous state, as established by electron diffraction.<sup>2–5</sup> In the solid state, all these crystallize in a disordered cubic high-temperature phase and an ordered orthorhombic low-temperature phase.<sup>6</sup> The  $d^1$ ,  $d^2$ , and  $d^4$  systems should deviate from octahedral symmetry if spin–orbit coupling is not considered. By comparing the structures obtained by neutron powder diffraction of  $\text{WF}_6$ ,  $\text{OsF}_6$ , and  $\text{PtF}_6$  at very low temperatures, a small structural effect could be observed for  $\text{OsF}_6$ , but the effect in comparison with the structure of octahedral  $\text{WF}_6$  is at the edge of the experimental precision.<sup>7</sup>  $\text{ReF}_6$ ,  $\text{OsF}_6$ ,  $\text{IrF}_6$ , and  $\text{PtF}_6$  are calculated to be distorted octahedral,<sup>5,8</sup> but the distortion is small, and so experimental proof is still lacking. Vibrational spectra of  $\text{ReF}_6$ ,  $\text{OsF}_6$ , and  $\text{TcF}_6$  have been interpreted as indicative of a dynamic Jahn–Teller effect.<sup>9</sup>

## The Problem of the Sterically Active or Nonactive Electron Pair in Main Group Octahedral Compounds

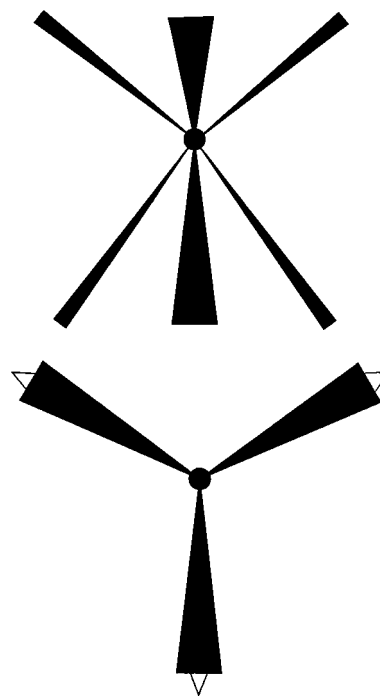
Structures of simple main group compounds can be predicted by the valence shell electron pair repulsion (VSEPR) model with surprising success, although the predictions remain qualitative.<sup>10</sup> The essence of this model is to look for the size differences of bonding and nonbonding electron pairs and how they influence the structure. The results are in all modern textbooks of

