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Structure and Bonding in [M_6X_8] Units of Nonmetallic Transition Metal Cluster Compounds*

W. BRONGER,* J. FLEISCHHAUER,† H. MARZI,† G. RAABE,†
W. SCHLEKER,† AND T. SCHUSTER*

**Institut für Anorganische Chemie der Technischen Hochschule Aachen and*
†Lehr- und Forschungsgebiet Theoretische Chemie der RWTH Aachen,
Professor-Pirlet-Strasse 1, 5100 Aachen, Federal Republic of Germany

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A simple quantum mechanical method, based on the Wolfsberg–Helmholtz approximation, has been applied to some nonmetallic 4*d* and 5*d* transition metal cluster compounds containing [M_6X_8] units. Our aim was to calculate bonding energies of M_6 clusters as a function of electronic configuration and symmetry. Energy sequences of clusters containing elements adjacent to each other in the periodic table are discussed, in particular, niobium and molybdenum as well as tungsten and rhenium. Compared with experimentally well-characterized compounds, the computional results show good qualitative agreement. So the occurrence of M_6 clusters with O_h or lower symmetry can be explained by electronic effects. © 1987 Academic Press, Inc.

Introduction

Among the transition metal cluster compounds those species containing M_6 units of ideal or distorted octahedral symmetry have attracted a considerable amount of interest. Our contributions regarding these solids were synthesis and characterization of compounds containing Re_6 units, which had been observed for the first time in ternary chalcogenides (*1–7*). Crystal structure determinations revealed framework structures in which [Re_6X_8] units are linked three-dimensionally via X or X_2 groups, respectively. The holes in this framework are occupied by alkali or alkaline earth metal ions to such a degree that an oxidation state of +3 results for the rhenium atoms. This leads to an evidently stable configuration with 24 valence electrons for each Re_6 octahedron.

The compound $Li_4Re_6S_{11}$ may be an example (*7*). The structure of this ternary sulfide is characterized by a $\{[Re_6S_8]S_{6/2}\}^{4-}$ framework, in which the Re_6 octahedra, enclosed by S_8 cubes, are linked three-dimensionally by sulfur bridges. The framework of $Li_4Re_6S_{11}$ with 24 electrons per cluster corresponds to those in Nb_6I_{11} (*8–10*) with only 19 valence electrons per M_6 unit and in $Mo_6Cl_{10}Se$ with again 24 electrons (*11*). All three compounds crystallize in structures with space group *Pccn*. Although the atomic parameters of corresponding positions are rather similar, closer examination of the interatomic distances reveals striking differences between the rhenium and the molybdenum compounds,

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on the one hand, and the niobium-containing solid, on the other hand. While in the case of the rhenium and molybdenum compounds the M_6 units form almost regular octahedra, a significant deviation from O_h symmetry was found for the Nb_6 clusters. It seems reasonable to assume that the distortion, for example in the case of Nb_6I_{11}, is due to the electronic structure of this compound rather than to the linkage of the M_6 octahedra, which is obviously identical in all three structures discussed.

If other $[M_6X_8]$ compounds ($M \hat{=}$ Re, Mo, or Nb) that are comparable from a structural point of view are included, these assumptions are strongly supported. Although in the case of 24 valence electrons the M_6 units constitute almost regular octahedra, marked deviations from regularity occur in the case of clusters with a smaller number of valence electrons. Naturally such a simple model cannot be used without modification for $[M_6X_8]$ compounds with metallic properties. In such cases calculation of the number of electrons per M_6 unit via oxidation numbers makes no sense.

In this paper we discuss the symmetry of M_6 units in terms of their electronic structure. Our argumentation is based on the assumption that the electronic structure of $[M_6X_8]$ clusters can be characterized by means of molecular orbital (MO) calculations of isolated units even if these are interconnected in the solid state. The model of isolated units has been extended by several authors, e.g., (*12–14*), in order to understand features of Chevrel phases like metallic properties or even superconductivity. Nevertheless, we used the simple model of Cotton and Haas (*15*) to calculate the relative total energies of M_6 units for different symmetries.

