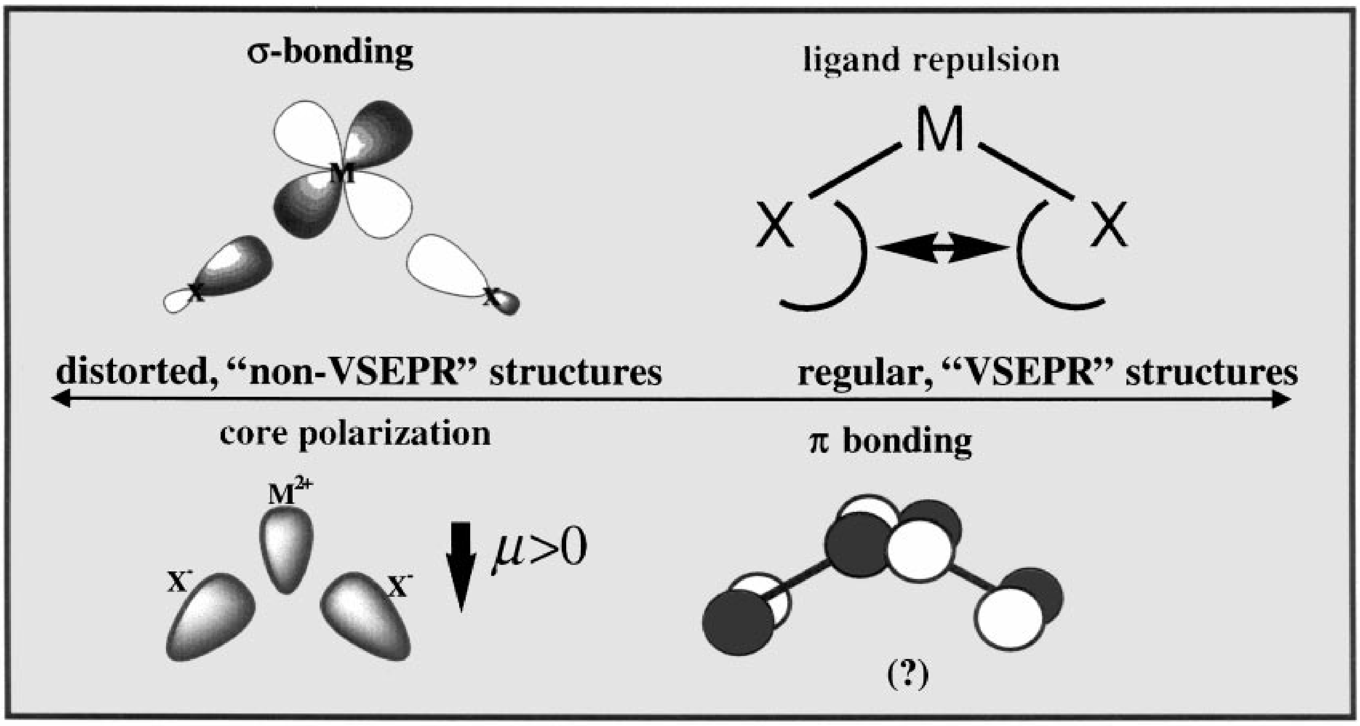
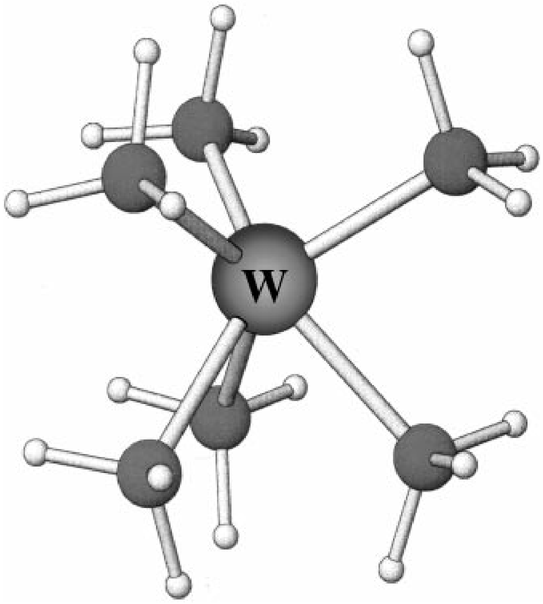
The fascinating structures of systems with formal d^0 configurations may be traced back largely to the interplay of four factors:



Examples include the distorted trigonal-prismatic structure of $[W(CH_3)_6]$ (see picture), bent structures of gaseous alkaline earth dihalides, and those of many more molecules and solids.



The structural distortions have important consequences for homogeneous and heterogeneous catalysis, bioinorganic chemistry, and materials properties.

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"Non-VSEPR" Structures and Bonding in d^0 Systems

Martin Kaupp*

Dedicated to the memory of Marco Häser (1961–1997)

Under certain circumstances, metal complexes with a formal d^0 electronic configuration may exhibit structures that violate the traditional structure models, such as the VSEPR concept or simple ionic pictures. Some examples of such behavior, such as the bent gas-phase structures of some alkaline earth dihalides, or the trigonal prismatic coordination of some early transition metal chalcogenides or pnictides, have been known for a long time. However, the number of molecular examples for "non-VSEPR" structures has increased dramatically during the past decade, in particular in the realm of organometallic chemistry. At the same time, various theoretical models have been discussed, sometimes controversially, to explain the observed, unusual structures. Many d^0 systems are important in homogeneous and heterogeneous catalysis, biocatalysis (e.g. molybdenum or tungsten enzymes), or materials science (e.g. ferroelectric perovskites or zirconia). Moreover, their electronic structure without formally nonbonding d orbitals makes them unique starting points for a general understanding of structure, bonding, and reactivity of transition metal compounds. Here we attempt to provide a comprehensive view, both of the types of deviations of d^0 and related complexes from regular coordination arrangements, and of the theoretical framework that allows their rationalization. Many computational and experimental examples are provided, with an emphasis on homoleptic mononuclear complexes. Then the factors that control the structures are discussed in detail. They are a) metal d orbital participation in σ bonding, b) polarization of the outermost core shells, c) ligand repulsion, and d) π bonding. Suggestions are made as to which of the factors are the dominant ones in certain situations. In heteroleptic complexes, the competition of σ and π bonding of the various ligands controls the structures in a complicated fashion. Some guidelines are provided that should help to better understand the interrelations. Bent's rule is of only very limited use in these types of systems, because of the paramount influence of π bonding. Finally, computed and measured structures of multinuclear complexes are discussed, including possible consequences for the properties of bulk solids.

Keywords: bond theory · d^0 complexes · density functional calculations · transition metals · VSEPR Model

1. Introduction

The development of improved models for chemical bonding has always benefited from specific cases in which the existing models fail. One well-known example is the failure of the widely used valence-shell electron-pair-repulsion (VSEPR[1]) model and also of simple ionic models to predict the bent structures of some of the molecular dihalides of the heavy alkaline earth metals (Ca, Sr, and Ba) in the gas phase.[2–10] Many more complexes with a formal d^0 configuration of the central metal (and also with d^1 and d^2 configurations) have since been found, both experimentally and computationally, which do not conform to the simple structural models. These interesting "non-VSEPR" d^0 systems and the electronic factors that control their shapes are the topic of this article.

Figure 1 shows the part of the periodic table, in which metals with a formal d^0 configuration may be found. The configuration assignment is based on the usual oxidation state formalism, which assumes a heterolytic distribution of the bonding electrons in favor of the ligands.[11] The number of different metals for which such a configuration is possible is remarkable indeed, and ranges from the heavier members of "main" Groups 1 and 2 through the genuine transition metals Groups 3–8 to the lanthanides, and even to the later members of the actinides.[12, 13] Many compounds with a formal d^0 configuration are of practical importance, for example, as

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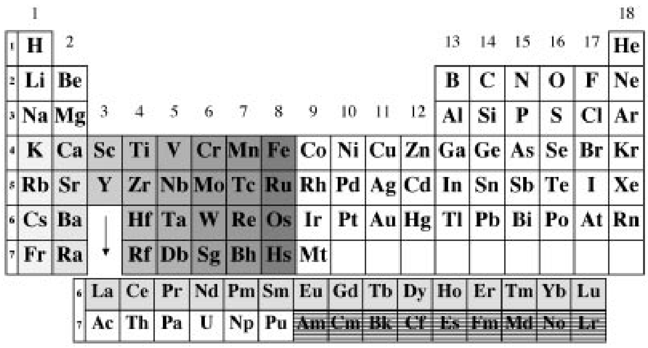

Figure 1. Range of occurrence of systems with formal d^0 configuration throughout the periodic table. Shaded areas indicate the range found. Darker shading indicates increasing covalency.

catalysts, in important materials (see Section 5), or in biological systems.[14, 15] Moreover, as d^0 complexes lack nonbonding d electrons by definition, one may view them as the simplest transition metal compounds and thus as convenient starting points for a better understanding of transition metal chemistry in general. It is therefore worthwhile having a closer look at the performance of simple models in describing bonding and the molecular shapes of such systems.

Very different views have been put forward on how to explain the "non-VSEPR structures" of certain d^0 systems. These range from modified ionic models through "extended VSEPR" approaches to molecular-orbital (MO) and valence-bond (VB) models emphasizing the covalent bonding contributions. Based on the results of a large number of quantum-chemical calculations during the past years by many research groups, herein we will attempt to provide a unified view of the factors that control the structures of d^0 systems. Initially we will focus mainly on the simplest mononuclear, homoleptic complexes. Recently there has been increased interest in more complicated heteroleptic, as well as in multinuclear complexes; preliminary discussions will be given in Sections 4 and 5, respectively, of the new considerations that come into play for such systems. Rather than giving a comprehensive choice of examples, we will try to be systematic with respect to what is known about the electronic origin of the structural preferences (mainly in Section 3).

We will provide many experimental examples (mainly in Sections 2, 4, and 5). Our emphasis, however, will be on the interrelation between structure and bonding. It should be noted that the interaction between experimental and quantum-chemical studies has been tremendously fruitful in this area of research on d^0 systems. In particular, ab initio and density functional theory (DFT) computations have been shown in a considerable variety of cases to be at a stage, where rather detailed, qualitative and quantitative, structural predictions can be made. Some of the aspects of the unusual structures of d^0 complexes have already been mentioned in other contexts in previous reviews (see, e.g., refs. [10a, 16–18]). d^1 Complexes and low-spin d^2 complexes frequently exhibit distortions very similar to those of their d^0 analogues, although the single or double occupation of one nonbonding d orbital typically reduces the tendency to distort. We will concentrate on d^0 complexes but will occasionally also mention d^1 and d^2 examples.

2. Examples of Homoleptic Complexes with "Non-VSEPR Structures"

In this Section we will give some examples, both from experimental and from computational studies, for homoleptic d^0 systems that depart from the expected "VSEPR structures". The literature available has grown tremendously during the past few years. We will therefore not attempt to review all the compounds studied but rather try to cover all the important *types* of systems. The examples will be grouped in the order of increasing coordination numbers.

2.1. Bent Dicoordinate Complexes

Let us start with the well-known case of the gaseous, monomeric alkaline earth dihalides. Table 1 summarizes the current knowledge (see ref. [10] for more details) about the

Martin Kaupp, born 1962 in Stuttgart, studied Chemistry in Stuttgart and Cincinnati. After his diploma thesis 1989 in Stuttgart in theoretical chemistry with Hermann Stoll, he moved to Erlangen, where he received his doctorate 1992 performing quantum-chemical studies with Paul von Ragué Schleyer. Following a stay 1992/1993 at the Max-Planck-Institut für Festkörperforschung in Stuttgart with Hans-Georg von Schnering, further postdoctoral work was carried out 1993/1994 with Dennis Salahub in Montréal. After the return to Stuttgart, the completion of the Habilitation in theoretical chemistry followed in 1997. Since the end of 1999, he is a Professor at Universität Würzburg. Research interests cover a wide-range of theoretical and computational chemistry. The topic of the present review reflects a general interest in structure, bonding, and reactivity throughout the entire periodic table. A further central field of research is the development and application of density functional methods for the calculation and interpretation of NMR and EPR parameters, extending their applicability to compounds of heavier elements. In this context, but also in many other areas of chemistry, he is is particularly interested in the influence of relativistic effects, and in their quantum-chemical treatment.

Table 1. Preferred structures of the monomeric alkaline earth dihalides $[MX_2]$.[a]

X: M:	F	Cl	Br	I
Be	linear	linear	linear	linear
Mg	linear	linear	linear	linear
Ca	quasilinear	quasilinear	quasilinear	quasilinear
Sr	bent ($\Delta E_{lin} = 6.6$)	quasilinear	quasilinear	quasilinear
Ba	bent ($\Delta E_{lin} = 20.9$)	bent ($\Delta E_{lin} = 6.8$)	bent ($\Delta E_{lin} = 4.5$)	quasilinear

[a] Linearization energies ΔE_{lin} [kJ mol^{-1}] are from Configuration interaction singles-doubles (CISD) calculations.[5] Species for which computed energy changes are below approximately 4 kJ mol^{-1} upon angle changes of more than 20° around linearity have been termed "quasilinear".

linear versus bent structures of these molecules, mainly based on the results of ab initio calculations[4, 5] (the various available experimental techniques all have their problems with the quantitative structure determination in the case of shallow potential-energy surfaces[5, 10]). As expected, the Be and Mg dihalides are linear. However, the halides of the heavier metals deviate increasingly from a rigid linear structure, the heavier the metal and the lighter the halogen is.[2] As a result, $[BaF_2]$[*] may be called genuinely bent, with a linearization energy of about 20 kJ mol^{-1}, whereas several other "intermediate" species should be better termed "quasilinear" in view of energy changes below approximately 4 kJ mol^{-1} upon bond-angle changes over more than 20°.[4, 5] These computational results confirmed the more qualitative conclusions of the early electric quadrupole deflection (EQD) experiments of Klemperer et al.,[2] which initiated the interest in the shapes of the gaseous alkaline earth dihalides. The quantum-chemical calculations may thus be considered to have settled the long-standing dispute on the structures of these molecules. We note in passing that the use of even larger basis sets and a better inclusion of electron correlation than in these studies are expected to give an even slightly larger preference to bent arrangements (as well as slightly shorter bond lengths in some of the systems).

The lanthanides in their +II oxidation state may be considered to be valence isoelectronic with the heavy alkaline earth compounds. Consequently, their gaseous dihalides are also bent, or at least they exhibit a relatively flat bending potential curve (i.e. they are quasilinear). This structure has been confirmed at various computational levels[19] (again, various experimental techniques give partly inconclusive results, but EQD experiments indicate bent structures for the difluorides[20]). The alkaline earth dihydrides have been studied computationally as the simplest model systems for the dihalides.[3, 7–9] While $[CaH_2]$[3, 7–9] should be considered quasilinear, the heavier homologues are increasingly bent. For example, $[BaH_2]$ was computed[3] to have a bending angle of around 119° and a linearization energy of more than 25 kJ mol^{-1}. Thus, it is slightly more bent than $[BaF_2]$. A matrix-isolation infrared (IR) and density functional study has found bent structures also for almost all lanthanide dihydrides.[21]

A computational comparison of a range of $[MX_2]$ complexes[6] ($M = Ca, Sr, Ba$; $X = Li, BeH, CH_3, NH_2, OH, F$) has indicated that the dimethyl complexes $[M(CH_3)_2]$ also exhibit an even larger tendency to bend than the corresponding difluorides, for reasons we will discuss in Section 3.8. Indeed, Eaborn et al.[22] have prepared a number of unsolvated $[MR_2]$ complexes ($M = Ca, Eu, Yb$) with very bulky alkyl ligands ($R = C[Si(CH_3)_3]_3$) and structurally characterized them by X-ray diffraction. All of these compounds exhibit bent structures in the solid state. In the case of the alkaline earth diamides $[M(NH_2)_2]$, a significant dependence of the bending on the orientation of the amide group has been found computationally,[6] a point we will discuss in detail in Section 3.8. Complex potential-energy surfaces have been computed for the $[M(CN)_2]$ molecules, with side-on coordination and bent structures dominating for $M = Sr, Ba$.[23]

If we regard the cyclopentadienyl ligand as occupying one coordination site at the metal, the Group 2 and lanthanide(II) metallocenes $[MCp_2]$ ($Cp = \eta^5\text{-}C_5H_5$) may also be viewed as dicoordinate $[MX_2]$ complexes. Indeed, the observation[24, 25] of bent solid-state structures of a number of substituted, base-free alkaline earth and lanthanide(II) metallocenes stimulated considerable interest, although it could not be ruled out that intermolecular contacts may be partly responsible for the bending. Gas-phase electron diffraction (GED) studies also suggested bent structures.[26] Ab initio calculations on $[MCp_2]$ at the MP2 level[27] indicated bent minimum-energy structures for $M = Sr, Ba, Sm, Eu$, but linear structures for $M = Ca, Yb$ (see refs. [26d, 28] for further computations). In all cases the bending potential was extremely shallow, and thus these complexes should best be classified as quasilinear, with shallow potential-energy surfaces. As a consequence, the problem of shrinkage effects[10] makes a reliable determination of the bending angles by GED difficult for such systems.

In contrast, calculations on the isoelectronic but more covalently bonded, hypothetical cations $[MCp_2]^+$ ($M = Sc, La$)[29] indicated significantly bent arrangements with large linearization barriers. Thus, the preference for bent structures increases with increasing covalency (cf. Section 3.7). Bent structures have also been computed for the heteroleptic model systems $[CpM(NH)]$ ($M = Y, La$).[30] Similarly, the cations $[YH_2]^+$,[31c] $[ScF_2]^+$,[9f, 32] and $[ScH_2]^+$[32, 33] have been computed to be significantly bent. Small angles and large linearization energies have been found computationally and partly experimentally for $[MO_2]$ ($M = Ti, Zr, Hf$).[34–36] Even more strongly bent structures have been found for the ions $[MO_2]^+$ ($M = Nb, Ta$),[37] and were predicted for the hypothetical $[MO_2]^{2+}$ ($M = Mo, W$).[38] Earlier Hartree–Fock–Slater calculations also gave a significantly bent structure for $[CeO_2]$,[7] but this method probably overestimates the bending.[39]

d^0 Systems with neutral ligands may also exhibit bent structures, with relatively shallow bending potentials but quite low bending angles. This has been found computationally for the hypothetical cations $[M(L)_2]^{m+}$ ($M^{m+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}, Sc^{3+}, Y^{3+}, La^{3+}$; $L = HF, H_2O, NH_3$).[40] Even the

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[*] Note: molecular metal compounds will be considered as coordination complexes and thus written in square brackets.

corresponding Group 1 cations $[Rb(L)_2]^+$ and $[Cs(L)_2]^+$ were computed to exhibit deviations from linearity, albeit with extremely shallow potential wells.[40b] The same holds for the bis(diethyl ether) complexes.[41]

2.2. Pyramidal Tricoordinate Complexes

The importance of ligand repulsion increases with increasing coordination numbers (cf. discussion in Section 3.7). The conditions for the pyramidalization of tricoordinate complexes are therefore already significantly more restrictive than those for the bending of dicoordinate species. Thus, Group 3 or lanthanide trihalides tend to be planar[13, 19, 32, 42, 43] (ref. [10] provides extensive further literature) or only very slightly pyramidalized, with shallow potential wells ("quasiplanar"). Slightly pyramidalized structures in the solid state have been found for a number of substituted rare earth metal tris(amido)[44, 45] and tris(phenolato)[46] complexes. However, the available evidence (e.g. NMR spectra in solution[44] or disorder in the solid-state structures[44–46]) indicates that the barrier to planarity must be small. Planar structures are expected for the corresponding isoelectronic Group 2 $[MX_3]^-$ ions.

