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

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

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

Conclusion

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

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

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

Note Added in Proof. Recently, the green "isomer" of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ was spectroscopically and chromatographically characterized as a mixture of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and *mer*-MoCl$_3$(PMe$_2$Ph)$_3$.[17] Experimental studies of the W system are currently in progress (Enemark, J. H.; Wieghardt, K. Personal communications).

Acknowledgment. We thank the National Science Foundation (Grant No. CHE 86-19420) and the Robert A. Welch Foundation (Grant No. A-648) for financial support and M. F. Guest for providing the GAMESS package of programs. This research was conducted in part using the Cornell National Supercomputer Facility, a resource of the Center for Theory and Simulation in Science and Engineering at Cornell University, which is funded in part by the National Science Foundation, New York State, and IBM Corp. We also thank Cray Research for a grant of computer time on the Cray Y-MP2/116 computer at the Supercomputer Center of Texas A&M University. We also thank G. Parkin for a preprint of ref 5 prior to publication.

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

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Received January 24, 1991

The d^0 early-transition-metal polyoxometalates which are reversibly reducible are constructed from octahedra having only one terminal oxygen atom. Such MO$_6$ octahedra each contain a single nonbonding d orbital. Overlap of these d orbitals results in delocalization, which may be regarded as binodal aromaticity and which is much weaker but topologically related to the aromaticity from overlap of the anodal sp hybrids of the boron atoms in the $B_nH_n^{2-}$ anions ($6 \le n \le 12$) or the uninodal carbon p orbitals in benzene. The improper 4-fold symmetry of these d orbitals leads to polyhedra of O_h symmetry and all vertices of degree 4 for the basic building blocks of binodal orbital aromatic systems corresponding to the octahedra found in polyoxometalates of the type $M_6O_{19}^{n-}$ (n = 8, M = Nb, Ta; n = 2, M = Mo) and the cuboctahedra found in Keggin ions of the type $XM_{12}O_{40}^{n-}$ (n = 3–7; M = Mo, W; X = B, Si, Ge, P, Fe^{III}, Co^{II}, Cu^{II}, etc.).

Introduction

The heteropoly- and isopolyoxometalates of early transition metals[2,3] have been known for well over a century and have become of increasing interest in recent years. Their structures are characterized by networks of MO$_6$ octahedra in which the early transition metals M (typically V, Nb, Mo, and W) are typically in their highest (d^0) oxidation states. A characteristic of many, but not all, of such structures is their reducibility to highly colored mixed oxidation state derivatives, e.g., "molybdenum blues"[2,4] and "tungsten blues".[2] The redox properties of these polyoxometalates make them important as catalysts for a number of oxidation and dehydrogenation reactions of organic substrates.[5,6]

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

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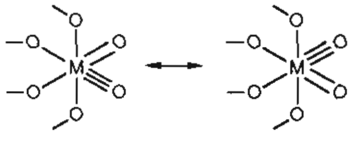
Pope[7] first noted that the reducibility of early-transition-metal polyoxometalates requires the presence of MO_6 octahedra in which only one of the six oxygen atoms is a terminal oxygen atom. Such an MO_6 octahedron can be related to mononuclear L_5MO species[8] in which there is an essentially nonbonding metal d orbital to receive one or two electrons. Nomiya and Miya[9] developed the idea of a structural stability index based on interpenetrating loops –O–M–O–M–O– around the polyoxometalate cage and suggested the analogy of closed loops of this type to macrocyclic π-bonding systems. The relationship of such macrocyclic π-bonding systems to aromaticity such as that found in certain organic annulenes[10] suggests that readily reducible polyoxometalates have some kind of aromatic properties. Thus the ready one-electron reducibility of a colorless to yellow polyoxomolybdate or polyoxotungstate to a highly colored mixed-valence "blue" may be viewed as analogous to the one-electron reduction of benzenoid hydrocarbons such as naphthalene or anthracene to the highly colored corresponding radical anion.

In previous papers[11-14] I have used ideas derived from topology and graph theory to show how deltahedral boranes, carboranes, and certain metal clusters exhibit three-dimensional electron delocalization or "aromaticity" completely analogous to the two-dimensional aromaticity of planar hydrocarbons such as cyclopentadienide, benzene, and tropylium. This paper indicates how related ideas can be used to describe the electron delocalization in the readily reducible early-transition-metal polyoxometalates. A recent paper[15] summarizes some experimental evidence for electron delocalization in heteropoly 12-molybdophosphate anions.