As can be seen from the following discussion, such a simple treatment, despite its severe approximations, leads to results that qualitatively fit nicely a lot of experimental findings when applied to a group of structurally very similar compounds. To judge the results it is necessary to discuss energy sequences of M_6 clusters of adjacent elements in the periodic table relative to each other. For this reason we confine ourselves to the following section of the periodic table:

Nb Mo
W Re

Computational Method

As mentioned, the molecular orbitals of the M_6 units have been calculated using the method of Cotton and Haas (*15*). Starting from a basis consisting of 24 metal *d* atomic orbitals we formed a set of symmetry-adapted linear combinations (for choice of the coordinate system, see Fig. 1). We therefore performed our calculations using a basis consisting of one a_{1g}, one a_{2g}, two sets of e_g, one set of t_{1g}, one set of t_{2g}, and two sets of t_{1u} and t_{2u} functions. The calculated orbital energies (ε) relative to the diagonal elements of the **H** matrix

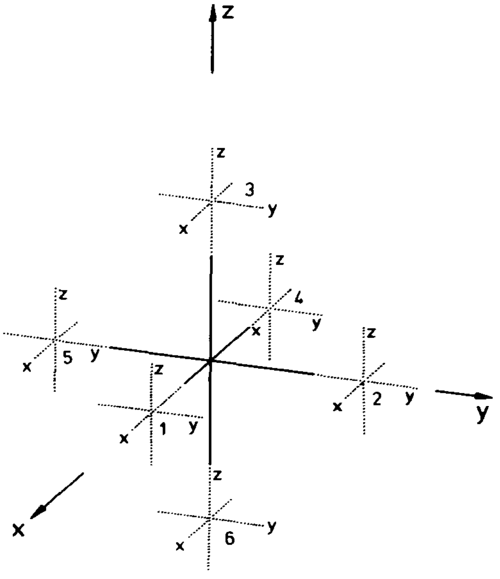

FIG. 1. Coordinate system used.

$[E_{\mathrm{rel}} = (\varepsilon - H_{dd})/|H_{dd}|$, with $H_{dd} = \langle nd|\hat{H}|nd\rangle]$ for ideal octahedral symmetry and principal quantum numbers $n = 4$ (4*d* functions) and $n = 5$ (5*d* functions) are plotted in Figs. 2a and 3a as functions of $p = \xi \cdot R$, where ξ is Slater's exponent (*16*) and R the distance between nearest neighbors in atomic length units. R is calculated according to Pauling's equation $[d(n) = d(1) - 0.60 \log n]$ which gives a good approximation to experimentally determined distances (*17*). In the case of the 4*d* metals with effective principal quantum number $n_{\mathrm{eff}} = 3.7$, the energy curves (Fig. 2a) have not been calculated directly, but were derived from those for effective principal quantum numbers $n_{\mathrm{eff}} = 3.0$ (3*d* functions) and $n_{\mathrm{eff}} = 4.0$ (5*d* functions) by interpolation. We checked the orbital energies calculated in this way by approximating the *d* functions for $n_{\mathrm{eff}} = 3.7$ as a linear combination of those for $n_{\mathrm{eff}} = 3.0$ and $n_{\mathrm{eff}} = 4.0$. The superposition coefficients were obtained with a least-squares procedure. The one-electron energies calculated by this method widely agree with those from the interpolation procedure. In the following calculations, therefore, we used only interpolated values.

Beside calculations of molecular orbitals of M_6 units with O_h symmetry, calculations of analogous systems of lower symmetry also have been carried out. Representative examples are given in Figs. 2b and 3b where the orbital energies of the clusters with D_{3d} symmetry (shortening of a threefold axis by 5%) for principal quantum numbers 4 and 5 are plotted as a function of p. In addition, we calculated the one-electron energies for clusters with D_3 symmetry (shortening of a threefold axis, combined with an oppositely directed torsion of the two triangular planes normal to this axis), D_{2h} symmetry (derived from regular octahedral symmetry by oppositely directed