In contrast to the trihalides, significantly pyramidal structures have been computed for hydrido species such as $[ScH_3]$,[32] $[LaH_3]$,[42c] several other lanthanide trihydrides (supported by matrix IR data[21]), $[TiH_3]^+$[32] and $[ZrH_3]^+$,[31c] or for the trialkyl ions $[Ti(CH_3)_3]^+$[32] and $[Ta(CH_3)_3]^{2+}$.[47] Indeed, the unsolvated trialkyl complexes $[M\{CH(Si(CH_3)_2)\}_3]$ (M = La, Sm) have been found experimentally to be distinctly pyramidal in the solid state.[48] This greater preference for pyramidal structures with hydride or alkyl ligands is to a large extent a result of the absence of π bonding[32] (cf. Section 3.8). The computed preference for pyramidal structures of species such as the ion $[TiCp_2R]^+$ (R = alkyl) has been suggested[49] as a possible origin of the syndiotacticity of propene polymerization using related metallocene catalysts (see also ref. [50]). In contrast, model calculations gave planar structures for neutral species like $[ScCp_2R]$ or $[TiCp_2R]$, and a correspondingly lower stereospecificity was considered.[49] Some more computational examples for pyramidal heteroleptic Group 3 and Group 4 complexes have been provided.[30, 51] Pyramidal structures have also been computed for the hypothetical cations $[ML_3]^{m+}$ ($M^{m+} = Sr^{2+}, Ba^{2+}, La^{3+}$; L = H_2O, NH_3)[40a,b] (and $[Ln(MeCN)_3]^{3+}$[52]). For the more covalent Group 6 systems $[CrO_3]$, $[MoO_3]$, and $[WO_3]$, calculations indicated significantly pyramidal structures[53–55] (see also refs. [30, 56] for further examples).

2.3. Tetracoordinate Complexes

Deviations from conventional "VSEPR" structures are least likely for tetracoordination, as both ligand repulsion and covalent considerations lead to a large preference for tetrahedral arrangements. Indeed, tetrahedral structures dominate the tetracoordination of d^0 complexes. Hybridization arguments (cf. Section 3.5) suggest a square pyramid (with the metal at the apex) or a trigonal pyramid (with the metal at the basis) as possible alternatives to the tetrahedron.[31c] However, these configurations have considerably larger ligand repulsion. DFT calculations on the $[NbH_4]^+$ ion indicate a square pyramidal structure as lowest-energy minimum.[57] Already for the heavier homologue $[TaH_4]^+$, the tetrahedron is computed to be lowest in energy, with the square pyramid about 30 kJ mol^{-1} above.[31c] While $[Ti(CH_3)_4]$ has been computed to be tetrahedral, its distortion requires considerably less energy than for analogous main group compounds.[58] Interesting deviations from an ideal tetrahedron may be found for tetracoordinate complexes when inequivalent ligands are present (see Section 4.1).

2.4. Square-Pyramidal Pentacoordinate Complexes

The VSEPR model predicts the trigonal-bipyramidal (TBP-5) structure to be the most stable arrangement for pentacoordinate d^0 complexes. However, even for main group compounds, square-pyramidal (SP-5) structures are only very slightly higher in energy (usually by a few kJ mol^{-1}). As a result, many $[MX_5]$ main group complexes are fluxional, often by the well-known Berry-pseudorotation pathway[59] (see ref. [60] for early reviews and excellent bonding discussions). The same behavior, that is, a TBP-5 minimum and low-lying SP-5 transition states, is found for d^0 pentahalides, both experimentally[61] and computationally[62] (see also ref. [60a]).

In contrast, the TBP-5 structure has been computed to be only a higher-order saddle point for $[TaH_5]$, more than 80 kJ mol^{-1} above the SP-5 minimum.[62] This preference for an SP-5 arrangement survives for $[Ta(CH_3)_5]$[62–64] which is experimentally known and has been structurally characterized by GED.[64] Among other factors, the larger ligand repulsion compared to the hydride (see discussion in Section 3.7) reduces the TBP-5 versus SP-5 energy difference (MP2 calculations give ca. 30 kJ mol^{-1},[62, 63] recent DFT calculations provide ca. 53 kJ mol^{-1} [65]). Based on ab initio calculations, it has been suggested[66] that the activation barrier for unimolecular methane elimination from $[M(CH_3)_5]$ (M = Nb, Ta), to give Schrock-type carbene complexes, is enhanced significantly by the fact that the ground states have SP-5 structures, whereas the transition states for the elimination reaction are closer to TBP-5. The recently reported structure[58] of the $[Ti(CH_3)_5]^-$ ion in the solid state ($[Li(Et_2O)_2]^+[Ti(CH_3)_5]^-$) is remarkable, as it exhibits two crystallographically different ion pairs. Of these, one is closer to SP-5, the other closer to TBP-5. Calculations for the free anion indicate SP-5 to be lower than TBP-5 by only about 10 kJ mol^{-1}.[58] A structure close to SP-5 has been found by X-ray diffraction for another $[TaR_5]$ alkyl complex (R = CH_2-*p*-$C_6H_4CH_3$).[67] The d^1 complex $[Mo(CH_3)_5]$ has recently also been found to favor SP-5, and computations suggest that the stabilization relative to TBP-5 is large.[65]

Interesting computational results are available for some further hypothetical hydride complexes: For the ion $[TiH_5]^-$, an SP-5 minimum has been calculated by DFT methods, with

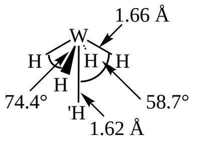

Figure 2. DFT-optimized lowest-energy structure of [WH$_5$]$^+$.[31c]

the TBP-5 approximately 30 kJ mol^{-1} less stable.[68] The more ionic [HfH$_5$]$^-$ prefers TBP-5, probably in part because of ligand repulsion (cf. Section 3.7).[57] In contrast, DFT calculations for the cation [WH$_5$]$^+$ suggest an unusual "umbrella-like" C_{4v} structure to be lowest in energy (Figure 2), but with several other low-lying minima (including the SP-5 structure) at less than 10 kJ mol^{-1} higher energy[31c] (see also ref. [57]).

Another interesting result is the computational observation of low-lying transition states of C_{2v} symmetry for the interconversion of equivalent SP-5 minima in [TaH$_5$] (Figure 3).[62] These transition structures may be classified as edge-bridged tetrahedral (EBT-5).[68] Therefore, this system has been predicted to be fluxional, in spite of the high energy of the TBP-5 structure.[62] Similar pivoting mechanisms may be expected for other five-coordinate d^0 complexes (as confirmed, for example, by computations[68] on the [TiH$_5$]$^-$ ion). Related EBT-5 arrangements may even become minima on the potential-energy surface for heteroleptic five-coordinate systems including both σ- and π-donor ligands[68, 69] (see Section 4.2).

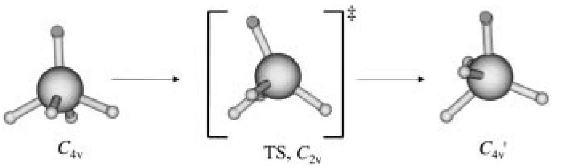

Figure 3. Low-lying C_{2v} symmetrical transition states (TS) on the energy surface of [TaH$_5$].[62]

2.5. Nonoctahedral Hexacoordinate Complexes

The increasing number of known nonoctahedral hexacoordinate d^0, d^1, and d^2 complexes represents probably the most spectacular failure of the traditional structure models in this area of the periodic table. The octahedron, which is clearly favored by ligand repulsion,[70] has been, and still is by far the predominant geometry for this coordination number, both in main group and in transition metal chemistry. It remains the dominant coordination mode even for most d^0 [MX$_6$] complexes, for example, with X = halide,[10, 62, 71] OR,[72] NR$_2$,[73]. However, as has been pointed out,[71] there are indications that the energy difference between octahedral and trigonal-prismatic arrangements for such d^0 systems is already considerably lower than for typical main group species, that is, the complexes are less rigid towards intramolecular rearrangements (presumably via D_{3h} transition states; however, see ref. [70]). A controversy arose,[62, 74–76] about whether the structure of [CrF$_6$] is octahedral or trigonal prismatic. This was mainly because the computational treatment of electron correlation is relatively difficult for this 3d system with a low HOMO – LUMO gap. The experimental information was also controversial. However, meanwhile both experiment[77] and theory[62, 76] agree with an octahedral structure. The conversion from octahedron into trigonal prism is computed[62, 76] to require actually somewhat higher energy than, for example, in [WF$_6$].[78] Table 2 summarizes activation barriers calculated for the trigonal twist of the Group 6 hexahalides. The regular trigonal prism is generally a transition state for this process (for [CrBr$_6$], [CrI$_6$], and [MoI$_6$], the DFT calculations did not converge for the O_h structure). Notably, with Mo and W, the barrier is larger for the heavier halogens than for fluorine (Section 3.8). For a given halogen, the barrier is larger with W than with Mo (Section 3.7). Obviously, these numbers indicate that a trigonal twist is much more facile than for main group hexahalide complexes, for which the barriers range typically from 100 to 300 kJ mol^{-1},[71] and thus dissociative processes become likely alternative pathways for ligand scrambling.

Table 2. Relative energies [kJ mol^{-1}] between D_{3h} and O_h structures of Group 6 hexahalide complexes.[a]

	Cr	Mo	W
F	61.6	27.1	42.9
Cl	56.4	62.6	78.7
Br	–[b]	61.9	74.9
I	–[b]	–[b]	66.4

[a] DFT calculations, see appendix. The O_h structure has been characterized as a minimum, whereas the D_{3h} structure is a transition state. [b] No self-consistent field (SCF) convergence within O_h symmetry at this computational level.

The earliest experimental examples of trigonal-prismatic coordination of early transition metals were provided by the extended solid-state structures of various d^0, d^1, and d^2 metal chalcogenides and pnictides (e.g. for the mineral molybdenite, MoS$_2$). An early overview on these solid-state compounds, and a very perceptive discussion of their electronic structure, has been given by Huisman et al.[79] (see also discussion in ref. [70]). Although the stoichiometric composition often does not lead directly to a d^0 – d^2 configuration of the metal, the local electronic situation may well correspond to it. Strongly distorted octahedral metal coordination is ubiquitous in binary or ternary Group 4 – 6 oxides, e.g. for ZrO$_2$, WO$_3$, MoO$_3$, BaTiO$_3$, or KNbO$_3$[80, 81]. These examples are relatively clear-cut d^0 cases. The distortions have been studied extensively in many cases because of their impact on technologically important materials properties. Such extended solid-state structures will be discussed in more detail in Section 5.

The first molecular d^0 complexes with trigonal-prismatic (or close to prismatic) structures were those of dithiolate (or diselenolate) chelate ligands,[82–85] originally with an unsaturated organic backbone (dithiolene or diselenolene[86] ligands). In this case, the nature of bonding is delocalized, and the assignment of a formal oxidation state and d configuration

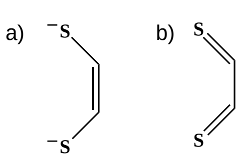

Figure 4. Two extreme bonding situations for dithiolene chelate ligands: a) dianionic dithiolene, b) neutral dithiodiketone.

is not straightforward (Figure 4 shows two extreme formulations of the state of the ligands). A formal treatment of the ligands in their dianionic form is advantageous for our present purpose[85], and gives a d^0 electron count for tris(dithiolene) systems such as $[Mo(S_2C_2H_2)_3]$ or $[Nb(S_2C_2H_2)_3]^-$.[87] Meanwhile, a significant number of nonoctahedral complexes with saturated dithiolates[83, 88] have been structurally characterized. Their bonding may be discussed in somewhat simpler terms. Part of the ongoing interest in dithiolate and dithiolene complexes is related to the importance of dithiolene coordination for the molybdopterin cofactor of various oxidase and reductase enzymes[84, 89–91] (Section 4.4). More recently, the first nonoctahedral hexacoordinate complexes of monodentate thiolate ligands have been reported.[92]

Typically, the structures found for tris(dithiolate), hexathiolate or tris(dithiolene) complexes, and for related complexes of more unysmmetrical ligands, may be assigned, at least approximately, C_3 symmetry. Depending on the actual electron configuration, on the type of ligand, on the metal, and on counter-ion contacts, these structures cover the entire range from octahedral to trigonal prismatic coordination. Whether a structure is closer to the trigonal prismatic or octahedral ("trigonal antiprismatic") extreme may often be expressed most conveniently in terms of a trigonal-twist angle δ between the two appropriate trigonal faces (Figure 5).[82–84] For monodentate ligands, $\delta = 0°$ and $\delta = 60°$ denote clearly the trigonal prismatic and antiprismatic limits, respectively. For chelate ligands, the octahedral limit has to be set at $\delta < 60°$, depending on the ligand bite angle (ca. 49° for a typical bite angle of ca. 81°).[93] The angle between *trans* coordination sites will in this case be around 170° rather than 180°. This has to be compared to a typical *trans* angle of about 136° for a regular trigonal prism.

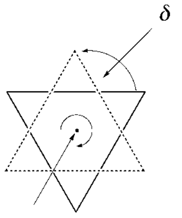

Figure 5. Definition of trigonal twist angles δ along C_3 axis for tris(dithiolene) and related systems intermediate between octahedron and trigonal prism.

Complexes with unsaturated dithiolene ligands exhibit structures closer to the trigonal prism than those of saturated dithiolate ligands. This is related to π bonding (Section 3.8). A particularly fascinating set of systems is provided by compounds containing the $[M(ndt)_3]^-$ ion (M = Nb, Ta; ndt = norbornane-*exo*-2,3-dithiolate).[94] Depending mainly on the counter ions, several unusual structures are possible, in one of which the three chelate ligands coordinate in nonequivalent modes.[94] In this case, the distortion is more in the direction of a bicapped tetrahedron than of a trigonal prism. Similar types of distortion have been observed[95] and are more important for heteroleptic complexes (Section 4.3).

Most of the early discussions of the nonoctahedral structures of tris(dithiolene) complexes have focused on the notion of some special property of the ligands, for example, on the idea of "interligand bonding",[86a, 96] rather than on a genuine preference of the central metal for a prismatic coordination (however, see refs. [70, 79]). In view of the more recent observations of nonoctahedral complexes with simpler, monodentate ligands (see below), it is now clear that tris(dithiolene) and related complexes may be understood along the general lines set out in Section 3.

Apart from complexes of sulfur-based ligands, various complexes of other chelate ligands have been found to exhibit structures along the octahedral/prismatic twist coordinate. Examples are the tris(dialkoxide) complexes $[W(OCH_2CH_2O)_3]$ ($\delta \approx 37°$)[97] and $[W(OCMe_2CMe_2O)_3]$ ($\delta \approx 34°$),[98] which are more on the octahedral side. More on the prismatic side are tris(9,10-phenanthrene-quinone)molybdenum,[99] tris(buta-1,3-diene)molybdenum,[100, 101] tris(*ortho*-xylyl)tungsten,[102] tris(methylvinylketone)tungsten[103] (all $\delta \approx 0°$), or the recently characterized tris(4,4′,5,5′-tetramethyl-2,2′-bisphosphinine)tungsten ($\delta \approx 15°$; Figure 6).[104] In all of these cases, we may arrive at a formal d^0 configuration of the metal by regarding the chelate ligands in their dianionic form. For the butadiene ligand, this would lead to a metallacyclopentene-type rather than to a butadiene π-complex bonding situation (Figure 7). Therefore, one might expect shorter central than terminal C–C bonds, as is common for butadiene complexes of early transition metals.[105] The available experimental data[100, 101] indicate short terminal and long central bonds. However, these distances are probably unreliable. Recent DFT and MP2 calculations give the expected shorter central bonds.[106] The structures of tris(*ortho*-xylyl)tungsten[102] and tris(methylvinylketone)tungsten[103] exhibit short central bonds and thus support a first approximation as d^0 complexes with chelating dialkyl and enolate ligands, respectively. Similar to the situation for dithiolene ligands (see above), one may generally approach the bonding either by starting from a neutral ligand and then include extensive π backbonding, or from a dianionic ligand and then include π delocalization within the ligand (Section 3.8).[70]

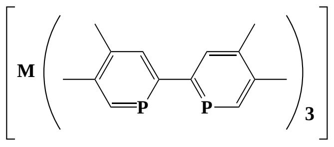

Figure 6. Group 6 tris(4,4′,5,5′-tetramethyl-2,2′-bisphosphinine) complexes.[104]

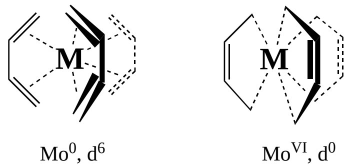

Figure 7. Two limiting resonance structures and formal d configurations for $[Mo(bd)_3]$ (bd = 1,3-butadiene).

In the 1980s, calculations predicted trigonal-prismatic structures (distorted, C_{3v}, or regular, D_{3h}) for simple hydride systems such as $[TiH_6]^{2-}$, $[VH_6]^-$, or $[CrH_6]$[107] (see refs. [31, 62, 71, 74, 108, 109] for further, related computational studies). The first experimental example of a trigonal-prismatic complex with only simple monodentate ligands was then provided by the solid-state structure of the $[Zr(CH_3)_6]^{2-}$ ion (further coordinated by $[Li(tmeda)]^+$ counter ions; TMEDA = N,N,N′,N′-tetramethylethylenediamine).[110] This observation spurred considerable interest. Subsequently, the neutral, valence-isoelectronic analogue hexamethyltungsten, $[W(CH_3)_6]$, received most of the attention, both experimentally[111–113] and computationally[31, 62, 114, 115] (the model system $[WH_6]$ and related species were also studied theoretically[31, 62, 71, 74, 108, 114]). While $[W(CH_3)_6]$ had been prepared in 1973 by Wilkinson and co-workers,[116] its structure had always been assumed to be octahedral.[116, 117] A GED study could then clearly rule out an octahedral arrangement.[111] A regular trigonal prism was favored (with D_{3h} skeleton), but a distortion of the skeleton towards C_{3v} could not be excluded. Initial Hartree–Fock (HF) optimizations supported the D_{3h} structure.[62] Calculations that include electron correlation later showed the skeleton to be distorted to C_{3v} symmetry (slightly tilted methyl groups reduce the overall symmetry to C_3).[114, 115] However, the system is fluxional, because a regular prismatic D_3-symmetrical transition state is only about 20 kJ mol^{-1} higher in energy and thus allows a rapid flipping process.[114, 115] Indeed, the VALBOND force-field calculations of Landis et al.[31] (Section 3.5) had even earlier suggested a distorted prism and fluxional behavior. The C_{3v} skeleton has been confirmed independently[112, 113] by a low-temperature X-ray diffraction study (see Figure 8 for a comparison of computed and experimental structure parameters). Among other things, the fluxional nature of $[W(CH_3)_6]$[114, 115] accounts for the relatively simple NMR spectra[111, 116, 117] at room temperature.

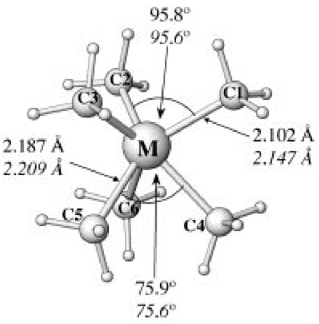

Figure 8. Comparison of experimental[113] and computed[114, 115] structure parameters for $[W(CH_3)_6]$. Computed parameters in italics. Experimental values have been averaged over three formally equivalent positions, and over the two molecules within the unit cell.