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general and inorganic chemistry and need not be repeated here. If a molecule or ion with six ligands has, by simple electron count, no nonbonding valence electrons or electron pairs left at the central atom, it is octahedral; examples include  $\text{AlF}_6^{3-}$ ,  $\text{SiF}_6^{2-}$ ,  $\text{PF}_6^-$ ,  $\text{SF}_6$ , and  $\text{ClF}_6^+$ , to name but a few. If, however, there is one electron pair left, as in  $\text{XeF}_6$ ,  $\text{BrF}_6^-$ ,  $\text{IF}_6^-$ ,  $\text{ClF}_6^-$ ,  $\text{SeF}_6^{2-}$ ,  $\text{TeCl}_6^{2-}$ , and  $\text{SbCl}_6^{3-}$ , then the prediction by the VSEPR model is a structure with seven “ligands”, one being a lone electron pair and six real ligands, and therefore the structures are nonoctahedral, since they are seven-coordinate. Clearly,  $\text{XeF}_6$  and  $\text{IF}_6^-$  are nonoctahedral. The exact structure of  $\text{XeF}_6$  has been the topic of many investigations and much speculation. The gas electron diffraction and the solid-state crystal structure of a material containing  $\text{XeF}_6$  as solvent molecules clearly show it to be nonoctahedral.<sup>11,12</sup> The X-ray single-crystal structure of  $(\text{CH}_3)_4\text{N}^+\text{IF}_6^-$  shows the distorted  $\text{IF}_6^-$  anion.<sup>13</sup> But isoelectronic  $\text{BrF}_6^-$  is octahedral beyond doubt in the solid state.<sup>14,15</sup> The vibrational spectra of  $\text{BrF}_6^-$  and also those of  $\text{ClF}_6^-$  show no features that suggest dynamic deviation from octahedral symmetry at  $-110^\circ\text{C}$ .<sup>16,17</sup>  $\text{SeF}_6^{2-}$ , however, is slightly distorted from octahedral symmetry toward  $C_{3v}$ ,<sup>15</sup> and the structure of  $\text{TeCl}_6^{2-}$  is dependent upon the crystallographic environment.<sup>18</sup> If the structure is found to be octahedral by X-ray crystallography, there are indications of dynamic distortions in the vibrational spectra of the dianion.<sup>18</sup> The VSEPR model can be rescued, if one allows that the influence of the nonbonding electron pair is dependent on the steric crowding: The large central atoms Xe and I in  $\text{XeF}_6$  and  $\text{IF}_6^-$  allow distortion from the octahedron, whereas the smaller Br atom in  $\text{BrF}_6^-$  does not. The slightly larger Se atom in  $\text{SeF}_6^{2-}$  is the borderline case. If the central atom sizes are kept equal, but the size of the ligand atom is increased as in  $\text{TeCl}_6^{2-}$ ,  $\text{TeBr}_6^{2-}$ , and  $\text{TeI}_6^{2-}$ , then again the structure changes toward octahedral.<sup>19,20</sup> The resulting prediction is also fulfilled, namely that with the increasing number of ligands, the steric activity of the nonbonding electron pair diminishes and disappears.  $\text{XeF}_5^+$  has a square pyramidal umbrella structure, with the sterically active lone pair occupying an apical site.  $\text{XeF}_6$  is  $C_{3v}$  or  $C_{2v}$  and distorted octahedral with weak steric activity of the nonbonding electron pair.  $\text{XeF}_7^-$  is capped octahedral, and the very weak steric activity of the nonbonding electron pair is observed by elongation of the  $\text{XeF}$  bond of the capping fluorine atom.<sup>12</sup>  $\text{XeF}_8^{2-}$ , finally, is regular square antiprismatic, as is  $\text{IF}_8^-$ , without any steric activity of the nonbonding pair.<sup>21,22</sup>

## $d^0$ and $d^1$ Transition Metal Complexes

These types of structures deviate more than just little from octahedral symmetry; indeed, they have a completely different basic structure! Nevertheless, the phenomenon has been detected only quite recently, and it is noteworthy that the first paper that dealt with the problem is a theoretical one based upon quantitative computational chemistry. Desmolliens, Jean, and Eisenstein were searching for a theoretical explanation of “agostic” behavior in



**FIGURE 1.** Schematic structure of  $\text{Mo}(\text{CH}_3)_6$  and  $\text{W}(\text{CH}_3)_6$ , viewed perpendicular to the three-fold molecular axis (above), and viewed from below along the three-fold axis. Note: The three bonds that appear shorter in this projection are indeed the longer bonds. This is due to the small angle between those bonds. Numerical values: for  $\text{Mo}(\text{CH}_3)_6$ ,  $\text{Mo}-\text{C}(\text{short}) = 210.9$  pm (mean of  $3 \times 3$  experimental values from single-crystal X-ray diffraction),<sup>41</sup>  $\text{Mo}-\text{C}(\text{long}) = 219.2$  pm (mean of 9),  $\text{C}(\text{short})-\text{Mo}-\text{C}(\text{short}) = 96.4^\circ$  (mean of 9),  $\text{C}(\text{long})-\text{Mo}-\text{C}(\text{long}) = 75.2^\circ$  (mean of 9); for  $\text{W}(\text{CH}_3)_6$ ,  $\text{W}-\text{C}(\text{short}) = 210.2$  pm (mean of 6),<sup>40</sup>  $\text{W}-\text{C}(\text{long}) = 218.7$  pm (mean of 6),  $\text{C}(\text{short})-\text{W}-\text{C}(\text{short}) = 95.8^\circ$  (mean of 6),  $\text{C}(\text{long})-\text{W}-\text{C}(\text{long}) = 75.9^\circ$  (mean of 6).