Structural and Chemical Aspects

The polyoxometalates of interest consist of closed networks of MO_6 octahedra where M is a d^0 early transition metal such as V(V), Nb(V), Mo(VI), or W(VI). These networks may be described by the large polyhedron formed by the metal atoms M as vertices. In general, the edges of this *macropolyhedron* are M–O–M bridges, and with rare exceptions as noted later, there is no direct metal–metal (M–M) bonding. The oxygen atoms are of three types: (1) terminal or external oxygen atoms, which are multiply bonded to the metal (one σ and up to two orthogonal π bonds) and directed away from the macropolyhedral surface; (2) bridging or surface oxygen atoms, which form some or all of the macropolyhedral edges; (3) internal oxygen atoms, which are directed toward the center of the macropolyhedron. The metal vertices of the macropolyhedron may be classified as L_5MO or *cis*-L_4MO_2 vertices depending on the number and locations of the terminal oxygen atoms (i.e., O = terminal oxygen atoms only and L = other (bridging and internal) oxygen atoms). In the *cis*-L_4MO_2 vertices all nine orbitals of the sp^3d^5 manifold of M are used for the σ and π bonding to the two terminal oxygen atoms and σ bonding to the four bridging and internal oxygen atoms leaving no orbitals for direct or indirect overlap with other metal vertices of the metal macropolyhedron corresponding to a resonance hybrid depicted schematically as



(1)

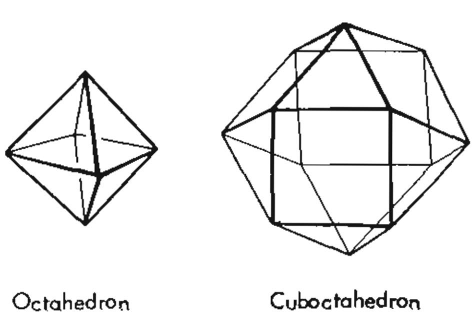
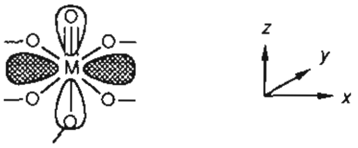


Figure 1. Regular octahedron and the cuboctahedron.

The *cis*-L_4MO_2 vertices in polyoxometalates correspond to the saturated CH_2 vertices in cyclohexanes and other cycloalkanes. In the L_5MO vertices only eight of the nine orbitals of the sp^3d^5 manifold of M can be used for σ and π bonding to the single terminal oxygen atom and σ bonding to the five bridging and internal oxygen atoms leaving one nonbonding d orbital (d_{xy} if the $M\equiv O$(terminal) axis is the *z* axis depicted below).



(2)

Thus an L_5MO vertex with a nominally nonbonding d_{xy} orbital in a polyoxometalate is analogous to an unsaturated CH vertex with a nonbonding p orbital in a planar aromatic hydrocarbon such as benzene.

These elementary considerations suggest that early-transition-metal polyoxometalates constructed from MOL_5 units have the potential for electron delocalization based on overlap of the nonbonding d_{xy} orbitals. However, since these polyoxometalates are constructed from macropolyhedra with relatively long M–O–M edges rather than normal metal polyhedra with the much shorter M–M edges, the direct overlap of the d_{xy} orbitals on different metal atoms is negligible. Instead the metal–metal interactions using these metal d_{xy} orbitals must also involve the orbitals of the oxygen atoms in the M–O–M bridges[16] and thus resemble the exchange coupling between metal atoms in antiferromagnetic systems.[17] Thus the electron delocalization in polyoxometalates with MOL_5 units is based on indirect M–O–M interactions using the metal d_{xy} and appropriate bridging oxygen p orbitals rather than direct M–M interactions such as those found in metal clusters. For this reason electron delocalization in reduced polyoxometalates is much weaker than that in either planar aromatic hydrocarbons or three-dimensional deltahedral boranes and carboranes. Nevertheless, the same ideas derived from topology and graph theory are relevant to all of these systems.