Meanwhile, the structures of several further d^0–d^2 hexamethyl complexes have been studied, both experimentally[113] and computationally.[115] DFT calculations have indicated the mono- and dianionic d^0 complexes $[M(CH_3)_6]^-$ (M = V, Ta) and $[M(CH_3)_6]^{2-}$ (M = Ti, Zr, Hf) to have regular trigonal prismatic structures, whereas neutral and cationic complexes $[M(CH_3)_6]$ (M = Cr, Mo, W) and $[M(CH_3)_6]^+$ (M = Tc, Re) distort to C_3 structures (with C_{3v} heavy-atom skeleton) to varying extents.[115] $[Nb(CH_3)_6]^-$ was computed to be a borderline case, just on the brink of distortion[115] (X-ray data confirm a slight distortion and show considerable thermal motion[113]). A regular prism was confirmed by X-ray diffraction for $[Ta(CH_3)_6]^-$.[113] Adding one or two electrons to the system quenches the distortion effectively, and thus d^1 $[Re(CH_3)_6]$ and $[Tc(CH_3)_6]$, as well as d^2 $[M(CH_3)_6]$ (M = Ru, Os), have been predicted to prefer regular prisms[114, 115] (an unusual C_{2v} structure was predicted computationally for $[OsH_6]$[109]). Indeed, while the initial X-ray structure determination for $[Re(CH_3)_6]$ had suggested a slightly distorted arrangement,[112] a more recent, better refinement confirms a regular prism.[113] Very recently, Roessler and Seppelt[118] reported the structure of $[Mo(CH_3)_6]$ and confirmed the computationally predicted C_3 structure[115] with a slightly larger distortion than that of the tungsten analogue. Most notably, in none of these cases can a distorted or regular octahedral structure compete energetically with the prismatic arrangements.

Partly because of β-hydrogen elimination as a potential low-energy pathway for decomposition, no further d^0 $[MR_6]$ complexes with simple alkyl ligands are known. However, regular trigonal prismatic structures were also observed by X-ray diffraction for the aryl complexes $[TaPh_6]^-$ and $[Ta(tolyl)_6]^-$.[119] Even more recently,[120] the anionic acetylide complexes $[Ta(tBu_3SiC{\equiv}C)_6]^-$ and $[M(tBu_3SiC{\equiv}C)_6]^{2-}$ (M = Zr, Hf) were examined in form of the salts $K[Ta(tBu_3SiC{\equiv}C)_6]$, $[K(crypt\,2.2.2.)][Ta(tBu_3SiC{\equiv}C)_6]$, $[Li(tBu_3SiC{\equiv}C)_3][Ta(tBu_3SiC{\equiv}C)_3]$, and $[\{Li(tBu_3SiC{\equiv}C)_3\}_2M]$ (M = Zr, Hf; crypt 2.2.2. = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane). While the bulky substituted acetylide ligands provide complexes closer to the trigonal prismatic extreme for the two tantalum systems (twist angles $\delta = 18°$), the more ionic Zr and Hf dianions exhibit almost regular octahedra. DFT and calculations on the simpler model complexes $[Ta(C{\equiv}CH)_6]^-$ and $[Zr(C{\equiv}CH)_6]^{2-}$ gave structures closer to the regular prism, but with the octahedron at lower relative energy for the dianion compared to the monoanion.[120]

2.6. Higher Coordination Numbers

For coordination numbers above six, there should be no significant surprises. Ligand–ligand repulsion is expected to dominate and to favor regular structures. Moreover, even the simplest structure models allow several different coordination arrangements (Figure 9) that usually do not differ much energetically. Nevertheless, we may ask to what extent additional electronic factors favor certain structures?

The only experimental examples of seven-coordinate, exclusively σ-bonded d^0 complexes are the ions $[M(CH_3)_7]^-$ (M = Mo, W).[118, 121] Both exhibit a singly capped distorted octahedral structure (SCO-7; C_{3v} skeleton), which has also been found in ab initio calculations to be the lowest-energy structure for $[MH_7]^-$ (M = Mo, W)[31d, 57, 122] The SCO-7 arrangement is "allowed" by the VSEPR model because it has relatively low ligand–ligand repulsions, in fact lower than those of the two alternative structures, the singly capped trigonal prism (SCTP-7) and the pentagonal bipyramid (PB-7). On the other hand, the structural parameters of the underlying distorted octahedra for $[M(CH_3)_7]^-$ are in striking agreement with one of the lower-lying stationary points on the

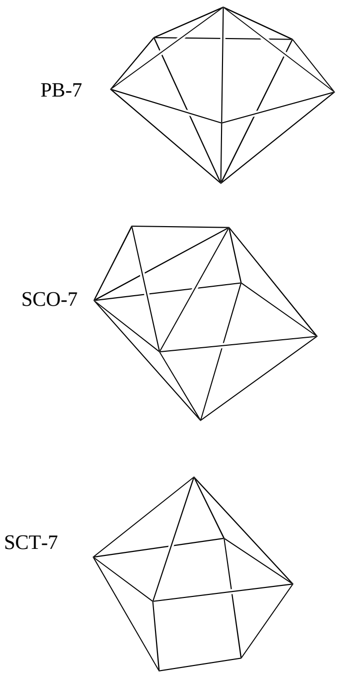

Figure 9. Preferred polyhedra for heptacoordination.

potential-energy surface computed for the hexamethyl complexes.[114, 115] This suggests that in addition to ligand repulsion there may also be some electronic factors that favor the SCO-7 structure. These structures contrast to those of heptacoordinate main group compounds such as $[IF_7]$, which usually prefer PB-7 (with distortions in the equatorial plane).[122, 123] Of the experimentally known d^0 heptafluorides, $[ReF_7]$[124] apparently prefers a distorted PB-7,[125] whereas $[WF_7]^-$ and $[MoF_7]^-$ favor the SCO-7.[126] The dianions $[NbF_7]^{2-}$ and $[TaF_7]^{2-}$ have been found to exhibit the SCTP-7,[127] whereas the PB-7 apparently is again favored for the trianions $[ZrF_7]^{3-}$ and $[HfF_7]^{3-}$ [128] (clearly, interactions with the counter ions are expected to be large for the polyanions).

The most notable computational result in this context is the finding that the SCO-7 is *strongly* favored (by ca. 150 kJ mol^{-1}) over PB-7 for $[WH_7]^-$, whereas the energy difference is only about 4 kJ mol^{-1} for $[WF_7]^-$ and around 18 kJ mol^{-1} for $[MoF_7]^-$.[122] This provides further support for the importance of electronic factors. More specifically, as the pentagonal bipyramid exhibits a 180° bond angle between the apical ligands, this arrangement is unfavorable for predominantly σ-bonded d^0 systems (Sections 3.4 and 3.5). Furthermore, it appears possible that π bonding is less effective for these high coordination numbers, because of competition with the σ bonds for the same metal orbitals (Section 3.8 and 4.1).

Nonclassical structures are most likely for simple hydrides, and quantum-chemical calculations on these systems are most easily carried out. Calculations on $[TcH_7]$ favor a C_{2v} structure that might be described best as distorted SCTP-7.[57] For ReH_7, a further slight distortion of this polyhedron was computed.[57] MP2-optimizations for the cations $[MH_7]^+$ (M = Ru, Os) converged towards nonclassical dihydrogen complexes and thus may not be compared directly.[57] If we regard the η^5-cyclopentadienyl ligand as occupying one coordination site, an experimentally known heteroleptic analogue of a d^0 $[MH_7]$ system is provided by $[ReCpH_6]$ (see also Section 4).[129] This system favors a structure derived from PB-7, but with the equatorial hydrogens bent away by more than 110° from the Cp ligand (which is a strong π donor, Sections 3.8. and 4). Calculations indicate SCO-7 to be higher in energy by about 66 kJ mol^{-1}.[130]

Ab initio calculations on $[OsH_8]$ and $[MH_8]^-$ (M = Tc, Re) indicate that irregular C_s structures are favored ($[RuH_8]$, $[RhH_8]^+$, and $[IrH_8]^+$ converge towards dihydrogen complexes).[57] σ Bonding disfavors the more symmetrical eight-coordinate arrangements, the dodecahedron (D_{2d}) and square antiprism (Section 3.4).[57] A distorted square-antiprismatic D_{2d} structure has been predicted computationally for $[OsF_8]$.[131] While a similarly distorted structure has been observed for the $[TaF_8]^{2-}$ ion in $Na_2[TaF_8]$,[132] a regular square antiprism was found for the d^0 $[WF_8]^{2-}$ and the d^1 $[ReF_8]^{2-}$ ions.[133] The d^1 octaalkyl complex, $[Re(CH_3)_8]^{2-}$ exhibits an almost regular square antiprism structure.[121] Finally, the nine-coordinate systems $[IrH_9]$, $[MH_9]^-$ (M = Ru, Os), and $[MH_9]^{2-}$ (M = Tc, Re) are computed to prefer tricapped trigonal prisms, D_{3h} symmetry (with low-lying C_{4v} transition states),[57] as found also experimentally[134] for the latter two systems.

3. Bonding Descriptions and Models

In the previous section, we have summarized computational and experimental evidence indicating that a considerable variety of homoleptic d^0 complexes exhibit structures that do not obey the VSEPR model nor simple electrostatic considerations. We will now discuss the factors that lead to these "non-VSEPR structures", as well as those factors that favor the more regular structures. Figure 10 illustrates the four major influences that need to be considered. Of these, core polarization and d-orbital participation in σ bonding have been found to favor the non-VSEPR arrangements, whereas ligand repulsion and π bonding tend to act against them. However, the effect of π bonding is more complicated and

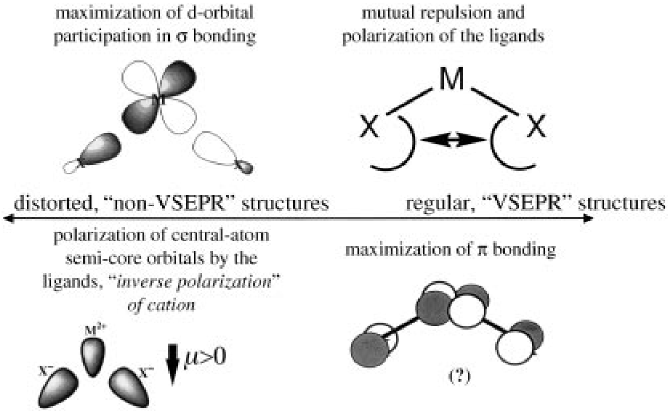

Figure 10. Illustration of the four important factors that control the structural preferences of d^0 complexes. The question mark for π bonding indicates that there are cases where π bonding may actually favor the "non-VSEPR" structures (see Section 3.8).

may even favor distorted structures (Section 3.8). Core polarization and σ bonding, and the models commonly employed to deal with them, are discussed in Section 3.1 – 3.6, ligand repulsion is addressed in Section 3.7, and π bonding in Section 3.8.

3.1. The "Classical" Models: Core Polarization versus d-Orbital Involvement?

Let us start again with the first examples given in Section 2, the bent structures of some alkaline earth dihalides. Historically, two very different explanations had been offered for the bent arrangements, which at first sight appear to be very difficult to reconcile. a) Klemperer and co-workers[2] explained the bent structures within the framework of a polarized-ion model (although they did not rule out other possible reasons).[135] Thus, as shown in Figure 11, a large, polarizable cation may be polarized by the anions. This is sometimes referred to as "inverse polarization", in contrast to the more common polarization of anions by cations. Only a system with a bent structure possesses a permanent dipole moment and thus exhibits nonvanishing charge – dipole and dipole – dipole interactions involving the dipole polarizability of the cation. These interactions will therefore stabilize the bent relative to the linear arrangement. This model has later been put on a more quantitative basis by Guido and Gigli,[136] using a Rittner-type approach,[137] and it was tested by other workers.[5, 7, 8] b) An alternative, covalent bonding model has been considered in detail by Hayes,[138] and by Coulson[139] (an even earlier, very perceptive discussion has been given by Skinner,[140] prior to the discovery[2] of the bent structures). While the lighter metals Be and Mg have only valence ns and np orbitals at their disposal for covalent bonding, the heavier metals Ca, Sr, and Ba may employ their "inner" $(n-1)$d orbitals[141, 142] (note the contrast to the "outer" nd orbitals that are frequently—most often unnecessarily—invoked in the qualitative discussion of "hypervalency" of the heavier p-block main group elements[143]). The highest occupied σ-bonding molecular orbital in these molecules has σ_u symmetry in the linear $D_{\infty h}$ structure and b_2 symmetry in the bent C_{2v} structure. Thus, as shown in Figure 12, while a valence p orbital is best for the formation of a linear structure, a d orbital may only participate at a bent structure (optimally at a bond angle of 90°). Depending on the availability of such "inner" d orbitals, covalent σ-bonding contributions would thus favor either a linear structure (e.g. for the Be and Mg systems) or a bent one (for Ca, Sr, and Ba). The symmetrical σ-bonding combination (of σ_g/a_1 symmetry), which also should be considered, has optimum overlap for a linear structure. However, the slight loss of overlap for this MO is expected to be greatly over compensated by the gain in overlap for the antisymmetric combination. These arguments may be extended in a straightforward manner to higher coordination numbers (see discussions of molecular orbital and valence-bond models in Sections 3.4 and 3.5, respectively).

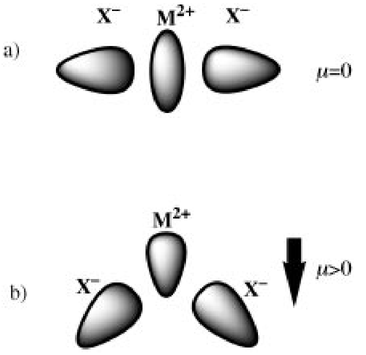

Figure 11. Schematic display of the polarized-ion model explanation of bending of alkaline earth dihalides. a) At a linear structure the system has no permanent dipole moment, and there is no stabilization because of interactions of the induced dipole of the cation with charge or dipole moment of the anions. b) At bent structures, a permanent dipole moment allows stabilizing charge – dipole and dipole – dipole interactions involving the induced dipole moment of the cation.

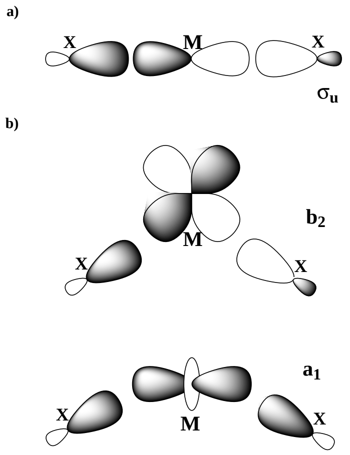

Figure 12. The d-orbital participation model[138, 139] to explain linear versus bent structures of the alkaline earth dihalides. a) Participation of a metal np orbital in the σ_u HOMO favors a linear structure (e.g. for the Be and Mg dihalides). b) Participation of a metal $(n-1)$d orbital in the b_1 HOMO favors a bent structure (e.g. for the Ca, Sr, and Ba dihalides).

3.2. Core Polarization *and* d-Orbital Involvement!

For a long time, these two models were discussed controversially. However, a careful analysis of results from ab initio calculations on $[MX_2]$ complexes indicated that a) the cation polarization and d-orbital participation arguments both are valid as two contributing aspects of the phenomenon,[3–5, 8] and b) the two aspects are not strictly separable.[144] The latter point may be appreciated best when considering radial density plots of the atomic valence and semi-core orbitals, shown for barium in Figure 13: The dipole polarizability, and thus the magnitude of any possible "inverse polarization" of a Ba^{2+} ion is largely determined by the outermost semi-core 5p atomic orbitals (AOs). For Ba^{2+}, the "inner" $(n-1)$d orbitals invoked in the covalent models are

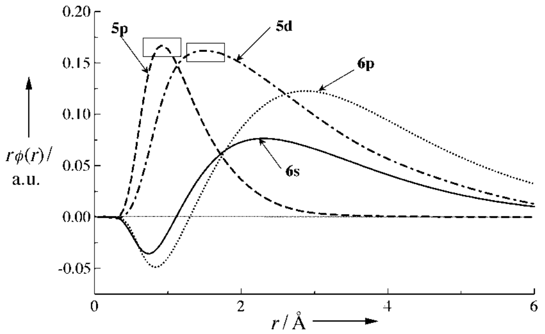

Figure 13. Radial distribution functions of atomic pseudo-valence orbitals for barium. Results of HF calculations with a small-core ECP and (6s6p5p1f) valence basis set. The 5p and 6s radial densities are from the ^1S ground state. The 5d and 6p radial densities have been computed for the lowest-lying ^3D and ^3P excited states, respectively. See ref. [145] for similar results for the calcium atom. Shaded boxes highlight the closeness of the maxima of the 5p and 5d curves.

the 5d orbitals. These orbitals have the same principal quantum number as the outermost core orbitals, and consequently their radial maxima are found in rather similar regions (Figure 13). This has been shown to be even more pronounced for the "3d metal" calcium.[145] Thus, in spite of a significant energy difference between these $(n-1)$p and $(n-1)$d orbitals (e.g. the HF orbital energies of the 5p semi-core orbitals computed for $[BaH_2]$ are in the range 23.5–24 eV, the valence orbitals near 7.5–8 eV), a clear geometrical separation of "semi-core" and valence space is not possible. Similar arguments hold for all transition metals (as well as for the lanthanides) and in particular for the early ones. Thus, it has been shown many times that in an effective-core-potential (ECP) ansatz,[146] the semi-core $(n-1)$p orbitals have to be treated together with the valence orbitals to get accurate results.[147] In the present context this means that a structure change resulting from involvement of the $(n-1)$d orbitals in bonding will invariably influence the semi-core $(n-1)$p orbitals. Turning the argument around, a polarization of the $(n-1)$p semi-core orbitals involves generally the mixing of $(n-1)$d-type orbitals into the wavefunction (the d-type basis functions have been termed "virtual orbitals of the core"[8, 145]). This represents a fundamental break down, in this region of the periodic table, of the chemists' usual valence-electron-only view.

In this context, it appears appropriate to term core polarization and d-orbital participation "two sides of the same coin".[8] Szentpály and Schwerdtfeger proposed the use of cation and anion softness as a unifying criterion, as this depends both on polarizability and the relative energies of different valence states.[8] Unfortunately, a quantitative analysis indicates that the proposed criterion does not account for the structures of the entire series of alkaline earth dihalides.[5] In spite of the inherent difficulties, there have been attempts to analyze, as far as possible, the influence of the two individual factors, core polarization and d-orbital participation, on the structural preferences of these alkaline earth $[MX_2]$ molecules. The most detailed analyses have been carried out for the simple dihydride model systems ($X = H$),[3] where complicating π-bonding contributions are absent. Various ECP approaches have been compared, with different ECP core sizes, with and without additional core-polarization potentials (CPP[148]), and with different sizes of valence basis sets. It turned out that, for example, the bent structure of $[BaH_2]$ is not reproduced with a frozen-core 2-valence-electron ECP ansatz for the metal (i.e. the innermost 54 electrons of barium are replaced by the ECP), even with a large metal d-orbital valence basis set.[3] Only when a CPP is added to simulate the polarization of the core by the valence electrons,[148] is a bent structure observed.[3] On the other hand, even with a CPP, such a 2-valence-electron ECP calculation fails to provide significantly bent structures when the metal basis does not contain d functions with large exponents (corresponding to genuine $(n-1)$d orbitals just as for the transition metals).[3]

This indicates that both core polarization *and* d-orbital participation act simultaneously to favor bent structures in these systems (keeping in mind that the two factors are not strictly separable, see above). Other investigations have supported this view,[4, 5, 8] for example, a comparison of bending-force constants obtained from a polarized ion model or from the ab initio values,[5] or analyses of model-core potential calculations.[4] Investigations of $[BaX_2]$ molecules[149] within Häser's elegant one-center expansion analysis procedure[150] of the one-particle density matrix have indicated clearly that the d-type metal populations have to be classified partly as genuinely "valence-type" as opposed to pure core-polarization contributions. This provides support for a "boundary role" of the heavy Group 2 atoms between main group elements, lanthanide, and transition metals.[3–5]

Obviously, the relative importance of core polarization versus d-orbital participation will depend on a) the metal, b) the nature of the ligands, and c) the overall charge of the system. Consider, for example, the alkali metal complex $[Cs(H_2O)_2]^+$, which calculations show to be bent, albeit with an extremely shallow bending potential.[40b] Clearly, covalent bonding contributions are very small in this system, and it appears more natural here to invoke the large polarizability of the cesium cation. Slightly bent structures of ionic compounds with large anions can be considered in a similar fashion, they are bent mainly because of the polarization of the central ion.[151]

On the other hand, if we move into the transition metal series, the importance of the covalent bonding contributions increases dramatically with increasing oxidation state and formal charge of the metal center. At the same time, core polarizability diminishes. Landis et al.[31c] have compared calculations with different ECP core sizes for the system $[WH_6]$. They found the distorted trigonal-prismatic structure for this complex to be favored even with an ECP including the $(n-1)$s and $(n-1)$p orbitals in the frozen core ("large-core" ECP). They concluded that core polarization is not very important for the structural preferences, which are then exclusively because of the covalent bonding contributions. As a note of caution, we have to mention that our own comparisons of "large-core" and "small-core" metal ECPs for $[W(CH_3)_6]$ and similar complexes indicate a large *overestimate* of the energetic preferences for distorted structures, and of the structural distortions, when using a large core. This is a result of the above mentioned fundamental break down of core-valence separation in these systems, which makes "large-core" ECP approaches unreliable quantitatively,[147] and which also does not allow a strict separation of core polarization and covalent bonding (see above). Nevertheless, it may be argued convincingly[31c] that in such relatively covalent systems the d-orbital participation in σ bonding is generally more important than the influence of core polarization in determining the "non-VSEPR" structures.