methyl and ethyl groups in titanium complexes.<sup>23</sup>  $\text{TiH}_6^{2-}$  was calculated as a model compound, initially with octahedral symmetry. It became clear that even by a restricted deviation of  $O_h$  toward  $C_{2v}$  symmetry, the energy of the system dropped dramatically, and a search for the global minimum was started. The results appeared in 1989,<sup>24</sup> and several other computational papers on this problem appeared later.<sup>25–34</sup> In the same year, the first experimental proof arrived when Mosse and Girolami isolated and crystallized  $\text{Zr}(\text{CH}_3)_6^{2-}$ .<sup>35</sup> The dianion has a trigonal prismatic structure. Long ago, Wilkinson and co-workers prepared  $\text{W}(\text{CH}_3)_6$  and  $\text{Re}(\text{CH}_3)_6$ .<sup>36,37</sup> These would be ideal molecules to settle the question, since no cation–anion interactions are present here. Electron diffraction studies on  $\text{W}(\text{CH}_3)_6$  were best accommodated by a trigonal prismatic structure.<sup>38</sup> Finally, the solid-state structure was solved, and  $\text{W}(\text{CH}_3)_6$  was found to be distorted trigonal prismatic.<sup>39,40</sup> Three  $\text{W}-\text{C}$  bonds in one hemisphere of the molecule can be called normal, with lengths around 210 pm and bond angles of  $94\text{--}99^\circ$  between them. The three bonds in the other hemisphere of the molecule are surprisingly long (218–220 pm) and have very small angles ( $75\text{--}76^\circ$ ) between them (see Figure 1). Qualitatively, this is exactly the  $C_{3v}$  structure predicted by Landis et al. a few

months before the experimental results were published.<sup>25</sup> Re(CH<sub>3</sub>)<sub>6</sub>, however, was found to be regular trigonal prismatic, with six almost equal bond lengths.<sup>40</sup> Later, the structures of Mo(CH<sub>3</sub>)<sub>6</sub>,<sup>41</sup> Nb(CH<sub>3</sub>)<sub>6</sub><sup>-</sup>,<sup>40</sup> and Ta(CH<sub>3</sub>)<sub>6</sub><sup>-</sup> appeared. Of these, Ta(CH<sub>3</sub>)<sub>6</sub><sup>-</sup> is closest to a regular trigonal pyramid. The *C*<sub>3v</sub> deviation of Nb(CH<sub>3</sub>)<sub>6</sub><sup>-</sup> is so small that it may be questioned (but see later for the computational prediction!). Mo(CH<sub>3</sub>)<sub>6</sub> has even a slightly stronger *C*<sub>3v</sub> distortion than W(CH<sub>3</sub>)<sub>6</sub>. The presence of several molecules in the asymmetric unit is usually a nuisance, but the appearance of virtually chemically identical but crystallographically different molecules, namely two in the W(CH<sub>3</sub>)<sub>6</sub> structure and three in the Mo(CH<sub>3</sub>)<sub>6</sub> structure, lends strong credibility to the crystallographic findings, since the influence of the packing on the molecular structure can be excluded. Even the structures of Ta(C<sub>6</sub>H<sub>5</sub>)<sub>6</sub><sup>-</sup> and Ta(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)<sub>6</sub><sup>-</sup> are derived from a trigonal prismatic geometry.<sup>42</sup> Very recently, WH<sub>6</sub> has been detected in a neon matrix, prepared from W atoms and H<sub>2</sub> molecules, and the IR spectra are in full agreement with the predicted *C*<sub>3v</sub> distorted trigonal prismatic structure.<sup>43</sup>

Any model or theory must explain the following structural features: WH<sub>6</sub> and W(CH<sub>3</sub>)<sub>6</sub> are *C*<sub>3v</sub> with a distorted trigonal prismatic structure. Anions with negative charges are undistorted trigonal prisms. Addition of one electron to the system, going from W(CH<sub>3</sub>)<sub>6</sub> to Re(CH<sub>3</sub>)<sub>6</sub>, also removes the distortion. And finally, the distortion of second-row transition metal compounds seems to be little stronger than that for otherwise identical third-row compounds.