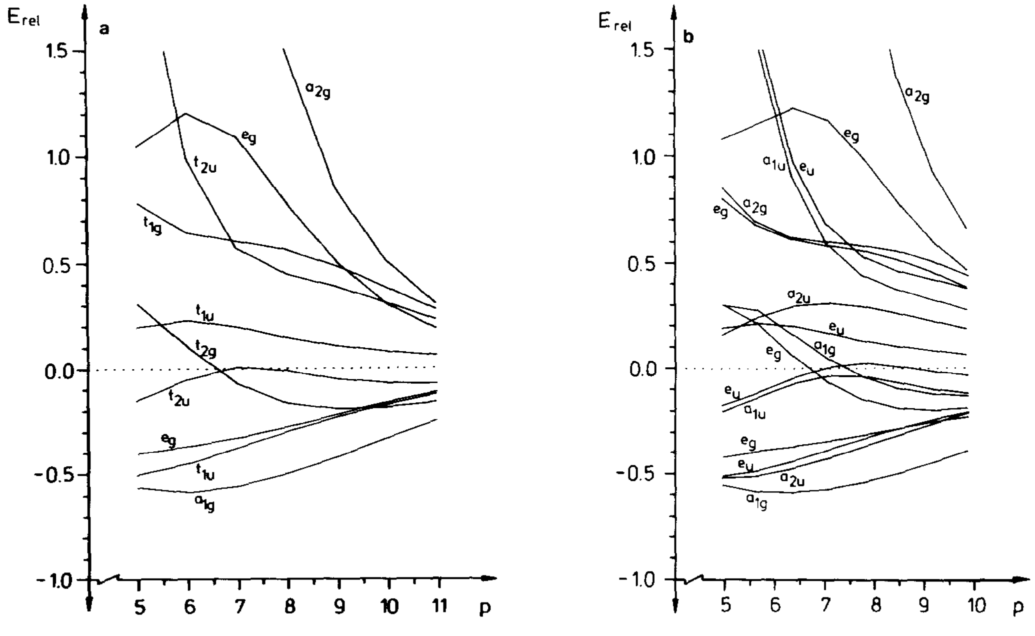

FIG. 2. (a) Relative orbital energies (E_{rel}) of an undistorted octahedral M_6 cluster as a function of p. Principal quantum number $n = 4$; effective quantum number $n_{\mathrm{eff}} = 3.7$. (b) Relative orbital energies (E_{rel}) of a M_6 cluster with D_{3d} symmetry as a function of p. Principal quantum number $n = 4$, effective quantum number $n_{\mathrm{eff}} = 3.7$.