3.3. Cases for an "Extended VSEPR Model"?

Recently, Gillespie, Bader, and co-workers have studied the Laplacian of the charge density, $\Delta\rho$,[152] as a basis to discuss "non-VSEPR" structures of the alkaline earth $[MX_2]$ compounds,[153] and of some more covalent d^0 systems.[154] The $\Delta\rho$ distribution does clearly show a nonspherical form of, for example, the Ba^{2+} ion in bent $[BaH_2]$.[153a] Indeed, similar results had been obtained [144] with the electron-localization function (ELF[155]). Such plots show very nicely that, in spite of the formal noble-gas electron configuration, the central atom in such d^0 systems is significantly nonspherical.

Gillespie et al. argued further[153, 154] that the observed maxima (attractors) in $-\Delta\rho$ allow the explanation of the distorted structures: the ligands are positioned as far removed as possible from maxima in the vicinity of the central atom, these maxima are termed "core charge concentrations". More generally, these workers had argued that maxima in $-\Delta\rho$ may be seen as a manifestation of the bonding and nonbonding electron pairs of Lewis theory (more recently termed electron pair "domains"[1d,e]), and thus also as a fundamental basis of an "extended VSEPR model".[152] Based on their calculations, Gillespie et al. then claimed[153, 154] that the observed Laplacian distributions show core-polarization to be the origin of the distorted structures, thus confirming an argument advanced earlier for the failure of the VSEPR model for transition metal compounds, that is, the nonspherical shape of the metal core.[1c–e]

Unfortunately, this view is a gross oversimplification. It neglects the more complicated situation delineated in Section 3.2, in which core polarization *and* d-orbital participation in covalent bonding are two contributing aspects of the problem, which moreover are not completely separable. As we discussed above, the exclusive focus on core polarization becomes increasingly less tenable the more covalent the bonding is. Moreover, very recently Bader et al. had to conclude[154c] that "core charge concentrations" in $-\Delta\rho$ of $[TiCl_2(CH_3)_2]$ are found even when a *frozen* spherical metal atomic core density is added to a "large core" ECP valence density. This obscures effectively any relation of these maxima in $-\Delta\rho$ to the core-polarization model, and it remains to be seen what their true significance is.

A more general weakness of the extended VSEPR model is that it lacks transparency and does not appear to be predictive: to obtain the $\Delta\rho$ distribution, a detailed quantum-chemical calculation has to be carried out, using the correct structure as input! Then the observed attractors in $-\Delta\rho$ may be used for a subsequent justification of the input structure. The usefulness of this approach is clearly quite limited, and no simple rules have emerged yet from these studies, which would allow structure predictions without the need for explicit calculations. Sometimes, incorrect structures have been employed as an input for analyses, thus invalidating the conclusions. For example, a regular trigonal-prismatic structure has been employed in the analysis of $[Cr(CH_3)_6]$,[153a] whereas accurate calculations clearly support a distorted prism.[115] Similarly, a distorted octahedron has previously been used in Laplacian analyses of the structure of the $[ClF_6]^-$ ion,[156] whereas accurate calculations indicate a regular octahedron.[157] Generally speaking, it may not be sufficient to know the charge density at a given molecular structure, but we need to know what factors have lead to this structure and charge density.[158]

We emphasize that analyses of "observable-based" quantities such as $\Delta\rho$ or ELF do provide very valuable insights into the bonding of complex systems. However, an "extended VSEPR model", even though based on such important quantities, does not presently appear to be suitable to rationalize or predict the structures of transition metal compounds in any detail. The exclusive focus on core polarization and ligand repulsion distracts from other important factors, such as the competition between σ- and π-bonding interactions (see Sections 3.4–3.8, 4.1).

3.4. Molecular Orbital (MO) Descriptions: Second-Order Orbital Mixing and Symmetry Arguments

The covalent bonding aspects favoring the "non-VSEPR" structures may be cast nicely[62, 63, 74, 107] into the language of perturbation molecular orbital (PMO) theory.[159] Thus, the bent structure of $[BaH_2]$ may be considered to arise from a stabilization of the b_2 HOMO upon bending by mixing in metal d_{yz} character in second-order perturbation theory (see Figure 12). This corresponds to Hayes' modified Walsh diagrams[138] for the alkaline earth dihalides including d orbitals (reasonable Walsh diagrams for ionic systems may be obtained[5] from ab initio wavefunctions when using Davidson's "internally consistent self-consistent-field" orbitals[160]). Similar PMO arguments may be used for other coordination numbers, for example, for square-pyramidal pentacoordinate,[62, 63] or for distorted or regular trigonal-prismatic hexacoordinate complexes.[63, 74] Figure 14 shows a correlation diagram for the $O_h \rightarrow D_{3h} \rightarrow C_{3v}$ distortion of a d^0 $[MH_6]$ system, as obtained in ref. [62] from extended-Hückel-type calculations. The HOMO at the octahedral structure is a t_{1u} orbital, with participation of metal p orbitals. The LUMO is the well-known t_{2g} orbital. In this situation the participation of metal d orbitals in metal–ligand σ bonding is very unsatisfactory. Symmetry lowering to D_{3h} allows more interactions of metal d orbitals with appropriate ligand orbitals. Further symmetry reduction to C_{3v}, as computed for $[WH_6]$, finally allows the metal d_{z^2} orbital to participate in bonding (the qualitative scheme in Figure 14 may overestimate the role of the metal p orbitals). Two preconditions for these distortions are a) a small energy gap between the occupied and virtual orbitals that are to be mixed upon symmetry lowering, and b) not too much energy raising for lower-lying MOs (this

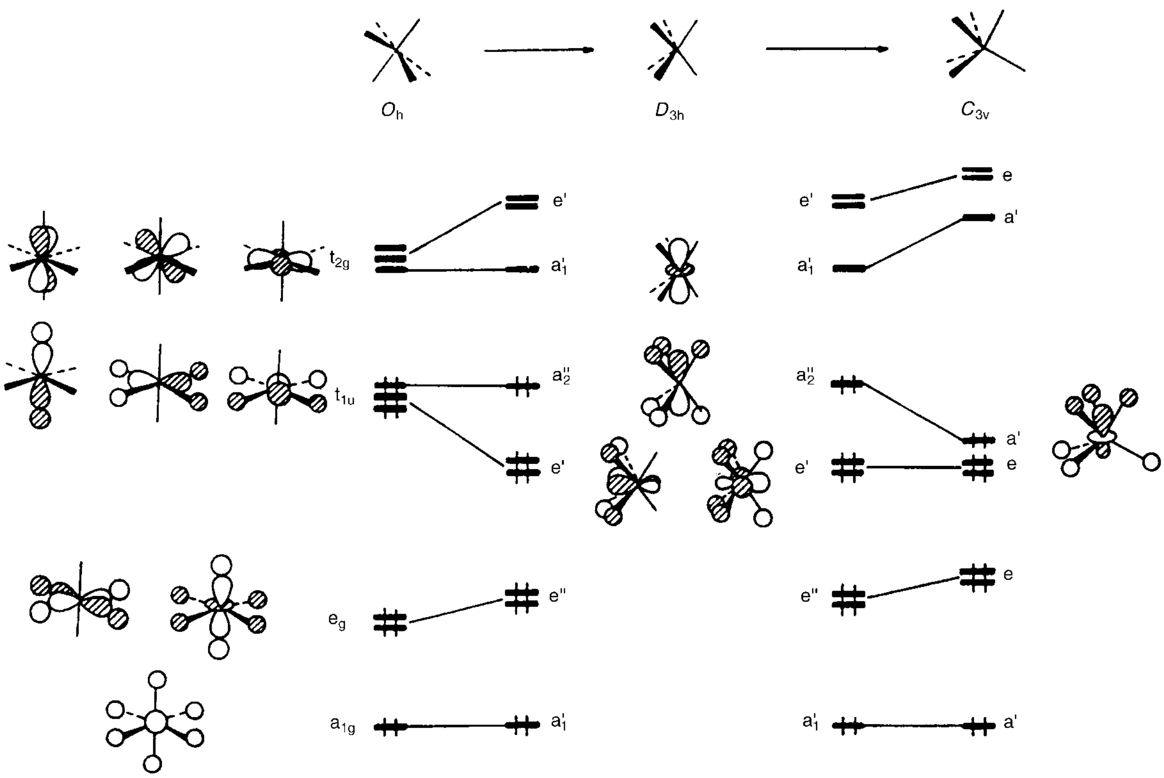

Figure 14. Qualitative MO correlation diagram for a purely σ-bonded d^0 [MH_6] system (reproduced with permission from ref. [62]).

corresponds to the ligand repulsion aspect discussed in Section 3.7). π Bonding (Section 3.8) enters this picture by a destabilization of the t_{2g} LUMO at O_h symmetry, thus raising the relevant energy difference and opposing the symmetry lowering.

The limitations of the PMO picture are clear: the contribution of core polarization is not incorporated in this scheme, as it is typically restricted only to the valence MOs of the highest energy. Obviously, as discussed above, this restriction becomes less and less important the more covalent the bonding situation, and the more dominant the d-orbital participation aspect is. Indeed, the extended-Hückel model, from which most of the PMO interpretations derive, is applicable only to relatively nonpolar bonds.

Symmetry lowering by orbital mixing in electronically nondegenerate systems is sometimes referred to as a second-order Jahn–Teller (SOJT) effect.[159] One may argue about the theoretical justification of the SOJT argument[161, 162] outside the scope of the PMO model (see discussion in ref. [157]). A loose orbital-type definition of the SOJT concept would also qualify the bent (pyramidal) structures of, for example, the H_2O (NH_3) molecules as a consequence of an SOJT effect,[159] even though the HOMO–LUMO gaps at the linear (planar) structures are appreciable. Thus, while a second-order perturbation theory argument is clearly a very useful way to view the covalent aspects of the "non-VSEPR" structures of d^0 systems, we are reluctant to employ the SOJT label.

A simple generalization of many of the above considerations is to say that lower symmetry of the coordination arrangement allows more metal d- and ligand orbitals to match in symmetry, and thus to provide stronger σ-bonding interactions. This statement may be found, in different disguises, in many previous works.[3–5, 7–9, 34, 50, 62, 70, 74, 79, 108a, 109, 138–140] Formalizations, applicable to simple homoleptic transition metal hydride and alkyl complexes, have recently been given by Bayse and Hall,[57] and by King.[163] Similar to the valence-bond concept of Landis (Section 3.5), the bonding is assumed to be dominated by the metal $(n-1)$d and ns orbitals. Metal np-orbitals are only of secondary importance, at least for systems up to a valence-electron count of 12,[57] as for most of the d^0 systems discussed here. For a given structure, metal s and d orbitals, and ligand σ-bonding orbitals are classified with respect to the irreducible representations of the appropriate point group. This provides symmetry allowed or forbidden structures, depending on how many metal and ligand orbitals match. Further criteria, such as ligand repulsion, have to be employed to discriminate between different "allowed" coordination arrangements. Table 3 provides "allowed" symmetries for d^0 [MH_k] ($k = 3-6$).[57] Note, for example, that the regular octahedron for [MH_6], the trigonal bipyramid for [MH_5], the trigonal planar structures for

Table 3. "Symmetry-allowed" structures for d^0 MH_n complexes.[a]

	Structures
[MH_3]	D_{3h}, C_{3v}, C_{2v}, C'_{2v}
[MH_4]	T_d, D_{2d}, C_{4v}, C_{3v}, C_{2v}, C'_{2v}, C''_{2v}
[MH_5]	C_{5v}, C_{4v}, C_{2v}, C'_{2v}
[MH_6]	C_{5v}, C_{3v}, C'_{3v}
[MH_7]	C_{5v}, C_{3v}, C'_{3v}, C_{2v}, C'''_{2v}
[MH_8]	D'_{2d}, C'_{4v}, C'_{2v}, C''_{2v}, C''''_{2v}
[MH_9]	D_{3h}, D'_{3h}, C'_{4v}, C_{3v}, C'_{3v}, C'_{2v}

[a] See ref. [57]. Further structures with lower symmetry are possible. Primed entries indicate more than one structure of a given point group, as described by Bayse and Hall.[57]

[MH_3], or the linear structures for [MH_2], are not allowed. At these more symmetric structures, metal d orbitals and ligand orbitals have insufficient match in σ-bonding interactions. In contrast, T_d symmetry is "allowed" for d^0 [MH_4] complexes.[57]

π Bonding may be included without problem in the MO framework (see Section 3.8), an advantage over the simple valence-bond model described in Section 3.5. On the other hand, many canonical (delocalized) molecular orbitals may have to be considered for larger systems. This limits the application of the MO description as a basis for "back-of-the-envelope" arguments, and explicit computations may be required.

3.5. A Simple Valence-Bond Model

Landis and co-workers[31] have explained the "non-VSEPR" structures of a considerable variety of simple homoleptic hydride and alkyl complexes using straightforward valence-bond arguments. Considering d^0 [MR_k] systems (R = H, alkyl) to be well-represented by k two-center two-electron bonds, and assuming that the bonding contribution by the metal valence p orbitals is negligible, the metal–ligand bonds may be regarded as originating from the interaction of k metal sd^{k-1} hybrids with the corresponding ligand AOs. The bonding with the ligands is optimized for minimal overlap between the different sd^{k-1} hybrids at the metal (Figure 15). This overlap leads to certain optimum bond angles. For example, the bonds in [BaH_2] would be qualified as being made up from metal sd-hybrid orbitals and hydrogen 1s orbitals, and thus an optimum angle of 90° would be predicted (this relatively ionic system may already be outside the scope of the model, see below). Similarly, the bonds in [WH_6] may be thought to be formed by metal sd^5 hybrids.[31] Figure 15 shows clearly that in this case the preferred interhybrid angles are 63° and 117°, far from the 90° and 180° required for an octahedron. This approach leads to a number of preferred coordination arrangements (cf. "symmetry-allowed structures" in the MO models given in Section 3.4). Among these one may then again discriminate further by other criteria, such as ligand repulsion. In this respect, the above MO models and the Landis' VB ansatz are rather similar. Differences arise in the treatment of metal p orbitals once the valence electron count of 12 at the metal is exceeded. While Bayse and Hall[57] prefer to include metal p orbitals in these cases, Landis et al. treat these "hypervalent" cases using three-center bonding.[31c] A general discussion has thus started on the importance of the outer metal p orbitals in transition metal chemistry (see also ref. [17]), in analogy to the much older discussion on the participation of outer d orbitals in main group chemistry.[143, 164] However, for the present d^0 systems it is usually sufficient to restrict the description to the d and s orbitals (exceptions have to be considered for coordination numbers seven and higher, or for extensive π bonding).

The preferred bond angles in simple alkyl and hydride transition metal complexes have been reproduced remarkably well by the simple VB model. Landis et al. have incorporated this "VALBOND" ansatz into a molecular-mechanics framework to model the angular-energy dependence around the central metal.[31] Indeed, VALBOND calculations had correctly predicted[31a,b] the distorted trigonal-prismatic structure of [$W(CH_3)_6$] prior to independent experimental[112, 113] and ab initio[114, 115] confirmation. Moreover, the inexpensive VALBOND method may be used conveniently in molecular-dynamics calculations and thereby has provided radial distribution curves for [$W(CH_3)_6$] and for [$Ta(CH_3)_5$][31a] in good agreement with GED experiments.[64, 111]

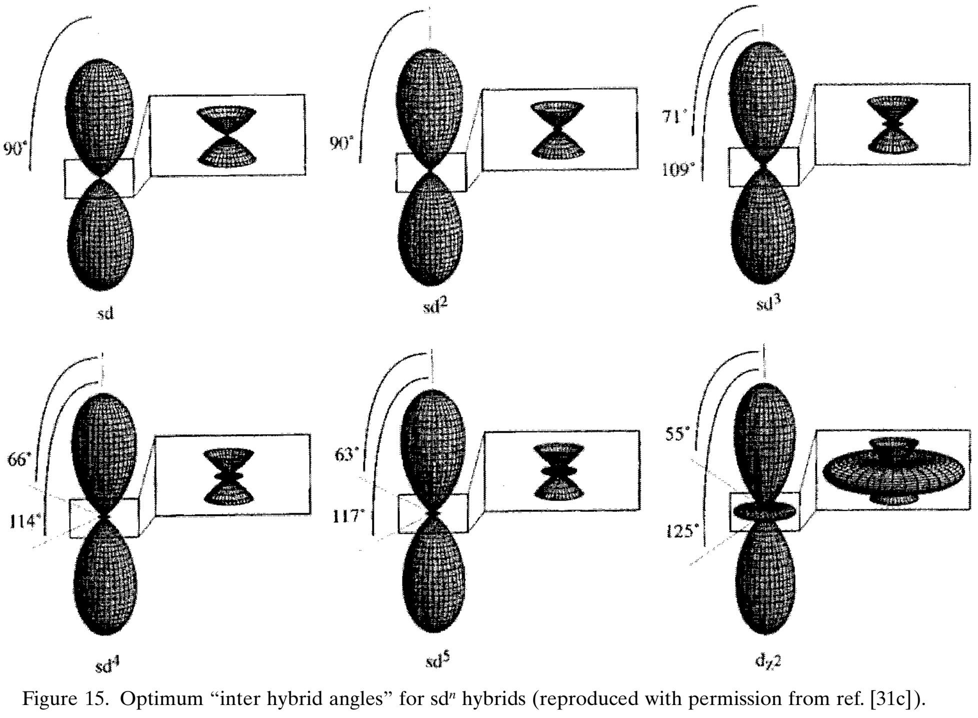

Figure 15. Optimum "inter hybrid angles" for sd^n hybrids (reproduced with permission from ref. [31c]).

Obviously, the simple valence-bond model must have severe limitations, most of which have already been discussed by Landis and co-workers.[31] Core polarization is clearly not incorporated. As for the above mentioned PMO model, this becomes a less problematic approximation the more covalent the bonding. The model appears to work well for simple homoleptic hydride and alkyl complexes, that is, systems which are well described by localized σ bonding only. It may be extended to "hypervalent" complexes by including covalent–ionic resonance,[31c] but it will become less useful for more strongly delocalized systems. As yet there have been no systematic applications of the model to transition metal systems including π bonding. Undoubtedly, valence-bond descriptions will be less straightforward in such cases, just as they tend to become clumsy for main group compounds when the bonding becomes more complex. The appreciable importance of π bonding for the structural preferences of d^0 complexes will be discussed in Sections 3.8 and 4.1.