As we will discuss later, computational chemistry (ab initio and density functional calculations) predicts that, for these systems, the energy of an octahedral structure is far higher than the less regular structure, so the octahedron is not even close to being an equilibrium structure. Values of more than 100 kJ mol<sup>-1</sup> between distorted trigonal prismatic and octahedral structures are calculated (see below). How can a simple model explain the fact that MoF<sub>6</sub> and WF<sub>6</sub> are octahedral, but isoelectronic with nonoctahedral Mo(CH<sub>3</sub>)<sub>6</sub> and W(CH<sub>3</sub>)<sub>6</sub>, only to point out the most obvious paradox? The Devil's advocate might argue, maybe WF<sub>6</sub> and MoF<sub>6</sub> are not octahedral. But the octahedral structure for both molecules has been proven beyond doubt. In addition, CrF<sub>6</sub> should be octahedral, despite earlier theoretical predictions,<sup>44</sup> but CrF<sub>6</sub> has so far never been prepared; even in matrix conditions, only CrF<sub>5</sub> is obtained.<sup>45</sup>

In these hexafluorides, the classical interconversion of an octahedron into a trigonal prism has a surprising low energy barrier, especially for MoF<sub>6</sub> and unknown TcF<sub>6</sub><sup>+</sup> (see Table 1).<sup>44,46</sup> At slightly elevated temperatures, MoF<sub>6</sub> should undergo the octahedral/trigonal prismatic interconversion. In such highly symmetric molecules, this is difficult to prove experimentally. But derivatives of the kind F<sub>5</sub>Mo-OR and F<sub>5</sub>W-OR (with R = CH<sub>2</sub>-CF<sub>3</sub> and C<sub>6</sub>F<sub>5</sub>) show coalescence of the chemically different fluorine atoms in the <sup>19</sup>F NMR spectrum not much above room temperature.<sup>46</sup>

**Table 1. Relative Energies (kJ mol<sup>-1</sup>) between Octahedral and Trigonal Prismatic Structure of Various Hexafluoride Complexes<sup>a</sup>**

|                               |                   |                               |
|-------------------------------|-------------------|-------------------------------|
|                               | CrF <sub>6</sub>  |                               |
|                               | 52.4              |                               |
|                               | 61.6 <sup>b</sup> |                               |
| NbF <sub>6</sub> <sup>-</sup> | MoF <sub>6</sub>  | TcF <sub>6</sub> <sup>+</sup> |
| 39.9                          | 25.0              | 15.5                          |
|                               | 27.1 <sup>b</sup> |                               |
|                               | WF <sub>6</sub>   |                               |
|                               | 43.8              |                               |
|                               | 42.9 <sup>b</sup> |                               |

<sup>a</sup> Becke 3LYP DFT calculations, 6-311 G(d,p) basis set for fluorine, and electron core potentials for the metal atoms from the Institut für Theoretische Chemie, Universität Stuttgart, Germany.  
<sup>b</sup> Ref 44.

Chemical thinking immediately brings up mixed substituted compounds (CH<sub>3</sub>)<sub>x</sub>MoX<sub>6-x</sub> and (CH<sub>3</sub>)<sub>x</sub>WX<sub>6-x</sub> (with X = F, Cl, OR) to answer the question, at what stage of substitution the change occurs from trigonal prism to octahedron or vice versa. Experimental data are still scarce on these types of molecules. (CH<sub>3</sub>)<sub>5</sub>MoOCH<sub>3</sub> and (CH<sub>3</sub>)<sub>5</sub>W-Cl are clearly distorted trigonal prismatic.<sup>47</sup> The OCH<sub>3</sub> and Cl ligands occupy a position in the hemisphere where the short M-C and opened C-M-C methyl groups reside in Mo(CH<sub>3</sub>)<sub>6</sub> and W(CH<sub>3</sub>)<sub>6</sub>, respectively. The only known example with two X ligands, (CH<sub>3</sub>)<sub>4</sub>Mo(OCH<sub>3</sub>)<sub>2</sub>, has a similar structure.<sup>47</sup> (CH<sub>3</sub>)<sub>3</sub>WCl(OCH<sub>3</sub>)<sub>2</sub> is an accidental oxidation product of (CH<sub>3</sub>)<sub>5</sub>WCl, it is the only compound currently known with x = 3, and it has a structure based on an octahedron.<sup>47</sup> Somewhere at this stage of substitution, the transition from trigonal prismatic to octahedral occurs, and a complicated isomer problem and dynamic behavior can be anticipated for these yet largely unknown compounds. As we will see in the next section, computational chemistry has given a fairly comprehensive answer on this special subject also. Finally, (MeO)<sub>6</sub>M (Me<sub>2</sub>N)<sub>6</sub>M (M = Mo, W) have *O<sub>h</sub>* structures. Thus, those compounds with ligands that can π-bond have *O<sub>h</sub>* structures.