Topological and Group-Theoretical Aspects

The nonbonding d_{xy} orbitals of the MOL_5 vertices in the reducible early transition metal polyoxometallates have two orthogonal nodes (see (2)) and thus have improper 4-fold symmetry. Matching this 4-fold orbital symmetry with the overall macropolyhedral symmetry requires macropolyhedra in which a C_4 axis passes through each vertex. A true three-dimensional polyhedron having C_4 axes passing through each vertex can have only O or O_h symmetry (the only point groups with multiple C_4 axes). The expected highly restrictive nature of this condition is confirmed by a recent study of Broersma, Duijvestijn, and Göbel,[18] who show that the only two polyhedra having less than 15 vertices meeting these conditions are the regular octahedron and the cuboctahedron (Figure 1). It is therefore not surprising that these two polyhedra form the basis of the specific early-transition-metal polyoxo-

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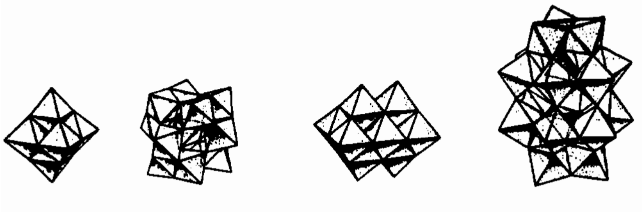
Table I. Types of Aromaticity

compound type	formulas	dimensionality	vertex atoms	overlapping orbitals type	overlapping orbitals nodes	adjacent atom interactions
deltahedral borane anions	$B_nH_n^{2-}$ ($6 \le n \le 12$)	3	B	sp	0	B–B
planar hydrocarbons	$C_nH_n^{6-n}$	2	C	p	1	C–C
macrooctahedral and macrocuboctahedral polyoxometalates	$M_6O_{19}^{n-}$ $XM_{12}O_{40}^{n-}$, (M = V, Nb, Mo, W)	3	M	d	2	M–O–M



$M_6O_{19}^{n-}$ $XM_{12}O_{40}^{n-}$ $V_{10}O_{28}^{6-}$ $P_2W_{18}O_{62}^{6-}$

Figure 2. Structures of the polyoxometalates of the types $M_6O_{19}^{n-}$, $XM_{12}O_{40}^{n-}$, $V_{10}O_{28}^{6-}$, and $P_2W_{18}O_{62}^{6-}$.

metalate structures containing only MOL_5 vertices (type I structures in the Pope nomenclature).

The specific building blocks for type I structures of interest are as follows. (A) Octahedron: $(MO^tO^b_{4/2}O^i_{1/6})_6^{n-} = M_6O_{19}^{n-}$ (n = 8, M = Nb, Ta; n = 2, M = Mo) where O^t = one terminal oxygen per metal atom, $O^b_{4/2}$ = one bridging oxygen along each of the 12 edges of the macrooctahedron, and $O^i_{1/6}$ = a μ_6-oxygen in the center of the M_6 macrooctahedron shared equally among all six metal vertices. (B) Cuboctahedron (Keggin Structure): $(MO^tO^b_{4/2}O^i_{1/3})_{12}X^{n-} = XM_{12}O_{40}^{n-}$ (n = 3 to 7; M = Mo, W; X = B, Si, Ge, P, Fe^{III}, Co^{III}, Cu^{II}, etc.) where O^t = one terminal oxygen per metal atom, $O^b_{4/2}$ = one bridging oxygen along each of the 24 edges of the macrocuboctahedron, and $O^i_{1/3}$ = an OM_3X oxygen bonded to three of the early-transition-metal atoms. The four oxygen atoms of this type surround the center of the cuboctahedron at the vertices of a tetrahedron. The heteroatom X is located in the center of the cuboctahedraon with tetrahedral coordination to these oxygen atoms.

The other type I structures considered by Pope[7] include $V_{10}O_{28}^{6-}$ formed by edge-sharing of two V_6 macrooctahedra and $X_2M_{18}O_{62}^{6-}$ (Dawson structure) formed by fusion of two M_{12} macrocuboctahedra. These four basic structures are depicted in Figure 2.

These structures containing only MOL_5 vertices can be contrasted with the nonreducible polyoxometalate structures containing only *cis*-MO_2L_4 vertices (type III structures in the Pope nomenclature[7]). These structures are necessarily more open, since only four of the six oxygens of the MO_6 octahedra can be bridging oxygens. The most symmetrical polyoxometalate structure with only *cis*-MO_2L_4 vertices is the icosahedral Silverton structure $M^{IV}(MoO^t_2O^b_{1/2}O^i_{3/3})_{12}^{8-} = M^{IV}Mo_{12}O_{42}^{8-}$ (M = Ce, Th, U) in which the central metal forms an MO_{12} icosahedron with the interior oxygen atoms. The 12-coordinate central metal is a large tetravalent lanthanide or actinide with accessible f orbitals.