Another implicit assumption of the simple valence-bond ansatz is the orthogonality of the metal hybrid orbitals employed. In other words, a comparable radial extent of the metal $(n-1)$d and ns orbitals is assumed such that only angular overlap needs to be considered.[31] Only in the case of orthogonal hybrids does a clear-cut relationship hold between the hybrid-orbital composition and the bond angles. Kutzelnigg[164, 165] has discussed in detail that hybrid orthogonality holds only when the AOs involved have the same overlap with the ligand orbitals, that is, they must have a comparable radial extent. For example, the condition of orthogonal hybrids does not hold for compounds of the heavier p-block elements, where the valence s orbitals are considerably more contracted than the valence p orbitals. In this case, the popular relations between hybrid composition and bond angles (e.g. $sp^3 \rightarrow 109.5^\circ$, $sp^2 \rightarrow 120^\circ$, $sp \rightarrow 180^\circ$) cease to apply.[164] As a typical example, the assumption of sp hybrids for linear $[HgX_2]$ complexes is far from reality, as the bonding is almost exclusively derived from the metal s orbitals, with very little p-orbital participation.[150, 166]

As yet, there have been no systematic studies of hybrid orthogonality for transition metal compounds. Natural population analyses (NPA[167]) suggest that the hybrid compositions for simple, relatively covalent hydride complexes often conform quite well to the expectations of the simple valence-bond model.[31c] Our own experience indicates that already for the somewhat more polar bonds in alkyl complexes,[69, 114, 115] the s-orbital participation in bonding is frequently *less* than that implied by the simplest valence-bond descriptions (however, the population analyses confirm the underlying assumption of the model[31] that the valence p-orbital participation in bonding is usually small in these systems). The more ionic the bonding, the less we may expect hybrid orthogonality to hold. Thus, for example, the basic valence-bond description will be less accurate for classical Werner-type coordination complexes.[31c] Landis et al. also point out that the size of $(n-1)$d and ns orbitals will be less compatible for 3d than for 4d or 5d complexes.[31c]

The simple valence-bond model will thus certainly be less widely applicable than, for example, the PMO approach. The great appeal of the model, however, lies in its simplicity. Moreover, the valence-bond approach appears to be particularly well suited as a basis for the parametrization of angular terms in molecular-mechanics force fields throughout the periodic table.[31, 168]

3.6. On the Isolobal Analogy Between Main Group and Early Transition Metal Compounds: A Little Caveat

A very useful way to break down conceptually complex transition metal systems into smaller fragments is the isolobal principle.[169] Two molecular fragments are termed isolobal, if their most important frontier MOs have similar shapes, orientations, and energies. This approach has been particularly efficient in relating the typically more complex transition metal systems to somewhat better understood main group compounds.[159, 169] The considerations of the previous two sections allow us to discuss a little caveat (restriction) that needs to be kept in mind when applying the isolobal analogy to compare main group and early transition metal complexes.

Consider the two radical species $[SiH_3]$ and $[ZrH_3]$ (Figure 16), which contain the central atoms from Groups 14 and 4 of the periodic table, respectively. Both molecules are computed to be pyramidal, and they both have one singly occupied nonbonding orbital of comparable energy pointing away from the three hydrogen substituents. As a good approximation we may consider these two fragments as being isolobal. However, let us examine the structural changes occurring upon removal or addition of one electron from or to these systems. The p-block main group cation $[SiH_3]^+$ is planar, as the s-orbital participation in bonding is maximized by leaving a p_z orbital perpendicular to the molecular plane empty (in valence-bond language, neglecting hybrid nonorthogonality,[164, 165] one would usually speak of sp^2 hybridization). Addition of one or two electrons to the system leads to increasing pyramidalization, as it is favorable for the now occupied nonbonding orbital to acquire more s character. In contrast, the $[ZrH_3]^+$ ion prefers a pyramidal structure, to maximize d-orbital participation (in valence-bond language, the metal may be considered to use sd^2 hybrids for bonding[31]). Adding electrons to the system reduces the pyramidality, as the nonbonding electrons attempt to acquire maximum d character. As a result, the hypothetical $[ZrH_3]^-$ ion is planar, with the nonbonding electron pair in a d_{z^2} orbital perpendicular to the molecular plane. Thus, while one would at first sight undoubtedly qualify the neutral $[EH_3]$ fragments as being isobal, the structural behavior of the two systems

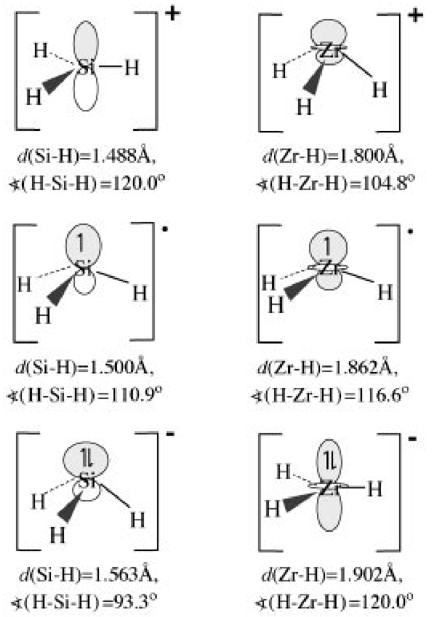

Figure 16. Opposite structural and electronic behavior of the SiH_3 and ZrH_3 fragments upon addition or removal of one electron. Structure parameters pertain to DFT optimizations (see appendix).

upon addition or removal of one electron is just the opposite, because of the different composition of the dominant valence orbitals.

3.7. The Role of Ligand Repulsion

The repulsion of bonding and nonbonding electron pairs is at the heart of the VSEPR model. Ligand repulsion is thus the most obvious factor that favors the conventional VSEPR structures and opposes the distortions. The nature of the repulsion may be both electrostatic (in particular for significantly polar bonds) and steric (mainly Pauli exchange repulsion). It is usually not straightforward to extract the magnitude of such repulsions directly from quantum-chemical calculations in a quantitative manner, although various schemes have been proposed to estimate, for example, Pauli exchange repulsion.[170] The systematic comparison of compounds with different metals, ligands, coordination numbers, and net charges provides some insight into the importance of ligand repulsion for the structural preferences. Ligand repulsion is probably also the chemically most intuitive of the factors involved. For example, it is clear that, all other things being equal, ligand repulsion increases rapidly for larger coordination numbers.

Our prototype dicoordinate systems, the alkaline earth dihalides, are more on the electrostatic side. The analysis of their bending force constants in terms of a polarized-ion model has provided an estimate of the Coulomb-repulsion and anion-polarization contributions that favor the linear arrangements.[5] Thus, for example, the anion–anion repulsion in the calcium dihalides is considerably more pronounced than for the corresponding Sr and Ba species, because of the shorter anion–anion distances involved. Therefore, the calcium dihalides are at best quasilinear, in spite of a large driving force towards a bent structure (a result of d-orbital participation and metal core polarization).[5]

The leading anion–anion repulsion terms may be removed when replacing the anionic halide ligands by neutral ligands such as HF, H_2O, or NH_3. Indeed, complexes like $[Ba(H_2O)_2]^{2+}$ have been computed to exhibit even lower bending angles than $[BaF_2]$ or $[BaH_2]$, in spite of their much smaller covalent bonding contributions and very shallow bending potential curves.[40] As a result, tricoordinate cations such as $[Ba(H_2O)_3]^{2+}$ are still slightly pyramidal,[40] while anionic species such as $[BaX_3]^-$ ($X = H$, F) are expected to be genuinely planar.

Within the range of the more covalent d^0 systems, it has also been shown that an increasing negative charge on the ligands disfavors the "non-VSEPR" arrangements. Thus, the preference for nonoctahedral structures of $3d^0$ hexahydride systems increases along the series $[ScH_6]^{3-} < [TiH_6]^{2-} < [VH_6]^- < [CrH_6] < [MnH_6]^+$.[71, 108c] Similar results were obtained in DFT calculations for Group 4–7 hexamethyl complexes, $[M(CH_3)_6]^n$ ($n = -2, -1, 0, +1$).[115] Only the cationic and neutral complexes prefer distorted trigonal prisms, whereas the mono- and dianionic systems have regular trigonal-prismatic structures (of the three Group 5 monoanions, only the 4d species $[Nb(CH_3)_6]^-$ shows some tendency to distort). While the octahedron is far from competitive for any of these hexamethyl complexes, its energy relative to the minimum structure is lowest for the dianions.[115] Experimentally, the $[Zr(CH_3)_6]^{2-}$ and $[Ta(CH_3)_6]^-$ ions prefer a regular trigonal prism,[110, 113, 119] whereas $[W(CH_3)_6]$[112] and $[Mo(CH_3)_6]$[118] are distorted (see Section 2.5). As the anionic systems have the most ionic bonding and bear significant negative charge on the methyl ligands, it appears reasonable to assume that increased electrostatic repulsion between the ligands prevents a distortion of the prism. However, at the same time the more ionically bonded anionic systems show the largest HOMO–LUMO gap at the regular prismatic structure[114, 115] (as discussed in Section 3.4, a small gap is important for the second-order orbital mixing upon distortion).[159]

Similar arguments have been invoked for the structural preferences of tris(dithiolene) complexes: a better match of the energy of ligand and metal valence orbitals for the more covalent complexes was made responsible for their larger deviations from an octahedron, for example, along the series $[Zr(S_2C_6H_4)_3]^{2-}$, $[Nb(S_2C_6H_4)_3]^-$, $[Mo(S_2C_6H_4)_3]$[171] (see also ref. [172]). This result shows that it is difficult to completely separate these influences. Another comparison may be made between the neutral $[Ta(CH_3)_5]$ and monoanionic $[Ti(CH_3)_5]^-$. The computed preference for the square-pyramidal over the trigonal-bipyramidal structure is considerably reduced for the Ti[58] than for the Ta[62, 63] complex. The hybridization of the ligand donor atom affects its electronegativity. For example, the structures of hexaacetylide d^0 complexes tend to be in between octahedral and prismatic,[120] whereas hexaalkyl complexes are more clearly prismatic. This difference may again be attributed to both a) larger ligand repulsion, because of the more polar M–C bonding in acetylides, and b) a larger gap between occupied and unoccupied MOs.

Interestingly, the bond polarity (and also the HOMO–LUMO gap) is larger for 5d than for 4d complexes, a result of the relativistic expansion[173] of the 5d orbitals. Relativity reduces metal–ligand covalency and thereby increases ligand repulsion.[115] As a consequence, $[Mo(CH_3)_6]$ for example, exhibits a more strongly distorted trigonal-prismatic structure than the heavier congener $[W(CH_3)_6]$[115, 118] (the trigonal distortion of octahedral $[MoX_6]$ complexes is also easier than that of their homologous $[WX_6]$ species, see Table 2). In contrast, the distortion has been predicted to be less pronounced for $[Cr(CH_3)_6]$, partly because of the smaller ligand–ligand distances and thus the larger ligand repulsion.[115] Similarly, the 4d complex $[Nb(CH_3)_6]^-$ is on the borderline to a distorted prism, whereas the 5d analogue $[Ta(CH_3)_6]^-$ clearly exhibits a regular prism structure.[113, 115] As another experimental example, we note that for the two tris(dithiolene) systems $[M(S_2C_6H_4)_3]^-$ ($M = Nb$, Ta), the 4d niobium system exhibits a structure that is considerably closer to the trigonal-prismatic extreme than that of its 5d tantalum homologue.[95, 174] Computational studies on the $[MH_4]^+$ ion ($M = Nb$, Ta) give preference to an unusual square-pyramidal structure for the 4d system but to the tetrahedron for the 5d complex.[31c, 57] Further examples of such 4d/5d comparisons in the regime of extended solid-state structures will be discussed in Section 5.

d^0-Metallocenes provide further examples, in which reduced negative charge on the ligands corresponds nicely with more distorted structures. While the neutral Ca, Sr, Ba, Eu, Sm, and Yb metallocenes [MCp_2] are shown by calculations to have at most quasilinear structures,[27] the hypothetical isoelectronic cations [$LaCp_2$]$^+$ and [$ScCp_2$]$^+$ have been computed to be significantly bent.[29] Similar comparisons can be made essentially for all examples discussed in Section 2: the more covalent the bonding, the larger the deviations from the conventional "VSEPR structures". In all cases it is difficult to separate the covalent and the ligand-repulsion contribution to the structural preferences (note the exceptional behavior of systems with neutral ligands[40]). Moreover it is also frequently difficult to separate the influences of ligand repulsion from those of π bonding (see Section 3.8).

Actual steric interactions in the sense of Pauli exchange repulsion become more important the more covalent the system gets. Obviously the size of the ligands may then be particularly important. A striking example is provided by substituted alkaline earth and lanthanide(II) metallocenes. While several permethylated complexes [MCp^*_2] (M = Sm, Eu, Yb, Ba; Cp* = η^5-$C_5(CH_3)_5$) have been found to exhibit bent structures in the solid state (keeping in mind possible influences by intermolecular interactions , see Section 2.1), larger alkyl substituents on the cyclopentadienyl rings eventually force linear metallocene structures as a consequence of the steric bulk of the ligands.[25]

It has been suggested[26b] that the ring–ring distances in [MCp^*_2] (Cp* = C_5Me_5) complexes are such that there may also be attractive van der Waals (vdW) interactions between the methyl groups on different rings. Indeed, it has been claimed, based on molecular-mechanics calculations,[175] that such vdW forces may be responsible for the bent [MCp^*_2] structures. It is unclear how reliable such estimates are. For example, a recently reported bent structure for a triple-decker sandwich without alkyl substituents at the central C_8H_8 ring has been taken as evidence *against* the importance of vdW attractions.[176] Even if weak attractive interactions are important, this implies that the other factors involved (covalent bonding, core polarization, ligand repulsion) act together to provide a very shallow bending potential curve,[27] such that the weak dispersive forces may become decisive. These arguments are certainly not applicable to the hypothetical cationic systems [MCp_2]$^+$ (M = Sc, La), which have been predicted to be strongly bent.[29] Here the covalent-bonding contributions undoubtedly dominate the bending process.

We note in passing, that the accurate ab initio treatment of systems with bulky ligands becomes increasingly cumbersome for larger systems. Recent methodological developments suggest, however, that such steric contributions to the structural preferences for large systems may be modeled reasonably well by integrated quantum-mechanics/molecular-mechanics (QM/MM) approaches.[177] Thus, while the electronically demanding part of the system (e.g. the immediate coordination sphere of the metal) is described at a sufficiently high ab initio level, more remote parts of the molecule (e.g. parts of bulky ligands) may be treated at a molecular-mechanics or lower quantum-chemical level of theory. A notable example of a QM/MM treatment for some heteroleptic d^0 systems has been given by Barea et al.[178] (see also Section 4.2). As another example of the influence of steric repulsion, recent DFT calculations also indicated a significant effect on the preferred coordination arrangement of a d^0 *cis*-diimido complex, when PH_3 was substituted for $P(CH_3)_3$.[179]

3.8. The Influence of π Bonding

π Bonding is considerably more important in early, high-valent transition metal complexes than for analogous (formally single-bonded) main group compounds.[180–182] This is easily understandable when we consider the orbitals available at the central atom. In p-block main group compounds, the *outer* d orbitals are too large and too high in energy to be available as efficient acceptors for π bonding. Thus, in the absence of regular $p_\pi - p_\pi$ bonding, it is mainly negative hyperconjugation that allows some π character to mixed into the bonds, at the expense of some σ bonding to the neighboring substituents.[183] In contrast, the coordinative unsaturation of early, high-valent transition metal complexes arises from the availability of low-lying *inner* d orbitals. This point has to be kept in mind to appreciate the potential influence of π bonding on structure (see also Section 4).

Besides ligand repulsion, π bonding is usually considered to be the second important factor that opposes a deviation from the VSEPR-conforming structures. This had already been noted by Jolly and Marynick[32] for di- and tricoordinate systems (e.g. for [ScX_2]$^+$ or [ScX_3]), and by Kang et al.[62, 74] for [MX_5] and [MX_6] systems with X = H, F (ref. [107] gives an even earlier, related discussion). In both cases, the hydride species adopt "non-VSEPR" structures (bent dicoordinate, pyramidal tricoordinate, square pyramidal pentacoordinate, distorted trigonal prismatic hexacoordinate), whereas the fluorides favor the regular VSEPR arrangements.[32, 62, 74] While one might attribute this to the larger ionicity of the fluorides, which leads to increased anion–anion repulsion (see Section 3.7), there is further evidence which points to the importance of π bonding (see below).

It appears that π bonding favors structures closer to the VSEPR requirements in most homoleptic systems. However, there are also a number of cases, with strong π-donor ligands, for which π bonding has been considered to *increase* the deviations from the VSEPR-type arrangements. The most well-known case is the strongly bent [MoO_2]$^{2+}$ unit found in many heteroleptic "molybdenyl" complexes. Calculations at various degrees of sophistication[38, 184] have suggested that the *cis* configuration with relatively small O-Mo-O angles (typically around 103°), also found in the isolated [MoO_2]$^{2+}$ fragment,[38] is partly caused by more efficient π bonding in the *cisoid* structure. Similar arguments may be applied to other dioxo, trioxo, or disulfido systems, for example, to chromyl complexes, [CrO_2X_2]. This tendency is also frequently discussed in the context of a large *trans* effect for strong π-donor ligands.[15]

We are thus facing the seemingly paradoxical situation that π bonding is considered to increase the bond angle in systems such as $[ScF_2]^+$ (compared to $[ScH_2]^{+}$[32]) but to decrease the angle in $[MoO_2]^{2+}$ and related species.[38, 184] To rationalize these findings, we have recently studied the interdependence of π bonding and bond angles in some detail by analyses of natural localized molecular orbitals (NLMOs[167]) as functions of bond angle for some simple model complexes.[180] Figure 17 shows those (canonical, delocalized) metal d orbitals which may potentially act as π acceptors in linear and bent d^0 $[MX_2]$ systems, respectively (cf. also refs. [38, 184]). In the case of cylindrical π donors such as oxo or halide ligands, four π-type lone pairs have to share two metal d orbitals in a linear arrangement (Figure 17a). Upon bending, the in-plane component of the former d_π set (d_{yz}, b_2 in C_{2v} symmetry) has essentially no overlap with the ligand π orbitals, and we will disregard it in the following. In contrast, the overlap of the out-of-plane component (d_{xy}, a_2 in C_{2v} symmetry, see Figure 17b) decreases only very slowly when reducing the angle. Thus, initially we expect a significant loss of in-plane π bonding and a very slight loss of out-of-plane π bonding. However, at smaller angles two more metal orbitals become accessible for π bonding: the d_{xz} orbital (of b_1 symmetry) becomes out-of-plane π bonding, whereas at even smaller angles a hybrid dominated by the d_{z^2}-orbital (a_1 symmetry) becomes in-plane π bonding (Figure 17b; note that π_{ip} and σ bonding contributions are not easily separable in such systems, as they involve MOs of the same symmetry). These two orbitals are the ones that have been invoked as reasons for the small angles of the $[MoO_2]^{2+}$ fragment.[38, 184]

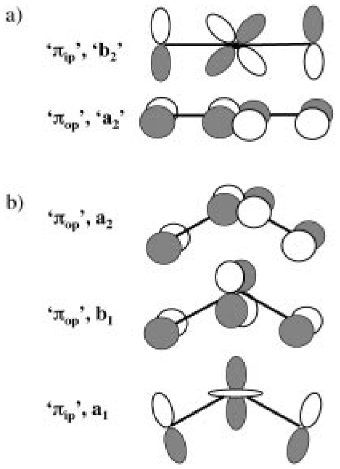

Figure 17. Metal d orbitals available for π bonding in d^0 MX_2 complexes. a) At an X-M-X angle of 180°. b) At X-M-X angles $<180°$ (cf. refs. [38, 180, 184]). Symmetry labeling as appropriate for C_{2v} point group; ip = in plane, op = out-of-plane.