## Theoretical Predictions

In the meantime, it has been shown that ab initio and especially density functional calculations can predict all of the known and unknown structures in great detail: The structures of and structural differences between W(CH<sub>3</sub>)<sub>6</sub>, Mo(CH<sub>3</sub>)<sub>6</sub>, Nb(CH<sub>3</sub>)<sub>6</sub><sup>-</sup>, Ta(CH<sub>3</sub>)<sub>6</sub><sup>-</sup>, Zr(CH<sub>3</sub>)<sub>6</sub><sup>2-</sup>, and Re(CH<sub>3</sub>)<sub>6</sub> are perfectly described (see Table 2).<sup>48</sup> Of course, these calculations can predict structures of unknown molecules, such as the trigonal prismatic structure for hypothetical Os(CH<sub>3</sub>)<sub>6</sub>. The calculations for methyl compounds seem to be presently even more accurate than the experimentally established structures, as they can fairly precisely predict the location of the hydrogen atoms in these compounds. Furthermore, the trigonal prismatic/octahedral interconversion of mixed substituted compounds is nicely predicted. Theory says that (CH<sub>3</sub>)<sub>3</sub>WCl<sub>3</sub> is still trigonal prismatic but that (CH<sub>3</sub>)<sub>2</sub>WCl<sub>4</sub> and CH<sub>3</sub>WCl<sub>5</sub> are octahedral.<sup>49</sup> The fact that there seems to be a disagree-

**Table 2.** Calculated Relative Energies (kJ mol<sup>-1</sup>) for Different Geometries of Hexamethyl Complexes<sup>48</sup>

| species  | distorted trigonal prism | regular trigonal prism | distorted octahedron |
|--|--------------------------|------------------------|----------------------|
| [Ti(CH <sub>3</sub> ) <sub>6</sub> ] <sup>2-</sup> |                          | 0.0                    | 52.8                 |
| [Zr(CH <sub>3</sub> ) <sub>6</sub> ] <sup>2-</sup> |                          | 0.0                    | 65.8                 |
| [Hf(CH <sub>3</sub> ) <sub>6</sub> ] <sup>2-</sup> |                          | 0.0                    | 43.4                 |
| [V(CH <sub>3</sub> ) <sub>6</sub> ] <sup>-</sup>   |                          | 0.0                    | 120.0                |
| [Nb(CH <sub>3</sub> ) <sub>6</sub> ] <sup>-</sup>  | 0.0                      | 0.8                    | 125.4                |
| [Ta(CH <sub>3</sub> ) <sub>6</sub> ] <sup>-</sup>  |                          | 0.0                    | 130.1                |
| [Cr(CH <sub>3</sub> ) <sub>6</sub> ]               | 0.0                      | 11.5                   | 98.6                 |
| [Mo(CH <sub>3</sub> ) <sub>6</sub> ]               | 0.0                      | 39.3                   | 110.3                |
| [W(CH <sub>3</sub> ) <sub>6</sub> ]                | 0.0                      | 24.6                   | 131.9                |
| [Tc(CH <sub>3</sub> ) <sub>6</sub> ] <sup>+</sup>  | 0.0                      | 112.2                  | 90.3                 |
| [Re(CH <sub>3</sub> ) <sub>6</sub> ] <sup>+</sup>  | 0.0                      | 93.0                   | 110.0                |
| [Tc(CH <sub>3</sub> ) <sub>6</sub> ]               |                          | 0.0                    | 148.1                |
| [Re(CH <sub>3</sub> ) <sub>6</sub> ]               |                          | 0.0                    | 169.5                |
| [Ru(CH <sub>3</sub> ) <sub>6</sub> ]               |                          | 0.0 <sup>a</sup>       | 136.3 <sup>b</sup>   |
| [Os(CH <sub>3</sub> ) <sub>6</sub> ]               |                          | 0.0 <sup>a</sup>       | 160.4 <sup>b</sup>   |