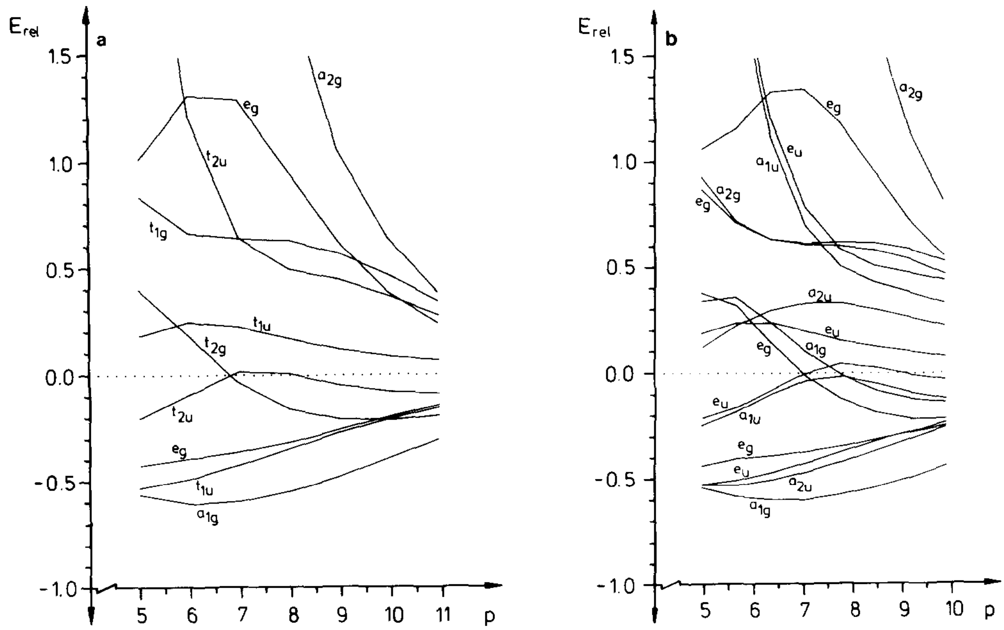

FIG. 3. (a) Relative orbital energies (E_{rel}) of an undistorted octahedral M_6 cluster as a function of p. Principal quantum number $n = 5$; effective quantum number $n_{\text{eff}} = 4$. (b) Relative orbital energies of a M_6 cluster with D_{3d} symmetry as a function of p. Principal quantum number $n = 5$; effective quantum number $n_{\text{eff}} = 4$.

TABLE I

DEPENDENCE OF RELATIVE TOTAL ENERGIES ($E_{\text{rel}}^{\text{total}}$) OF M_6 CLUSTERS WITH N ELECTRONS PER CLUSTER ON p FOR DIFFERENT SYMMETRIES

N	p	O_h	D_{3d}	D_3(TS)	D_3(T)	C_{2h}	C_1
Nb 18	6.21	5.70	5.97	6.02	5.75	5.70	6.01
Nb 19	6.07	5.70	5.94	5.98	5.74	5.73	5.98
Nb 24	5.42	5.37	5.59	5.65	5.41	5.36	5.66
Mo 18	7.41	5.13	5.19	5.23	5.12	5.11	5.22
Mo 24	6.56	5.14	5.10	5.08	5.08	5.13	5.07
Tc 18	8.65	4.52	4.74	4.74	4.50	4.51	4.75
Tc 24	7.73	5.03	5.04	4.99	4.97	5.02	5.00
Ru 24	8.79	4.69	4.83	4.76	4.63	4.68	4.77
Rh 24	10.1	3.82	4.17	4.12	3.78	3.81	4.13
Ta 18	5.79	6.45	6.76	6.76	6.48	6.45	6.76
Ta 24	5.47	5.42	5.73	5.83	5.50	5.41	5.85
W 18	6.93	5.33	5.52	5.66	5.47	5.33	5.66
W 22	6.36	5.38	5.60	5.67	5.43	5.44	5.62
W 24	6.12	5.12	5.13	5.24	5.10	5.13	5.21
Re 18	8.11	5.31	5.34	5.36	5.27	5.29	5.37
Re 24	7.24	5.27	5.23	5.19	5.21	5.26	5.20
Os 24	8.29	5.28	5.24	5.16	5.21	5.27	5.19
Ir 24	9.51	4.83	5.03	4.95	4.76	4.82	4.96

Note. $T \hat{=}$ torsion of the two angular planes normal to the threefold axis. $S \hat{=}$ shortening of the threefold axis by 5%.

displacement of two apical atoms parallel to the equatorial plane), and C_1 symmetry (generated by combination of the preceding distortions).

The relative total energies ($E_{\text{rel}}^{\text{total}}$) in each case were calculated by summation over the products of the eigenvalues of the occupied orbitals and their occupation numbers. The results for different clusters and different numbers of valence electrons are collected in Table I.

Discussion

The relative orbital energies for $n = 4$, which have been plotted as functions of p in Figs. 2a and b for O_h and D_{3d} symmetry, chosen as examples, lead to the following conclusion: For values of p smaller than ~6.5, eighteen electrons can occupy bonding levels in the case of O_h and D_{3d} clusters, whereas the same is true for 24 electrons in the range $p > 8$.

For metals with principal quantum number $n = 5$, the corresponding values of p are somewhat higher (cf. Figs. 3a and b).