Thus, π bonding is expected to depend in a nontrivial way on the bond angle, and of course also on the σ- and π-bonding ability of the ligands (and of the metal). Analyses of the "weak π-donor" prototype system $[ScF_2]^+$ indicated that the overall π-bonding covalency at the bent equilibrium structure is lower than at the linear structure, and therefore π bonding might be considered to favor the linear structure. In contrast, in the "strong π-donor" model $[ZrO_2]$ the sum of in-plane and out-of-plane π bonding apparently favors the bent arrangement, in agreement with the above mentioned notions for molybdenyl systems. But in both cases, $[ScF_2]^+$ and $[ZrO_2]$, the slopes of the NLMO "covalency" curves around the equilibrium structures indicated that π bonding tends to favor smaller angles.[180] Thus, even in such apparently simple systems, the interrelations between π bonding and bond angles are far from trivial, because of the variety of metal d orbitals and ligand orbitals involved. In more complicated systems, the bonding to additional ligands may further alter the situation significantly (cf. Section 4.1).[180]

In a recent DFT study, in-plane π bonding (π_{ip} bonding) was held responsible for the bent structures of alkaline earth metallocenes.[185] While the significantly bent structures found in that study appear to be an artifact[180] of the unbalanced basis sets employed in the calculations, one may indeed consider such interactions in the case of genuinely bent metallocene structures. Of course the discrimination between π_{ip} and σ bonding will be even more difficult in these cases than in the models discussed above. A similar type of π interaction at strongly pyramidalized structures of rare earth trihalides has been considered in Extended-Hückel calculations.[186] Unfortunately, the computed pyramidal structures again appear to have been artifacts of the theoretical approach employed. Similar arguments have been put forward to explain the pyramidal structure of the MoO_3 molecule.[55]

The clearest indication for π bonding may be obtained when different conformations are possible. HF calculations on the series of simple alkaline earth $[MX_2]$ molecules (M = Ca, Sr, Ba; X = Li, BeH, BH_2, CH_3, NH_2, OH, F) have indicated[6] the largest degree of bending in the absence of π bonding, for example, for the dimethyl complexes $[M(CH_3)_2]$ (for a given metal), whereas the linearization energies decrease from X = CH_3 to X = F (see Figure 18a). Moreover, the diamide species $[M(NH_2)_2]$ (M = Sr, Ba) show a strong dependence of the linearization energy and bending angle on the orientation of the NH_2 ligands. As shown in Figure 18b, a C_{2v} arrangement with the amide hydrogen atoms in the N-Ba-N molecular plane is the most stable structure and has the smallest N-Ba-N

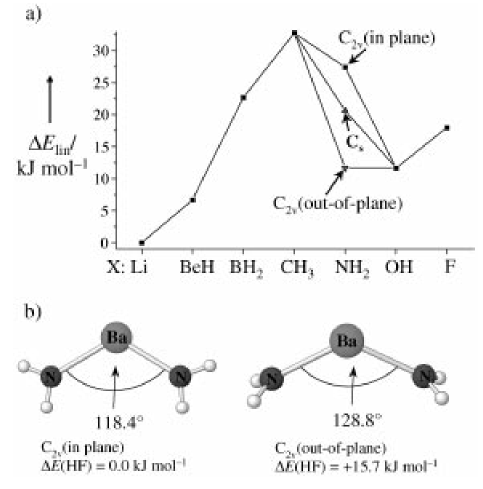

Figure 18. a) Linearization energies of $[BaX_2]$ molecules (HF results from ref. [6]). Different entries for $[Ba(NH_2)_2]$ pertain to different conformations (see (b)). b) Computed structure parameters for two rotamers of $[Ba(NH_2)_2]$.

angle, around 118° (and the largest linearization energy, ca. 27 kJ mol^{-1}). Rotation of the two amide groups out of the plane costs approximately 16 kJ mol^{-1} and increases the angle by about 7°.[6] This amounts to a surprisingly large rotational barrier for such an ionic system and indicates clearly the presence of π bonding. In the in-plane configuration, loss of π_{ip} bonding upon bending is avoided, and out-of-plane π bonding is retained (see above). Therefore, this arrangement is the most stable one, and the bending angle is coupled significantly to the amide group conformation. Somewhat stronger, cylindrical π donors such as cyclopentadienyl ligands appear to disfavor bending even more, with the result that, for example, the alkaline earth and lanthanide(II) metallocenes [MCp$_2$] are quasilinear.[27]

Within the PMO model of Section 3.4, the effect of π donation enters by a destabilization of some of the unoccupied orbitals of the more highly symmetrical structure.[62, 74, 107, 159] Thus, in the MO Scheme of an O_h symmetrical d^0 [MX$_6$] complex, the replacement of purely σ-donating hydride or alkyl ligands by σ-/π-donating halide ligands results in a significant destabilization of the π-antibonding t_{2g} LUMO (see Figure 14). As a consequence, the gap between the t_{1u} HOMO and t_{2g} LUMO increases, and the second-order mixing of these two MOs upon distortion to a trigonal prism becomes less favorable.[62, 74, 107] Therefore, simple d^0 hexahalides such as [WF$_6$] or [WCl$_6$] are octahedral, whereas the corresponding hexahydride and hexamethyl complexes prefer structures derived from a trigonal prism (Section 2.5). Again, one might attribute these differences simply to the larger ionicity and thus to larger electrostatic anion–anion repulsions in the halides. In this case, however, the distortion from an octahedron to a trigonal prism would be expected to require the largest energy for the most ionic systems, that is, with fluoride ligands. In disagreement with this expectation, our DFT calculations[78] (see Table 2) indicate almost twice the barrier for the trigonal twist of the tungsten or molybdenum chlorides or bromides than for the respective fluorides (our results for [WF$_6$] agree well with those of previous ab initio or DFT calculations[62, 187]). Thus, the prismatic structure is almost twice as favorable energetically for the fluoride as for the chloride, in spite of the much larger ionicity of the former (e.g., computed NPA metal charges at the O_h minima are +0.05, +0.25, +1.91, and +2.23 for [MoCl$_6$], [WCl$_6$], [MoF$_6$], and [WF$_6$], respectively). Moreover, an NPA/NLMO analysis[188] shows clearly that both a) π bonding at the octahedral structure, and b) the loss of π bonding upon distortion to a prism are much more pronounced for the chloride than for the fluoride. Thus, the π-donor abilities of the ligands appear to be more important here than the bond ionicities. This has the interesting consequence that successive alkyl substitution in mixed compounds [W(CH$_3$)$_m$X$_{6-m}$] leads to a transition from octahedral to prismatic structure at lower m value for X = F than for X = Cl (see Section 4.2).[78] These results are consistent with a recent study on metal–chalcogen bonding in related d^0 complexes.[181] DFT calculations for a series of homologous complexes [OsO$_3$E], [MCl$_3$E] (M = V, Ta), and [MCl$_4$E] (M = Cr, Mo, W, Re) with E = O, S, Se, Te, indicated that the strength of the M–E σ bonds decreased from E = O to E = Te. However, the M–E π bonding exhibited the maximum strength for E = S, Se. Relative to the σ-bond strength, the importance of π bonding increased even to E = Te.[181]

Halide ligands are moderate cylindrical π donors, whereas hydride and alkyl ligands are σ donors (slightly modified[189] by agostic interactions for alkyl ligands[63, 107, 114, 115, 189]). One may thus ask what structural preferences may be induced by single-sided π-donor ligands. One example has already been given above when discussing the alkaline earth [M(NH$_2$)$_2$] complexes.[6] Somewhat less clear-cut examples, which are particularly important in the regime of six-coordinate d^0 complexes, are thiolate ligands (see also Section 2.5). While an SR ligand has in principle two lone pairs available for bonding to the metal, the bending of the M-S-R moiety leads to considerable sulfur s character for the in-plane lone pair (Figure 19). Thus, only the lone pair perpendicular to the M-S-R plane remains truly effective as a π donor. Figure 20 shows the DFT-optimized structure of the model complex [Mo(SH)$_6$] (see

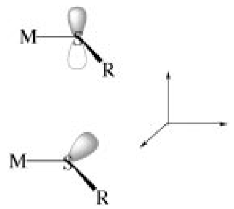

Figure 19. Formally nonbonded sulfur orbitals in a bent metal–thiolate fragment. Only the out-of-plane lone pair (top) is a suitable π donor, whereas the in-plane lone pair (bottom) obtains significant s character.

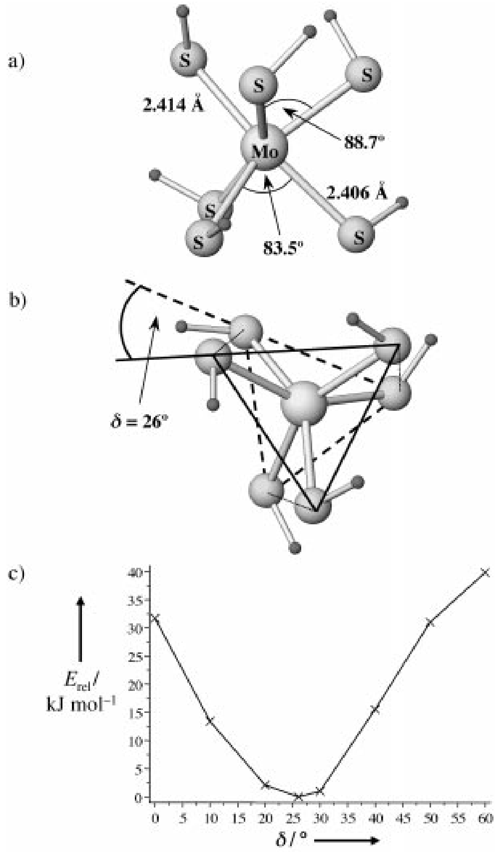

Figure 20. DFT optimized structure of the [Mo(SH)$_6$] model complex. a) Side view with key structural parameters. b) Top view showing the twist angle δ between the two triangular faces. c) Computed energy profile along the twist angle coordinate. The curve is the result of a "relaxed scan", in which the twist angle has been changed step-wise and, for a given twist angle, all other structural parameters have been fully optimized. See appendix for computational methods.

ref. [92] for experimentally observed homoleptic d^0 complexes of monodentate thiolates). The structure has C_3 symmetry, and its trigonal twist angle $\delta = 26°$ (Section 2.5) indicates that it lies between the octahedral ($\delta = 60°$) hexahalides and the trigonal prismatic ($\delta \approx 0°$) hexaalkyl structures. The energy profile in Figure 20c shows that the system is intermediate between octahedron and prism also from an energy point of view. Obviously, replacement of halide by thiolate is one way of partially switching off π-bonding contributions in such $[MX_6]$ d^0 complexes.

Similar considerations hold for the experimentally relevant chelating dithiolate ligands. As discussed in Section 2.5, for a given metal the complexes of the unsaturated dithiolene ligands appear to be closer to the trigonal prismatic extreme than their saturated dithiolate analogues[82, 83] (or of monothiolates[92]). Recent model calculations on the dithiolene complexes $[M(S_2C_2H_2)_3]$ (M = Mo, W) give twist angles $\delta \approx 0°$.[104] It appears reasonable to attribute this difference to the partial involvement of the sulfur lone-pair orbitals in intraligand π bonding and thus to reduced metal–ligand π-bonding contributions for the unsaturated dithiolene systems[104] compared to saturated dithiolates (keeping in mind the boundary conditions set to the twist angles by the bite angles of the bidentate ligands; Section 2.5). A further frequent distortion in dithiolene complexes is the nonplanarity of the ligands. Among other things, this has been attributed to improved overlap, in the nonplanar arrangement, of the sulfur π-type lone pairs with the metal d_{z^2} orbital in the trigonal prismatic arrangement.[190]

A structure close to trigonal prismatic has recently also been found for the complex [W(4,4′,5,5′-tetramethyl-2,2′-bisphosphinine)$_3$][104] (see Figure 6). For this system, the approximate ligand symmetry does indeed provide single-sided phosphorus π donors (we assume a dianionic formulation of the chelate ligand). The donor ability of the π-type lone pair should, however, be reduced because of delocalization within the ligand. For saturated phosphanide ligands, the interesting question arises, whether a pyramidal or a planar geometry around phosphorus will be found. While the former case would correspond essentially to a σ-only donor, significant π bonding would be expected for the latter case. Such systems thus appear to be attractive targets for computational and experimental studies (see also Section 5).

As mentioned in Section 2.5, the view of a d^0 complex with dianionic ligands is one extreme of a continuous description of the electronic structure of dithiolene complexes or related systems such as the above mentioned tris(bisphosphinine) complex, tris(buta-1,3-diene)molybdenum,[100, 101] tris(*ortho*-xylyl)tungsten,[102] or tris(methylvinylketone)tungsten.[103] At the d^0 extreme, a minimization of ligand-to-metal π bonding by delocalization of the relevant ligand lone-pair orbitals throughout an unsaturated chelate-ligand framework provides a driving force towards a prismatic structure. On the other hand, many years ago Hoffmann et al. approached the problem from the opposite extreme, and started from a d^6 system with neutral ligands.[70] They identified strong metal-to-ligand π back bonding to ligand orbitals of the appropriate symmetry as a means to move the structure away from the ubiquitous octahedron. Obviously, maximum back bonding will bring us back to the other extreme, a regular or distorted trigonal prismatic structure with d^0 metal configuration and dianionic ligands (see also Figure 7). This continuum of bonding descriptions provides part of the fascination of dithiolene and related ligands.

Finally, we may speculate on the importance of π bonding in various extended solid-state structures known with trigonal-prismatic coordination at the metal center.[79] The coordinating main group atoms are typically connected to more than one metal center, and their mutual orientations are restricted by the solid-state arrangement of the atoms. Thus it appears likely that the ligand lone-pair orbitals are not fully available for π bonding. This might explain the large variety of cases with trigonal-prismatic metal coordination in early transition metal chalcogenides, pnictides, and related systems. On the other hand, π bonding may in some cases enhance the distortions (see above). Such considerations may become important, for example, for distortions of octahedral coordination in extended oxide structures (Section 5).

4. Heteroleptic Systems

We have up to now concentrated on homoleptic complexes, as the major aim has been to discuss the general bonding features of d^0 species. Most of the compounds of practical interest, for example, in catalysis or bioinorganic chemistry, are heteroleptic systems. With the basic underlying factors reasonably well understood for the simpler homoleptic systems, future interest will concentrate on heteroleptic complexes. We will in this Section discuss some bonding features and structural peculiarities which need to be considered when dealing with more complicated d^0 systems. We will first focus on some simple tetracoordinate molecules (Section1 4.1) to highlight the influence of π bonding and electronegativity on bond angles. We will then turn to a number of interesting penta- and hexacoordinate systems that provide hints of what the future may bring in this field (Sections 4.2–4.4).

4.1. May Bent's Rule be Extended to Transition Metal Chemistry?

Let us examine briefly what considerations come into play when we have mixed sets of ligands. Two factors to be kept in mind are a) the different electronegativity and b) the relative σ- and π-bonding capabilities of the ligands (a third factor is the steric requirements). A suitable starting point is the distorted tetrahedral structure of $[Ti(CH_3)_2Cl_2]$. Computation[191] and GED[192] both indicate the C-Ti-C and Cl-Ti-C angles to be lower than the ideal tetrahedral value, and the Cl-Ti-Cl angle to be larger (Figure 21a). This is just opposite to what is normally observed in main group compounds, for example, for $[Si(CH_3)_2Cl_2]$ (Figure 21b).[191b, 193] Here the angle between the less electronegative alkyl ligands is larger than tetrahedral whereas the Cl-Si-Cl angle is smaller.

Structures of such main group compounds are often explained by Bent's rule.[194] It states that the bonds to the

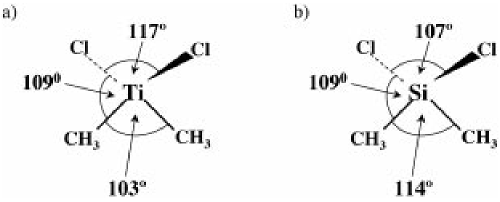

Figure 21. Bond angles from GED for a) [Ti(CH$_3$)$_2$Cl$_2$] and b) [Si(CH$_3$)$_2$Cl$_2$] (from refs. [191, 193]).

more electronegative substituents have more p character and thus make smaller angles, whereas the bonds to the less electronegative substituents obtain more s character and thus make larger angles (the valence p orbitals of the central atom are higher in energy and have a larger radial extent than the valence s orbitals).

Is it possible to extend Bent's rule to transition metal compounds? Jonas et al. argued,[191b] on the basis of natural bond orbital (NBO) hybridization analyses, that in this case Bent's rule has to be rephrased. As the $(n-1)$d orbitals are lower in energy and have a smaller radial extent than the *n*s orbitals, the bonds to the less electronegative ligands tend to acquire more d character and thus make lower angles, whereas the bonds to the more electronegative ligands have larger s character and thus make larger angles. This has been criticized by McGrady et al.,[192] and by Landis et al.[31c] In particular, Landis et al. argue that their orbital strength functions for the appropriate sd^k hybrids[31] show a preference for *larger* bond angles with increasing *k*, that is, with increasing d character. Thus, the less electronegative ligands should make larger angles, in agreement with Bent's rule! They further argue that the "inverse Bent's rule" structures of [Ti(CH$_3$)$_2$Cl$_2$] and of related compounds may be explained instead within a valence-bond picture by invoking ionic resonance structures (this would imply *lower* d character in the Ti–C than the Ti–Cl bonds).[31c]

Could Ti–Cl π bonding be responsible for the large Cl-Ti-Cl angles and thus resolve these contradictions? McGrady et al. rejected this possibility,[16, 192] based on the fact that related systems with strong π donors such as [CrO$_2$F$_2$] exhibit *small* angles between the π-donor ligands. However, as discussed in Section 3.8 the interrelation between π bonding and bond angles may be complicated in d^0 systems, because of the involvement of both in-plane and out-of-plane π bonding.[180] For example, for the "weak π-donor case" [ScF$_2$]$^+$, π bonding favors a linear arrangement over the bent equilibrium structure, whereas for the "strong π-donor case" [ZrO$_2$], the opposite is true. For the present, heteroleptic pseudotetrahedral systems, the out-of-plane π bonding (π_{op}) will now in addition have to compete with the σ bonding to the additional ligands (e.g. in [Ti(CH$_3$)$_2$Cl$_2$], π_{op}(Ti–Cl) bonding competes with σ(Ti–C) bonding).

The detailed analysis of NLMO compositions and of NBO deletion analyses has indicated indeed, that the overall effect of Ti–Cl π bonding in [Ti(CH$_3$)$_2$Cl$_2$] favors a large Cl-Ti-Cl angle.[180] In contrast, in [CrO$_2$F$_2$] and related systems with strong π donors and weakly donating competing ligands, the overall dependence of the bond angle on π bonding (the sum of in-plane and out-of-plane contributions) appears to be low, and thus the σ-bonding framework may dictate the small O-M-O angles.[180] Upon introduction of stronger σ donors as ancillary ligands, for example, in the model system [CrO$_2$H$_2$], in-plane M–O π bonding again starts to favor larger O-M-O angles.[80] Indeed, the O-Re-O angles in [CH$_3$ReO$_3$] have experimentally been found to be 113°, larger than the ideal tetrahedral angle (with C-Re-O angles of 105.6°).[195] Clearly, the preferred angles reflect not only the specific character of the π-donor ligands, but also the σ-donor abilities of additional ligands present. This conclusion should also apply to other coordination numbers (see Sections 4.2 and 4.3).