<sup>a</sup> Singlet state. <sup>b</sup> Triplet state.

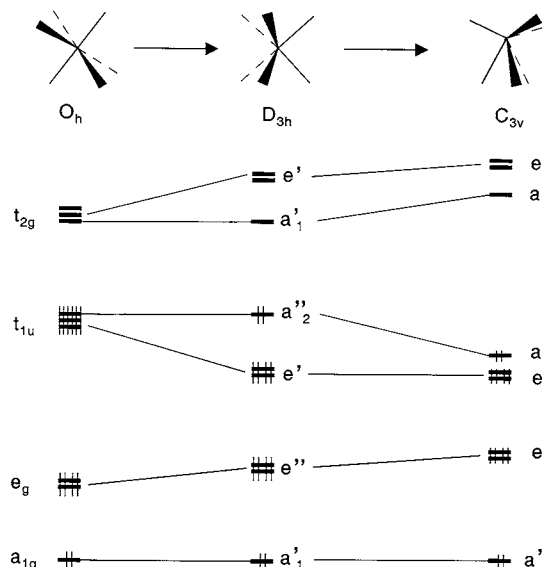
ment between the experimental octahedral (CH<sub>3</sub>)<sub>3</sub>WCl-(OR)<sub>2</sub> and the calculated trigonal prismatic (CH<sub>3</sub>)<sub>3</sub>WCl<sub>3</sub> structures is easily explained by one or both of the following two explanations: The compounds are similar, but not identical, so the compounds may indeed have different structures. Also, since it is obvious that there are several structural isomers of octahedral and trigonal prismatic structure which are very close in energy, it could happen that the accidental crystallization afforded an isomer which may not be the most stable one in the gas phase, which is the phase of the theory!

Finally, that the octahedral/trigonal prismatic interconversion barrier for MoF<sub>6</sub> is smaller than that for WF<sub>6</sub> is nicely predicted also: The onset of the relativistic effect in tungsten increases the polarity of the W-F bonds and thus the ligand repulsion, favoring the octahedron. A comprehensive discussion on the theoretical aspects of six- and other coordinated molecules is available.<sup>44</sup> The shortcoming of all these calculations is that they predict reliably, but do not give simple physical models that are useful to undergraduate students of chemistry. For an explanation, it is convenient to simplify the results to certain models. Such a model must at least have predictive value for a certain class of compounds.

## Models

The valence shell electron pair repulsion model certainly fails completely, since the octahedron is by far the most stable configuration in terms of ligand repulsion. Attempts have been made to rescue this model for such electron-deficient systems by introducing the core polarization.<sup>50</sup> The idea is that, on the position opposite of a ligand, a concentration of electron density is found which now is also stereochemically active. Besides the fact that this phenomenon has, so far, experimentally never been seen, it needs sophisticated computational methods, so it is really a modification of an existing model.

On the other hand, ligand repulsion can be used to explain why Ta(CH<sub>3</sub>)<sub>6</sub><sup>-</sup> is a nondistorted trigonal prism, and why the electron-rich (CH<sub>3</sub>)<sub>n</sub>Mo/WCl<sub>6-n</sub> ligands oc-



**FIGURE 2.** Qualitative MO diagram for d<sup>0</sup> MeH<sub>6</sub> molecules, cf. ref 29.

cupy positions with short bonds and wide angles in the hemisphere of the distorted trigonal prism. One could even go so far as to say that the ground state of WF<sub>6</sub> or MoF<sub>6</sub> should be C<sub>3v</sub> distorted trigonal prismatic, if there were not the considerable interligand repulsion of the quite polar M-F bonds, with a considerable negative charge of about 0.4 e<sup>-</sup> on each fluorine atom!