Binodal Orbital Aromaticity

Aromaticity may be regarded as stabilization through electron delocalization by overlapping atomic orbitals on adjacent atoms. Previous papers[14,19-21] have classified aromaticity by the dimensionality of the graph representing the orbital overlap. An alternative approach classifies aromaticity by the nodality of the atomic orbitals participating in the delocalization (Table I). Thus the three-dimensional aromaticity in the deltahedral boranes $B_nH_n^{2-}$ ($6 \le n \le 12$) involves overlap of the radial anodal sp hybrids in the center of the deltahedron[11-14] and thus may be regarded as anodal orbital aromaticity. Similarly, the two-dimensional aromaticity in the planar polygonal hydrocarbons $C_nH_n^{(n-6)-}$ ($5 \le n \le 7$) such as benzene (n = 6) involves overlap of the uninodal p orbitals on each vertex carbon atom and thus may be regarded as uninodal orbital aromaticity. The aromaticity in the type I polyoxometalates such as octahedral $M_6O_{19}^{n-}$ and cuboctahedral $XM_{12}O_{40}^{n-}$ is three-dimensional, involving overlap of binodal d orbitals, and thus may be regarded as binodal orbital aromaticity. Such binodal orbital aromaticity is much weaker than anodal or uninodal orbital aromaticity since the metal atom vertices furnishing the orbitals participating in the delocalization are much further apart, being separated by M–O–M bridges rather than M–M bonds. The Hückel treatment of aromatic delocalization may be related to the spectrum of the graph G describing the overlap topology of the relevant atomic orbitals by the relationship[11-14,22-24]

$$E_k = \frac{\alpha + x_k\beta}{1 + x_k S} \tag{3}$$

In eq 3, x_k is an eigenvalue of G, E_k is the corresponding molecular orbital energy parameter, and α and β are the standard Hückel parameters. Positive and negative eigenvalues x_k correspond to bonding and antibonding orbitals, respectively. The weakness of the binodal orbital aromaticity in type I polyoxometalates translates into a low β parameter in eq 3.

Figure 3 shows the spectra of the octahedron and the cuboctahedron, which are the basic building blocks of the delocalized polyoxometalates $M_6O_{19}^{n-}$ and $XM_{12}O_{40}^{n-}$, respectively. The octahedron is thus seen to have the eigenvalues +4, 0, and −2 with degeneracies 1, 3, and 2, respectively, whereas the cuboctahedron has the eigenvalues +4, +2, 0, and −2 with degeneracies 1, 3, 3, and 5, respectively. The most positive eigenvalue or *principal eigenvalue*[25] of +4 for both polyhedra arises from the fact that each polyhedron corresponds to a regular graph of valence 4.[26] This highly positive principal eigenvalue corresponds to a highly bonding molecular orbital, which can accommodate the first two electrons upon reduction of the initially d^0 polyoxometalates of the types $M_6O_{19}^{n-}$ and $XM_{12}O_{40}^{n-}$. The reported diamagnetism[27,28] of the two-electron reduction products of the $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, and $[(H_2)W_{12}O_{40}]^{6-}$ anions is in accord with the two electrons being paired in this lowest lying molecular orbital. Thus the overlap of the otherwise nonbonding d_{xy} orbitals in the $M_6O_{19}^{n-}$ and $XM_{12}O_{40}^{n-}$ d^0 early-transition-metal polyoxometalates creates

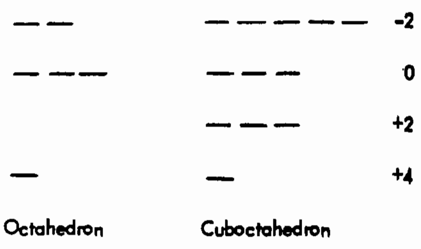


Figure 3. Spectra of the octahedron and cuboctahedron.

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a low-lying bonding molecular orbital which can accommodate two electrons, thereby facilitating reduction of polyoxometalates of these types.