Considerable further computational data on heteroleptic tetracoordinate complexes are available, which provide typical bond angles. For example, recent DFT calculations on d^0 and d^2 alkylidyne complexes [M(≡CH)(CH$_3$)$_2$(X)], and of bis(alkylidene) complexes [M(=CH$_2$)$_2$(CH$_3$)(X)], studied the influence of the ligands X on the computed bond angles.[196] Schrock-type carbene[197] and carbyne[198] complexes were studied systematically by MP2 calculations.

In view of the considerable importance of π bonding for their structural preferences, [Ti(CH$_3$)$_2$Cl$_2$], [CrO$_2$F$_2$], and similar complexes are not well suited to decide on the validity of Bent's rule in d^0 complexes. It would be better to compare heteroleptic systems without significant π-bonding contributions, but with significantly different electronegativities of the ligands. The choice of suitable models is rather limited. In ref. [180], the titanium complexes [TiH$_2$(CF$_3$)$_2$], [Ti(CH$_3$)$_2$(CF$_3$)$_2$], [Ti(SiH$_3$)$_2$(CH$_3$)$_2$], and [Ti(SnH$_3$)$_2$(CH$_3$)$_2$], as well as their silicon analogues were compared in DFT calculations. In the first case, the difference in substituent electronegativities is too small. The second and third system exhibit an inverse Bent's rule structure, but their silicon analogues also violate Bent's rule (probably the match of orbital size overrides the electronegativity differences[180]). Only the last system exhibits an inverse structure with titanium but a regular structure with silicon. It appears difficult to derive an extension of Bent's rule to d^0 systems from these examples. On the other hand, the potential usefulness of the rule would appear to be very limited anyway, because of the typically very large importance of π bonding for the bond angles (see Section 3.8).[180]

4.2. Pentacoordinate Heteroleptic Systems

Many of the factors discussed in Section 4.1 will also apply to other coordination numbers. Some examples of heteroleptic tricoordinate complexes have already been mentioned in Section 2.2. Clearly, the overall situation will become more complicated for higher coordination numbers, simply because more metal and ligand orbitals, as well as more potentially important geometrical structures have to be considered. Two recent computational studies have independently dealt with the structures of heteroleptic pentacoordinate complexes of the type [MX$_2$R$_3$][68] and [MXR$_4$],[69] where X denotes a σ-/π-donor ligand and R an essentially pure σ-donor ligand.

The main impetus for the first study[68] was the great importance of metallocene complexes of the type $[MCp_2R_3]$, in polymerization catalysis. Indeed, the η^5-C_5H_5 ligand may be considered a strong cylindrical π-donor X (Section 2.1). The typical structures of such pentacoordinate complexes, which appear to be also relevant for the transition state of sterospecific chain propagation in olefin polymerization,[199] are shown in Figure 22 (many theoretical studies have dealt with the orbitals of bent metallocenes; see for example ref. [50]). Ward et al. termed this structure *edge-bridged-tetrahedral* (EBT-5)[68] and studied many systems with related $[MX_2R_3]$ ligand arrangements, both by quantum-chemical calculation and by structure-correlation analysis. Starting from a trigonal bipyramid (TBP-5) the EBT-5 structure is reached by a reverse Berry pseudorotation. Detailed comparison of the d^0 MR_5 case (for which the EBT-5 structure is already a low-lying transition state,[62, 63, 68] see Section 2.4) and the $[MX_2R_3]$ case demonstrated clearly how the π-donor character of X favors EBT-5 over SP-5 (which lies along the regular Berry pathway). The stronger the π-donors, the larger the stabilization is. The structure-correlation analysis of published structures indicated many examples at different stages of the reverse Berry pathway.[68] $[ReO_2(CH_3)_3]$ is a clear-cut case for which a gas-phase EBT-5 structure has been determined recently (Figure 23).[200] The small C-Re-C angles are particularly obvious. Interestingly, the O-Re-O angle is larger than the 120° required by a regular trigonal bipyramid. This provides further support for the influence of the character of the ancillary σ-donor ligands on the bond angles (Section 4.1). In this case the strong σ-donor methyl ligands may lead to the observed preference for a larger O-Re-O angle. Weaker π-donor ligands may not be sufficient to force a nonclassical structure. For example, a regular TBP-5 with both chloride ligands in the axial positions was found by electron diffraction for $[Nb(CH_3)_3Cl_2]$.[16, 201]

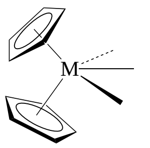

Figure 22. Preferred EBT-5 structure of $[MCp_2R_3]$ complexes.[68]

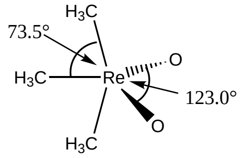

Figure 23. Gas-phase structure of $[Re(CH_3)_3O_2]$.[200]

We studied the $[MXR_4]$ system, in particular the structure of $[WO(CH_3)_4]$ and of related d^0 and d^1 systems.[69] While DFT calculations showed the hydride model system $[WOH_4]$ to exhibit strong deviations from a regular SP-5 structure (with the π-donor ligand in apical position), the distortions of the alkyl complex proceed along a rather shallow potential-energy surface. Nevertheless, the calculations show clearly that the regular SP-5 (C_{4v} symmetry) is not a minimum in these systems. Two directions of distortions were identified (Figure 24). One leads to a coordination arrangement that is close to the EBT-5 structure of Ward et al.[68] and exhibits C_s symmetry (C_s-1). The second distortion pathway leads to a different C_s structure (C_s-2) which may in fact become the lowest-energy structure for strong π-donor ligands X,[202] and for the d^1 model complex $[ReOH_4]$.[69] While the EBT-5-type arrangement provides three inequivalent sets of ligands R, two sets are obtained along the alternative distortion pathway.[69] Both types of distortions help to reduce antibonding interactions at the C_{4v} high-symmetry structure, which arise from the competition of M−X π bonding and M−R σ bonding. And both directions appear to provide closely comparable magnitude of stabilization.[69]

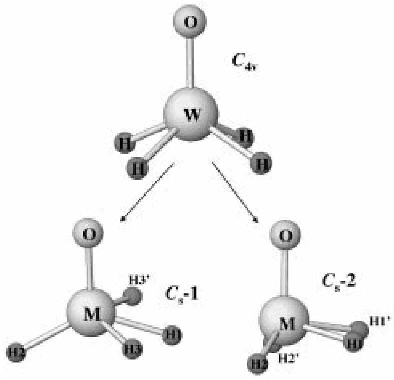

Figure 24. Possible distortions of the square pyramid for d^0 and d^1 $[MXR_4]$ complexes.[69]

The available evidence on $[MX_3R_2]$ systems indicates that the third π-donor brings us back into the regime of the TBP-5. However, there are significant differences depending on the type of σ and π donors. Thus, in the solid-state structure of the complex $[\{(CH_3)_2N\}_3Zr(SiPh_2tBu)_2]^-$, the three π-donor amide ligands are in equatorial position.[203] In contrast, two of the three π-donor chloride ligands in the gas-phase structure of $[Nb(CH_3)_2Cl_3]$ apparently are in axial positions, with *cis* Cl-Nb-Cl angles of about 96.5°.[16]

4.3. Hexacoordinate Heteroleptic Systems

Distortions from the regular octahedron in heteroleptic hexacoordinate d^0 complexes have played an important historical role in drawing the attention of theoreticians to possible deviations from the usual structures. For example, the strongly distorted octahedral structures of $[TiRCl_3(dmpe)]$ ($R = CH_3$, C_2H_5; $dmpe = (CH_3)_2P(CH_2)_2P(CH_3)_2$) initiated some of the earliest theoretical studies of nonoctahedral d^0 systems.[74, 107] Since then many more complexes have been studied, both experimentally and theoretically, in which different types of deviations from the regular octahedron are apparent. Generally, it is more difficult to discuss complexes with chelate ligands, as the preferred bite angle of the ligand may strongly influence the structure of the system, and works either against or with the electronic preferences of the central metal (Section 2.5).

The conceptually easiest distortions are probably those of unsymmetrical chelate ligands that remain largely along the trigonal twist discussed in Section 2.5. Examples are too numerous to be discussed here in detail.[84, 103, 204] It appears likely that the averaged σ- and π-donor abilities and bond ionicities of both inequivalent sides of the chelate ligand determine the twist angle. More interesting distortions are those in which formally equivalent chelate ligands coordinate in inequivalent modes (see Section 2.5).[94, 95] An interesting distorted trigonal-prismatic (C_{3v} symmetrical) system with one tridentate and three monodentate ligands is provided by $[(tbm)Ta(CH_3)_3]$ (tbm = tribenzylidenemethane).[47]

In Section 3.8 we have discussed the effect of replacing a cylindrical π-donor such as a halide by an effectively single-sided π-donor such as thiolate. This leads us into the range of structures intermediate between octahedron and trigonal prism, typically along the trigonal-twist pathway (see also Section 2.5). A recent DFT study explored a different route into this "no-man's-land":[78] starting from $[WCl_6]$ or $[WF_6]$, the halides were successively replaced by methyl ligands, to provide the heteroleptic series $[WX_{6-n}(CH_3)_n]$ ($n = 1-5$). The question was, how the structures proceed from the octahedral preference in $[WX_6]$ to the distorted trigonal prism of $[W(CH_3)_6]$. As indicated in Section 3.8, the trigonal prism has been computed to be a transition state for the trigonal twist in the hexahalides, approximately 80 kJ mol^{-1} and 43 kJ mol^{-1} above the O_h structure for $[WCl_6]$ and $[WF_6]$, respectively (the smaller difference for the fluoride being a result of the less efficient π bonding). Already after the first substitution of a halide by a methyl ligand ($[WX_5CH_3]$) this energy difference has almost vanished. Now a distorted octahedral minimum is only about 20 kJ mol^{-1} more stable than a trigonal-prismatic transition state for X = Cl, whereas the calculations already gave a very slight preference (by ca. 2 kJ mol^{-1}) to the prism for X = F. Even the C_s symmetrical octahedral structure (see Figure 25 for X = Cl) is characteristically distorted. This type of distortion also appears to be common for related heteroleptic systems (see below). While there is experimental evidence for the existence of both $[WX_5CH_3]$ complexes,[113, 205] no structures have been determined. With multiple substitution by methyl groups, the possibility of different isomers arises. Two minima of almost identical energy have been found computationally for $[WCl_4(CH_3)_2]$. One is a distorted *trans* octahedron of C_{2v} symmetry (analogous to the structure in Figure 25), whereas the second has C_2 symmetry and is intermediate between the trigonal prism and the *cis* octahedron. The structures of all of these complexes are presumed to be highly fluxional. Already with three methyl ligands, there appears to be a clearer preference for the trigonal prism, with the presence of different isomers of similar energy.[78] This preference is further enhanced upon substitution of the remaining halides by methyl groups, with no particularly surprising structures found along the way.[206] These computational data mark some of the possible intermediate structure situations in heteroleptic systems. Depending on the actual combination of σ-donor and single- or double-faced π-donor ligands, we may expect a considerable variety of coordination arrangements. Very recently, Seppelt et al.[207] succeeded in carrying out initial solid-state structure determinations for four heteroleptic systems, $[MoOCH_3(CH_3)_5]$, $[WCl(CH_3)_5]$, $[Mo(OCH_3)_2(CH_3)_4]$, and $[MoCl(OCH_3)_2(CH_3)_3]$. While the first three complexes are close to the trigonal-prismatic limit, the latter complex appears to prefer a distorted octahedral arrangement, which resembles strikingly a low-lying transition state computed for $[WCl_3(CH_3)_3]$.[78]

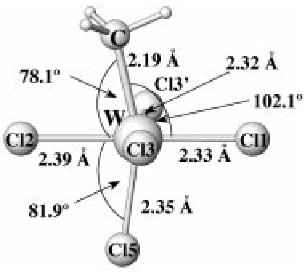

Figure 25. Distorted octahedral minimum structure computed for $[WCl_5CH_3]$.[78]

The type of distortions indicated in Figure 25 had already been observed earlier experimentally in a series of d^0 complexes of composition $[M(OAr)_2(H)_2LX]$ (M = Nb, Ta; L = $P(CH_3)_2Ph$, X = Cl, OAr),[208] and they have been the target of two independent computational studies on simplified model systems[209, 210] (see also ref. [107]). In these complexes, the two *trans* hydride ligands are bent characteristically towards the phosphane ligand L, away from the π-donor X ligand (Figure 26). With *trans* H-M-H angles of around 125–135°, the distortion is more pronounced than that computed for the *trans* alkyl ligands in the above mentioned $[WCl_4(CH_3)_2]$ (ca. 144°).[78] Replacement of the hydride ligands in these complexes by chloride ligands does not completely remove the bending but reduces it to a much less dramatic magnitude (*trans* Cl-M-Cl angles ca. 165°). The computational studies identified clearly the interplay between a maximization of the π bonding to ligand X and optimization of the σ overlap between the hydride ligands and appropriately hybridized metal d orbitals.[209, 210] Replacing X by a pure σ-donor ligand does not remove the distortion but reduces the energy preference for bending towards L. In several cases the calculations indicated the possible existence of a second isomer with the hydrides bent towards X.[210] The latter isomers became the preferred ones when X was replaced by a π-acceptor (see also ref. [18]).

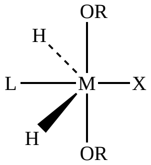

Figure 26. Distorted octahedral structures found for heteroleptic complexes $[M(OR)_2(H)_2LX]$ (M = Nb, Ta; L = $P(CH_3)_2Ph$, X = Cl, OAr).[208–210] While R = aryl group in the experimentally studied systems, DFT calculations employed R = H.

The results of these studies confirm a preference for angles below 90° and below 180° between *cis* and *trans* σ-donor ligands, respectively (see also Section 3.4 and 3.5). At the same time, the distortions allow the competing π-donor ligands to enhance their bonding to the metal. These conclusions are consistent with more general notions about the alleviation, by structural distortions, of conflicts between different π-donor ligands (or between σ- and π-donor ligands) competing for a given set of metal d orbitals.[211] The prototypical example for this type of competition is that discussed for distorted octahedral dioxomolybdenum complexes, in which the two strong π-donor oxo ligands prefer a *cisoid* arrangement (Section 3.8), and the two weakest co-ligands are located *trans* to the oxo ligands, with typically small angles between them[211a, 212] (see also ref. [179] for a theoretical study on a *cis* diimido complex).

Either structures close to the trigonal prism or characteristically distorted octahedral arrangements have been found for the complexes $[MX_2(Me_4taen)]$ ($Me_4taen = 5,7,12,14$-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene; M = Zr, Hf).[213] The cavity of the tetradentate macrocyclic ligand Me_4taen is too small to completely enclose the metal. The additional ligands X are attached in a *cis* arrangement on one side of the macrocycle. The dihedral angles are close to the trigonal prismatic extreme for X = Cl, CH_2Ph, with the ligands X each pointing in between two of the nitrogen atoms of the macrocycle. In contrast, in complexes with presumably stronger π-donors[213] (X = $N(CH_3)_2$, O*t*Bu) the ligands X eclipse almost two of the macrocyclic nitrogens, creating an octahedral structure distorted in the direction of a doubly capped tetrahedron.

An interesting example of a d^2 complex with five σ-donors and one π-/σ-donor is provided by $[CpOsH_5]$.[214] Calculations indicate a strongly distorted pseudo-octahedral structure with the equatorial hydrogens strongly bent away (by ca. 115°) from the apical Cp ligand, to enhance their σ bonding to the metal.[215] The system is thought to fluctuate even at low temperatures, via low-lying trigonal prismatic transition states.[215]

A very different class of heteroleptic d^0 systems may be derived from more strongly ionic complexes of the heavier alkaline earth metals (M = Ca, Sr, and Ba) or of the lanthanides. For example, in a series of complexes $[M(N\text{-carbazolyl})_2(L)_n]$, a clear transition from a mutual *trans* arrangement of the formally anionic carbazolyl ligands in $[Ca(N\text{-carbazolyl})_2(pyridine)_4]$ via a bent *transoid* arrangement in $[Sr(N\text{-carbazolyl})_2(NH_3)(dme)_2]$ to a *cis* arrangement in $[Ba(N\text{-carbazolyl})_2(dme)_3]$ was found by X-ray diffraction (dme = 1,2-dimethoxyethane).[216] Based on the increasingly bent structures of the gas-phase alkaline earth dihalides with increasing atomic number of the metal (see Section 2.1), it has been suggested that the same effects (small covalent σ-bonding contributions involving metal d orbitals and core polarization, Sections 3.1 and 3.2) survive when additional weakly bonded, neutral co-ligands are present.[216] This idea has been supported by ab initio calculations on the model complexes $[M(NH_2)_2(HF)_4]$ (M = Ca, Ba). While the calcium complex prefers an almost regular octahedral structure with *trans* NH_2 ligands, the barium complex favors a distorted *cis* arrangement. Even for the less stable *trans* structure, the N-Ba-N angle was computed to be only about 146° (the energy differences involved are in the range of only ca. $10\,kJ\,mol^{-1}$).[216] It appears that the electronic requirement to have the two anionic ligands in a bent arrangement dominates over the requirements of the additional neutral ligands (provided the latter are not too bulky) in controlling the preferred structure. This is consistent with a distinction between regular covalent and dative bonding.[217] Some more experimental examples in agreement with these ideas have been provided.[216] Recently, a number of hexacoordinate bisthiolate and bisselenolate complexes $[M(thf)_4EMes^*_2]$ (M = Ca, Sr, Ba; E = S, Se; Mes* = 2,4,6-$tBu_3C_6H_2$) have been structurally characterized.[218] While the Ca, Sr, and Ba complexes all exhibit a *transoid* arrangement of the anionic thiolato or selenolato ligands, the X-M-X angle decreases from Ca to Ba, and from selenolate to thiolate complexes, consistent with the above discussion.

4.4. Mononuclear Molybdenum and Tungsten Enzymes

We have already mentioned examples, in which the "non-VSEPR structures" of certain d^0 complexes were considered relevant for practical questions, for example, for the stereospecificity of olefin polymerization (Section 2.2), or in the context of α-elimination of alkyl compounds to produce carbene complexes (Section 2.4). Another case, in which the nonclassical structure preferences of d^0 systems are of potential interest, is the fascinating field of molybdenum and tungsten enzymes. We will disregard here the multinuclear molybdenum nitrogenases but will concentrate on the mononuclear active sites of the other large class of molybdenum enzymes and the closely related tungsten enzymes.[89, 90] In these enzymes, sometimes referred to as oxomolybdenum (oxotungsten) or oxotransferase enzymes, the single metal atom is coordinated by a unique bioligand termed pterin cofactor. Most notably, the coordination is of the dithiolene type, and this is one of the reasons for the large amount of research carried out on dithiolene complexes (Section 2.5). In their oxidized state, the active sites of the enzymes feature Mo^{VI} and W^{VI}, respectively, that is, they may be assigned a d^0 configuration.