But the MO model can explain the observed structures. Starting with the A<sub>1g</sub>, E<sub>g</sub>, T<sub>1</sub>, T<sub>2g</sub> sequence of molecular orbitals in an octahedron, this geometry prevails if all orbitals are occupied in an 18 valence electron system, e.g., W(CO)<sub>6</sub>. The octahedral geometry of WF<sub>6</sub> then calls for a considerable back-donation of electron density from the F ligands to the central atom via π-bonding. If, however, this mechanism is not available due to a lack of nonbonding electrons, as in W(CH<sub>3</sub>)<sub>6</sub>, then we have to deal with a pure 12 electron system (see Figure 2).

Distortion of the octahedron along one three-fold axis gives a trigonal prism and qualitatively an energy gain, since occupied orbitals are lowered and virtual orbitals are raised in energy.<sup>29</sup> Further distortion into the C<sub>3v</sub> distorted trigonal prism results in another gain of energy. This qualitative picture explains nicely why Re(CH<sub>3</sub>)<sub>6</sub> is nondistorted trigonal prismatic, and the same prediction holds for unknown Os(CH<sub>3</sub>)<sub>6</sub>. Unknown Ir(CH<sub>3</sub>)<sub>6</sub> could be octahedral, and the 18 electron anion Pt(CH<sub>3</sub>)<sub>6</sub><sup>2-</sup> certainly is octahedral, in agreement with the vibrational data, but a crystal structure is lacking.<sup>51</sup> In this picture, the octahedral structures of WF<sub>6</sub> and WCl<sub>6</sub> are explained by the occurrence of a considerable amount of π-back-donation of electron density.

The valence bond model is even simpler, and it accounts for the geometry by addressing the question of orbital parentage. If the bonding in W(CH<sub>3</sub>)<sub>6</sub> is made up solely from s and d orbitals, and no p orbitals are involved in the bonding, a picture that is close to the truth according to natural bond orbital analyses in ab initio and DFT calculations, then a set of sp<sup>5</sup> hybrid orbitals have

preferentially angles of  $63^\circ$  and  $117^\circ$  ( $=180 - 63^\circ$ ) with each other. From these angles, four principal structures can be constructed, of which the distorted trigonal prism is chemically the most reasonable one: ideally the  $C_{3v}$  distorted trigonal prism would have  $63^\circ$  between one set of bonds and  $117^\circ$  between the other set of bonds. In  $W(CH_3)_6$ , these angles change to  $75^\circ$  and  $95^\circ$  due to steric repulsion of the ligands. The calculated structure of  $WH_6$  that is in accord with the matrix IR spectrum of this compound has angles of  $62.4^\circ$  and  $114.7^\circ$ .<sup>43</sup>