The spectrum of the cutoctahedron corresponding to the topology of the $XM_{12}O_{40}{}^{n-}$ derivatives has not only the single +4 eigenvalue but also the triply degenerate +2 eigenvalue corresponding to three additional bonding orbitals which can accommodate an additional six electrons. For this reason eight-electron reduction of the $XM_{12}O_{40}{}^{n-}$ d^0 early-transition-metal derivatives might be expected to be favorable since eight electrons are required to fill the bonding orbitals of the cuboctahedron, i.e., the four bonding orbitals corresponding to the positive eigenvalues +4 and +2. However, experimental evidence indicates that when six electrons are added to a sufficiently stable $XW_{12}O_{40}$ derivative, rearrangement occurs to a more localized $XW_9{}^{VI}W_3{}^{IV}O_{40}{}^{n-}$ structure in which the three W^{IV} atoms form a bonded triangle[29] with W–W = 2.50 Å similar to the W–W of 2.51 Å in the tungsten(IV) complex[30] $[W_3O_4F_9]^{5-}$. This bonded W_3 triangle corresponds to one of the triangular faces of the W_{12} macrocuboctahedron in $XW_{12}O_{40}{}^{n-}$. This rearrangement of the $XW_{12}O_{40}{}^{n-}$ derivatives to a more localized structure upon six-electron reduction is an indication of the weakness of the binodal orbital aromaticity in these polyoxometalates corresponding to a low value for β in eq 3. Thus a configuration with three W–W localized two-center-two-electron σ bonds is more stable than a delocalized configuration with six electrons in the bonding molecular orbitals generated by binodal orbital overlap; i.e., $\beta_\sigma \gg \beta_d$ where $\beta_\sigma = (\Delta E_{\text{bonding}} - \Delta E_{\text{antibonding}})/2$ for a W–W σ bond and β_d is the energy unit in eq 3 from overlap of the d_{xy} orbitals on the 12 tungsten atoms.

The concept of binodal aromaticity in reduced early-transition-metal polyoxometalates may be related to their classification as mixed-valence compounds. Robin and Day[31] classify mixed-valence compounds into the following three classes: class I, fully localized corresponding to an insulator in an infinite system; class II, partially delocalized corresponding to a semiconductor in an infinite system; class III, completely delocalized corresponding to a metal in an infinite system. ESR studies on the one-electron reduced polyoxometalates $M_6O_{19}{}^{n-}$ and $XM_{12}O_{40}{}^{n-}$ suggest class II mixed-valence species.[15,32,33] Although such species are delocalized at accessible temperatures, they behave as localized systems at sufficiently low temperatures similar to semiconductors.[15,32,33] This is in accord with the much smaller overlap (i.e., lower β in eq 3) of the metal d_{xy} orbitals associated with binodal orbital aromaticity as compared with the boron sp hybrid anodal internal orbitals in the deltahedral boranes $B_nH_n{}^{2-}$ or the carbon uninodal p orbitals in benzene.

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Ab Initio Study of the Coordination Modes of Tetrahydroborato Ligands: The High-Spin Complex $V(BH_4)_3(PH_3)_2$

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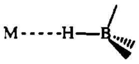
Received February 14, 1991

The structure of the high-spin complex d^2-$V(BH_4)_3(PH_3)_2$ is studied by means of ab initio UHF calculations including correlation energy at the MP2 level. This complex is used as a model for the complex $V(BH_4)_3(PMe_3)_2$ recently characterized by Girolami and co-workers, in which the three tetrahydroborato ligands are coordinated in an η^2 fashion. Thirteen structures which differ in the coordination mode of the $BH_4{}^-$ ligands (η^1, η^2, or η^3) are optimized by an analytical gradient method. In agreement with experimental data, the (η^2,η^2,η^2) structure, where all bridging hydrogens are lying in the plane of the boron atoms, is found to be the most stable. This result, together with the energy ordering of the other structures, is rationalized both through usual electron counting and through molecular orbital analysis. Average bond lengths are given for each coordination mode, and the mechanisms for exchange between bridging and terminal hydrogens in the $BH_4{}^-$ group are briefly discussed.

In recent years, there has been a considerable interest in transition-metal tetrahydroborato complexes. Several complexes have been synthesized and characterized by X-ray[1-20] or neutron diffraction[21-23] or by IR and NMR spectroscopy.[24-33] Besides their importance in homogeneous catalysis, these complexes are of great interest because three modes of coordination of the $BH_4{}^-$ moiety have been proved, depending on the number of bridging hydrogens between the metal and boron atoms. These coordination modes are called η^1, η^2, and η^3 (**1–3**).



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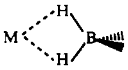
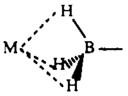


2



3

Until the 1980s, the coordination mode was mostly determined on the basis of IR data. However, this method may be imprecise, since the B–H stretching vibrations cannot be uniquely related to one coordination mode.[7b,23] X-ray diffraction studies may also be imprecise because of the hazardous location of the H atoms

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