Hille[89] has classified the known molybdenum enzymes broadly into three families, based on the known structural features of their active site. In the M^{VI} state, the "xanthine oxidase family" and the "sulfite oxidase family" both exhibit *one* chelating dithiolene (pterin) ligand, two terminal oxo (or sulfido) ligands, and one or two additional ligands. The structures determined may be termed distorted octahedral, partly because of the specific requirements of the strong π-donor oxo- and/or sulfido-ligands. These active sites fit well the category of d^0 dioxo complexes discussed above (Section 4.3), and a considerable number of synthetic model complexes has been structurally characterized[211, 212] or studied computationally.[211, 219]

In contrast, the "dimethylsulfoxide (DMSO) reductase family"[89] of molybdenum enzymes exhibits coordination by *two* pterin ligands, usually in a bischelating dithiolene mode (Figure 27). The additional ligands X and Y may be one oxo, sulfido, or selenido ligand (or potentially protonated forms like hydroxy or aqua ligands) plus one monoanionic ligand coming from the protein surroundings, for example, serinate, cysteinate, or selenocysteinate. Because of the restricted π-donor abilities of dithiolene ligands (Section 3.8), "non-VSEPR structures" are most likely for this last family of molybdenum enzymes, or for related tungsten active sites. Indeed, based on recent protein X-ray structure determinations, several of the active sites studied have been termed "distorted trigonal prismatic".[89, 90] In particular, the following cases have been discussed: 1) the structure of formate dehydrogenase H of *Escherichia coli*, where the two additional co-ligands to molybdenum(VI) center were either hydroxy and seleno-cysteinate, or nitrite and seleno-cysteinate (nitrite is considered an inhibitor, closely

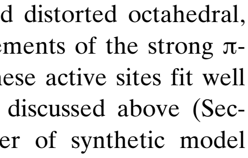

Figure 27. General coordination pattern of the Mo^{VI} active sites of molybdenum enzymes in the DMSO reductase family.[89]

analogous to the substrate formate).[220] 2) The structure of DMSO reductase from *Rhodobacter sphaeroides*, where the two co-ligands to the Mo^{VI} center have been considered to be one oxo and one serinate ligand.[221] 3) The structure of the tungsten(VI) active site of aldehyde ferredoxin oxidoreductase from *Pyrococcus furiosus*,[222] the structure of which has been considered to be very close to that of the Mo active center of DMSO reductase from *Rhodobacter sphaeroides* (see above).

Unfortunately, in none of these crystallographic studies of proteins is the structural resolution obtained sufficiently high to unequivocally discriminate near-octahedral or near-trigonal-prismatic coordination of the metal center. Nor does the additional spectroscopic information allow this classification to be made. Structure analyses of synthetic model complexes with suitable ligand combinations could provide the necessary insight, but as yet the data is limited for systems with a d^0 metal center, two dithiolene ligands and two appropriate additional co-ligands.[223–226] Those $[M(dt)_2XY]$ model complexes studied crystallographically (dt = dithiolene-type ligand; X, Y = monodentate co-ligands) had either two oxo ligands,[223, 224] or one oxo ligand plus a "monoanionic" ligand like alkoxide, siloxide, or chloride.[225, 226] In all cases, the structures may be best characterized as distorted octahedral.

Based on the predominantly trigonal-prismatic structures of tris(dithiolene) complexes (Section 2.5) and the structural role of π bonding (Section 3.8), we can speculate about possible structures of $[M(dt)_2XY]$ complexes. In particular, we expect that complexes in which X and Y are relatively weak π donors (that is, not oxo or sulfido ligands) will be closest to the trigonal-prismatic extreme. Thus, for example, the combination between a monoanionic co-ligand X (e.g. serinate, cysteinate, seleno–cysteinate) and a monoanionic (e.g. hydroxide, nitrite) or neutral (e.g. H_2O) co-ligand Y might provide a suitable electronic situation for a prismatic structural preference.[227] Clearly, in the actual situation in the protein, hydrogen bonding may further modify the π- and σ-donor abilities of the ligands. It is presently an open question, to what extent the structure preference of the active site of such molybdenum or tungsten enzymes may alter the reactivity of the system. However, as the fully reduced d^2 states (Mo^{IV}, W^{IV}) of the enzymes are likely to exhibit structures derived from the square pyramid (SP-5), it is not unlikely that oxo-transfer or related reactions will be modified in going from a distorted trigonal prismatic to an octahedral structure of the oxidized state.

5. Multinuclear d^0 Complexes: Moving towards the Extended Solid

As discussed in Section 2.5, the first "non-VSEPR" cases observed for d^0–d^2 systems were extended solid-state structures with trigonal-prismatic metal coordination.[79] It is to be expected that the factors discussed in Sections 2–4 may also be relevant for other extended solid-state systems. All other things being equal, an increase in coordination number increases ligand repulsion and thus tends to decrease the tendency towards nonclassical structures. In the case of MoS_2 and its relatives, the large covalency of metal–ligand σ bonding obviously helps to stabilize the prismatic coordination even in the bulk material (Section 3.7).[79] However, there are indications that even relatively small covalent-bonding contributions may be sufficient to have an influence on the structural preferences. Multinuclear complexes may be considered as intermediate states of aggregation, between molecule and extended solid. They are thus a convenient starting point for our discussion.

Still on the covalent side, some di- and trinuclear thiolato complexes of Ti and Zr should be mentioned, in which the central metal adopts either a distorted or a regular trigonal-prismatic coordination geometry.[92b,c] As discussed in Section 3.8, it appears likely that the influence of π bonding may be diminished compared to corresponding mononuclear analogues, as angular constraints do not allow the π-type lone pairs on sulfur to participate fully in bonding. A related heteroleptic example is provided by the trimer $[\{(Me_2N)_3Zr(\mu\text{-}H)(\mu\text{-}NMe_2)_2\}_2Zr]$, in which the central metal is in a trigonal prismatic and the outer metals in a trigonal antiprismatic environment.[228]

DFT[36] and HF[229] calculations have dealt with the monomers, dimers, and trimers of $[TiO_2]$. The electrostatically most favorable planar, doubly bridged D_{2h} structure (Figure 28a) is not a minimum on the dimer potential-energy surface, and it distorts to a C_{2h} structure (Figure 28b), with trigonal-pyramidal metal coordination. However, a triply bridged structure with C_{3v} symmetry (Figure 28c) is even more favorable energetically. Related structures have been computed for the trimer, $[Ti_3O_6]$[36, 229] and for its zirconium analogue.[230] In bulk TiO_2 modifications, Ti is octahedrally coordinated, but with deviations from the ideal polyhedron (the distortions are most notable in the brookite structure[80]). The 4d homologue ZrO_2 is also polymorphic. Except for the high-temperature cubic form, the coordination of the metal is highly irregular. In the low-temperature monoclinic modification (cf. the mineral baddeleyite; the same structure is realized by HfO_2), the metal is irregularly coordinated by seven oxygen neighbors.[80, 81, 231, 232] Ionic models have not performed well in describing the phase transitions of ZrO_2.[233] This has been taken as evidence for the importance of Zr–O covalency in describing the low-symmetry structures.[234] The phase transitions of ZrO_2 are of tremendous technological importance, as they are intrinsically related to the mechanical properties of zirconia (ZrO_2), one of the most widely used ceramic materials.[235] A vast literature exists on various factors affecting the stability of the different phases, which include the stabilization of the cubic structure by impurities. A review of this field is beyond the scope of the present article.

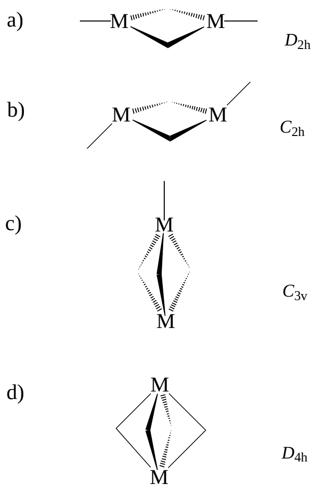

Figure 28. Preferred structures for d^0 $[M_2X_4]$ systems.[252]

The more covalent MoO_3, and particularly WO_3, also exhibit a strikingly rich structural chemistry, again with highly unsymmetrical coordination of the metal center in many cases.[80, 81, 232, 236] And again, the structural distortions are coupled to important technological applications (e.g. WO_3 is used in electrochromic devices,[237] and MoO_3 is an important oxidation catalyst[238]). In most cases, the metal coordination environment may be described as distorted octahedral. In several phases of WO_3, and in the metastable β-MoO_3,[236] the metal is displaced towards a face of the oxygen octahedron. An extended-Hückel study,[239] and several more recent HF and DFT studies[55, 240] have dealt with the instability of the high-symmetry cubic ReO_3-type structure for WO_3 or MoO_3. The preference for lower coordination symmetry in the d^0 systems has in all cases be traced to improved covalent M–O interactions. While the extended-Hückel work of Wheeler et al. emphasized the π-type interactions,[240] more recent HF solid-state calculations suggested that also the metal-oxygen σ bonding is improved in the lower-symmetry structures.[240a] Both notions are consistent with the discussions in Section 3. Notably, the deviations from a regular octahedral coordination are more pronounced for the 4d system MoO_3[236] than for the 5d system WO_3, probably because of the relativistic expansion of the 5d orbitals and the resulting larger bond ionicity and band gap in the tungsten compound (Section 3.7). Addition of one electron, to give a formal metal d^1 configuration, stabilizes the classical cubic structures of ReO_3 or of $NaWO_3$, with regular octahedral metal coordination. This has been traced to M–O antibonding contributions from the conduction band.[239, 240b]

In close relationship to the distorted structure of WO_3 are the ferroelectric d^0 perovskites.[241] The prototype is $BaTiO_3$, one of the economically most important ceramic materials, because of its ferroelectric transition near room temperature. At normal pressure, $BaTiO_3$ exhibits three phase transitions.[242] Notably, in the thermodynamically most stable low-temperature rhombohedral phase, the titanium atom has shifted towards one of the faces of the distorted oxygen coordination octahedron (the other ferroelectric transitions correspond to movements towards a corner or an edge, respectively). In this and related cases, the computed band gap increases upon distortion of the cubic structure.[243] Regarding the origin of the low-symmetry distortions, the same considerations apply as for WO_3 or MoO_3 above. Wheeler et al.[239] have classified the distortions as representative for a more general picture of second-order Jahn–Teller distortions. More recent DFT studies also emphasized the improved covalent M–O bonding in the distorted structures[243] (unfortunately, in most chemistry textbooks, the distortions are still rationalized as being because the "Ti^{4+} ion" is too small to adequately fill the octahedral interstices).

Among the other ferroelectric perovskites, we should mention $KNbO_3$, which exhibits the same series of ferroelectric phase transitions upon cooling, and the same distorted metal coordination in the low-temperature phases as $BaTiO_3$,[244] caused by the same tendency to improve M–O covalency. Interestingly, the heavier 5d homologue, $KTaO_3$, does not distort from the high-symmetry cubic perowskite form, even at very low temperatures.[245] However, a soft phonon mode[246] indicates that $KtaO_3$ is just on the brink of also favoring a low-symmetry distortion (it has been termed an "incipient ferroelectricum"). The dielectric properties of unrestricted solid solutions of $KNbO_3$ and $KTaO_3$ (a pseudobinary alloy termed "KTN") may be adjusted conveniently by concentration.[247] Ferroelectric behavior is already found at Nb concentrations above 1%. We may again attribute the differences between the 5d and 4d systems to slightly more ionic bonding in the former (caused by the relativistic expansion of the 5d orbitals), as well as to the related larger band gap (3.79 eV in $KTaO_3$[248] relative to 3.3 eV in $KNbO_3$[249]), which disfavors a "second-order Jahn-Teller distortion" (Sections 3.7 and 3.4, respectively). Similar differences apply to the comparison of $LiNbO_3$ and $LiTaO_3$. While both substances are known to exhibit one ferroelectric phase transition, the transition temperature is lower for $LiTaO_3$ (950 K) than for $LiNbO_3$ (1480 K), consistent again with a shallower well on the potential surface for the Ta compound.[250] Ferroelectrically distorted structures have recently been found also for $CsTaQ_3$ (Q = S, Se, Te).[251] A detailed appreciation of the vast amount of experimental and theoretical work centered on the ferroelectric distortions in perovskites and related materials is outside the scope of this article.

Many further d^0 oxides exhibit low-symmetry distortions of the metal coordination environment. Examples are the complex structural chemistry exhibited by Nb_2O_5 or Ta_2O_5 (again with notable differences between the 4d and 5d system[80]), the Group 3 sesquioxides (e.g. Sc_2O_3, Y_2O_3, La_2O_3), numerous iso- and heteropolyions of Nb, Ta, Mo, and W, or the rich structural chemistry of the vanadates. Even the different structures of the 4d oxide Tc_2O_7 and the 5d oxide Re_2O_7 in the solid state should be mentioned in this context. A detailed discussion of the extensive literature on these compounds is beyond the scope of this article (see, for example, ref. [80]).

Herein we have concentrated mainly on the local bonding environment of the d^0 metal, and therefore we have not considered long-range Coulombic interactions in detail. Moreover, the structural distortions of the metal coordination sphere are intrinsically coupled to those of the neighboring unit cells (this touches also the question of first- and second-order phase transitions). The structures are undoubtedly influenced by packing effects and thus by the relative sizes of the different atoms. Nevertheless, it is clear that the covalent bonding aspects discussed in Sections 2–4 have a high impact on the structural preferences, and thus on the materials properties of these substances. The discussion of the structural chemistry of d^0 oxides would benefit from a better consideration of covalent bonding.

Structures similar to $[Ti_2O_4]$ (see above) have been found for the ionic dimeric compounds of the heavier alkaline earth metals. HF calculations on the dihydride dimers indicated the triply bridged C_{3v} structure (Figure 28c) to be lowest in energy for $[Sr_2H_4]$, and in particular for $[Ba_2H_4]$, followed by the doubly bridged C_{2h} structure (Figure 28b) with pyramidal metal coordination environment.[252] Even a quadruply bridged D_{4h} structure with no terminal ligands (Figure 28d) has been computed to be almost as viable energetically as the ground-state structure for the heavier metals. The regular D_{2h} structure (Figure 28a) is preferred slightly for $[Ca_2H_4]$ and strongly for the Be and Mg systems but is not a minimum for [Sr_2H_4] or [Ba_2H_4]. Very similar results have been obtained in recent DFT calculations on the difluoride and dichloride dimers,[253] with increasing preference for the triply bridged structure with the heavier metals and lighter halogens. This is exactly the same type of tendency found for the bending of the monomers (Section 2.1).

Experimental examples for these types of structure preferences encompass oligomeric diamides, diphosphanides, and dialkoxides of the heavier alkaline earth metals: the dimers of bulky diamides, $\{M[N(SiMe_3)_2]\}_2$, exhibit the doubly bridged structure, with increasing pyramidalization of the metal center (C_{2h} heavy-atom skeleton) along the series Ca < Sr < Ba.[254] In contrast, the corresponding phosphanides $\{M[P(SiMe_3)_2]\}_2$ exhibit significantly reduced P–M π bonding, a result of the preferred pyramidalization around phosphorus atoms. Indeed, the known X-ray structures indicate triply bridged structures (Figure 28c), but with additional solvent molecules attached to the open metal site.[255] Further examples of these triply bridged types of dimers, and of related larger aggregates, are provided by a number of alkoxides of the heavier alkaline earth metals.[256]

Will the "non-VSEPR" preferences of alkaline earth MX_2 compounds also survive in the bulk solid? In this context, the covalent σ-donor hydride ligands are the most likely candidates for unusual coordination. Indeed, the solid-state structures of the heavy alkaline earth and lanthanide(II) dihydrides exhibit remarkably unsymmetrical metal coordination, typically described as a very irregular 6+3 or 7+2 coordination in a distorted $PbCl_2$ structure type.[80, 81] There appears to be no good reason based on ionic bonding forces alone that would explain these unusual structures. The unsymmetrical metal coordination in many lead dihalides or related compounds with the $PbCl_2$ structure type may be rationalized by the stereochemical activity of the metal lone pair. It seems likely that the irregular structures of the heavy Group 2 dihydrides in the bulk phase are because of d-orbital participation in σ bonding and to core polarization. These are the same factors that make the monomeric and dimeric molecules violate the usual structure rules.

The dihydrides are not alone in exhibiting irregular structures in the bulk solid. While ionic bonding forces appear to dominate the regular structures of alkaline earth and lanthanide(II) difluorides, the other barium halides, as well as $EuCl_2$ and $SmCl_2$, have $PbCl_2$-type structures similar to the hydrides, with very unsymmetrical coordination of the metal center.[80, 81] Wells noted that "The alkaline earth halides are surprisingly complex from a structural viewpoint, the twelve compounds exhibiting at least six different structures."[80] Complex structural situations also pertain to the known Group 3 and lanthanide(III) trihalides. For example, $LaCl_3$ and $LaBr_3$, as well many 4f trichlorides and trihydroxides, prefer the UCl_3 structure type, which is related to the $PbCl_2$-type. Even the fluorides tend to exhibit irregular coordination. It is notable, for example, that the highly irregular YF_3 structure type is the same as that also adopted by the main group fluorides TlF_3 and β-BiF_3,[80] where the unsymmetrical metal coordination might be attributed to stereochemically active lone pairs.

6. Final Remarks

The number of examples of "non-VSEPR structures" of d^0 and related systems provided in Sections 2–5 show that we are not dealing with a mere curiosity or exotic phenomenon. In many cases, the low-symmetry distortions appear to be related to important processes, for example, in homogeneous or heterogeneous catalysis (e.g. olefin polymerization or oxide-surface catalyzed oxidations), in bioinorganic chemistry (e.g. molybdenum enzymes), or in materials research (e.g. ferroelectric oxides). Future research will bring us more examples, in particular of heteroleptic complexes with numerous applications. We also have to accept that even those complexes that obey the classical structural models, may nevertheless exhibit potential-energy surfaces that differ sharply from those of related main group compounds. It is therefore mandatory that improved bonding principles are provided for such systems. These models should enable the preparative chemist, the catalyst designer, or the materials researcher to predict structure, reactivity, and properties of high-valent early transition metal compounds with good accuracy.

While the bonding in homoleptic, σ-bonded complexes appears to be well described by relatively simple MO or VB models, in conjunction with ligand repulsion (Sections 3.1–3.7), the influence of π bonding on structure (in particular on bond angles and conformation) needs further scrutiny before we will understand all its intricacies (Section 3.8). This holds in particular for heteroleptic complexes, where the outcome of the competition between σ-bonding and σ-/π-bonding ligands for the metal d orbitals is still hard to predict, because of the multitude of possible solutions, and often a result of relatively small energy differences between different structures (Section 4). Once the structural preferences have been put on a firm theoretical basis, our understanding of reactivity and stereoselectivity will benefit as well, for example, in the case of the molybdenum enzymes discussed in Section 4.4. Another area that deserves more work, also from a quantum-chemical point of view, are the multinuclear complexes, and the bulk phases discussed in Section 5. It appears possible that many solid-state structures, that up to now defy clear-cut interpretations, will become tractable along the lines set out in Section 3.

Generally, quantum-chemical calculations have played an enormously important role in uncovering the concepts described in Section 3 (and in Section 4.1). Moreover, the quantitative accuracy of modern ab initio or DFT calculations in structure predictions has been shown to rival experiment in many cases. In future we will need even better tools, in particular to extract suitable, improved qualitative chemical models from such quantitative calculations.

7. Appendix: Details of the DFT Calculations

All molecular calculations performed specifically for the present paper have been carried out with the Gaussian 94 program,[257] at the same computational level used in refs. [69, 114, 115]. That is, the gradient-corrected BP86 functional[258] was used with quasirelativistic small-core metal ECPs,[147a, 259] and also with ECPs for the main group atoms F, Cl, and S.[260] Valence basis sets employed were of the sizes (8s7p6d)/[6s5p3d] for the transition metals,[147a, 259] and (4s4p1d)/[2s2p1d] for the p-block main group atoms.[260, 261] Hydrogen basis sets were of the size (4s)/[2s][262] augmented by one p-function ($\alpha = 1.0$) for hydrogen atoms directly bound to the metal center. NPA and NBO analyses[167] have been carried out with the built-in subroutines of the Gaussian 94 program.[257]

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