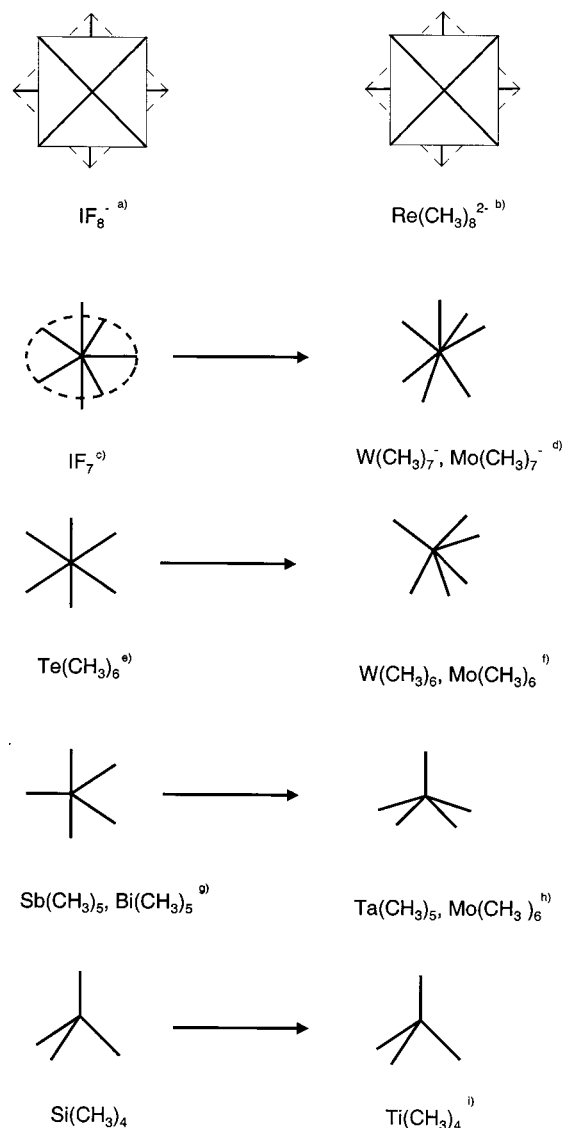
## Conclusions

The latter model predicts, of course, the octahedron for main group compounds, since the p-orbital-dominated bonds have a preference for  $90^\circ$  and  $180^\circ$  angles,  $Te(CH_3)_6$  being chemically the closest compound to the one described here, and it is of course octahedral.<sup>52,53</sup> The *gerade* character of f orbitals (like p orbitals) would predict octahedral symmetry for corresponding lanthanides and actinide compounds. Such purely f-bonded compounds do not exist, but it does not come as a surprise that the rare earth anions  $RE(CH_3)_6^{3-}$  are octahedral.<sup>54,55</sup>

Looking backward, one might ironically say that there has never been a reason for six-coordinated transition metal compounds to be octahedral, when no  $\pi$ -bonding is involved! Since the vast majority of such compounds also have  $\pi$ -bonds, the “wrong” picture is so dominant.

Anionic W and Mo trithiolate complexes often have structures between octahedral and trigonal prismatic. This old observation was originally explained by the special nature of the chelating ligands.<sup>56,57</sup> But now it appears to be an intrinsic characteristic of these anions, possibly because sulfur atoms are fairly weak  $\pi$ -donors.<sup>53</sup> A thiol complex with nonchelating ligands, as in  $Zr[SC(CH_3)_3]_6^{2-}$ , has a disordered crystal structure, and the anion can arbitrarily be described as octahedral or trigonal prismatic.<sup>58</sup> The authors prefer the trigonal prismatic description because of slightly different occupancy factors in the crystal. Unsubstituted  $Mo(SH)_6$  (unknown) should have, according to DFT calculations, a  $C_3$  structure just between octahedral and trigonal prismatic.<sup>44</sup> Other monodentate hexathiolato complexes are clearly close to trigonal prismatic.<sup>59–61</sup>

Applying the simplistic valence bond model avoiding  $90^\circ$  and  $180^\circ$  angles in the case of transition metal compounds with coordination numbers of 4–8 gives an interesting picture (see Figure 3). Only for the coordination numbers 4 (tetrahedron) and 8 (square antiprism) are the structures alike. It must be kept in mind, however, that  $Ti(CH_3)_4$  has not been isolated as a free molecule. The calculated tetrahedral structure is much softer, meaning that it is more easily deformed than are those of  $Si(CH_3)_4$  or  $Ge(CH_3)_4$ .<sup>62</sup> For coordination numbers 5 and 7, the observed geometries are known to be close in energy, but the rule of avoiding  $90^\circ$  and  $180^\circ$  bond angles for the transition metal compounds prevails. Only in the cases of coordination number 6 are the discrepancies very strong. If we stay with the valence bond model, this is so



**FIGURE 3.** Schematic structures of main group (left) and transition metal  $d^0$  and  $d^1$  compounds: (a) ref 63; (b) ref 64; (c) refs 65, 66; (d) refs 41, 64; (e) refs 52, 53; (f) refs 39, 41; (g) refs 67–69; (h) refs 68, 70; (i) refs 62, 71.

because the octahedron has twelve  $90^\circ$  angles and three  $180^\circ$  angles.

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