To achieve better insight, it is useful to compare the relative total energies in Figs. 4a and b (cf. also Table I). For $n = 4$ and values of p smaller than about 7, M_6 clusters with 24 electrons are less favorable

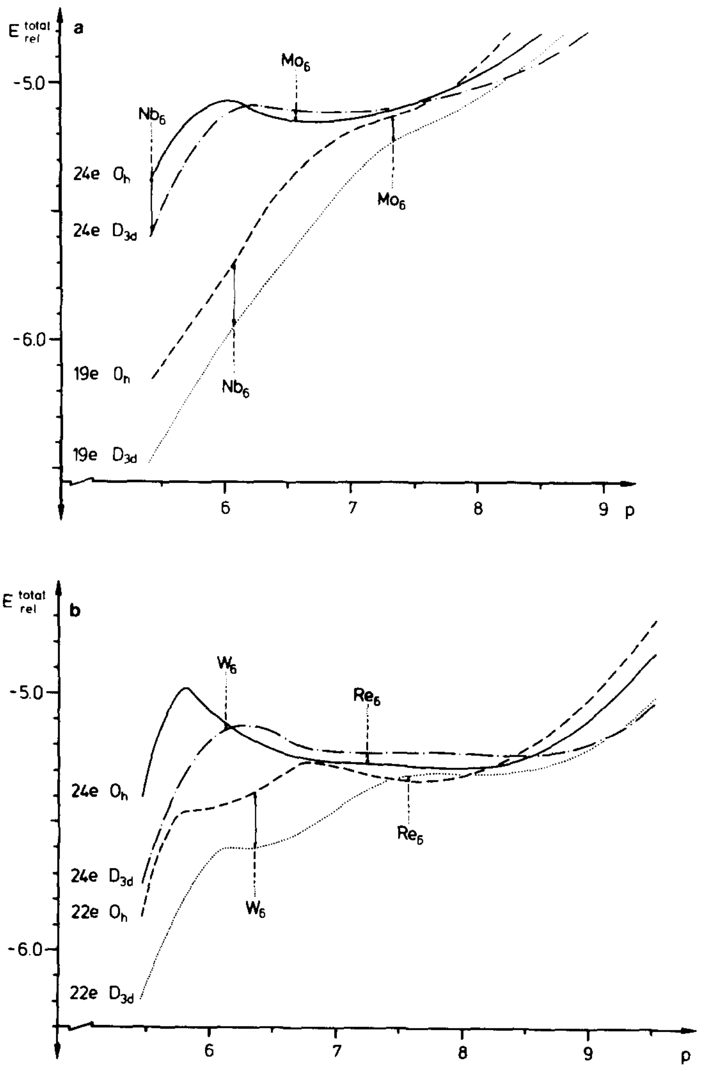

FIG. 4. (a) Relative total energies (E_{rel}^{total}) of M_6 clusters with O_h and D_{3d} symmetry containing 19 and 24 electrons as a function of p. Principal quantum number $n = 4$; effective quantum number $n_{eff} = 3.7$. The curves for systems with 19 and 24 electrons have been chosen because Mo_6 and Nb_6 clusters with 24 and 19 electrons, respectively, are compared in the text. (b) Relative total energies (E_{rel}^{total}) of M_6 clusters with 22 and 24 electrons as a function of p. Principal quantum number $n = 5$; effective quantum number $n_{eff} = 4$. Here the curves for systems with 22 and 24 electrons have been chosen because in the cases of Re_6 and W_6, clusters with 24 electrons have been characterized experimentally and, moreover, for W at least one system with 22 valence electrons is known.

from an energetical point of view than those with a smaller number of valence electrons. For p values between 6.5 and 8 the relative total energies of clusters with 24 electrons depend only weakly on p. The reason lies in the fact that within this range of p values the functional dependence on p of the lower occupied orbitals opposes that of the higher ones so that, on the whole, the relative total energy almost remains constant (cf. Figs. 2a and b). Available experimental data coincide qualitatively with our computational results. So, for example, the data in Table I and the plot in Fig. 4a clearly show that in the case of Nb_6 a cluster containing fewer than 24 valence electrons should be preferred and that, moreover, an additional distortion of the O_h symmetry is expected to cause an additional lowering of the energy.

The structure determinations of compounds like Nb_6I_{11} (*8–10*), HNb_6I_{11} (*10, 18*), and $CsNb_6I_{11}$ (*19*) confirm our calculated data. For the Nb_6 unit in Nb_6I_{11}, containing 19 valence electrons, for example, a distortion similar to that leading to D_3 symmetry has been found. According to the data in Table I it is just such a deviation from octahedral symmetry that should cause a significant decrease in the bonding energy. Things are different for the Mo_6 clusters. As can be seen from Table I for the species containing 24 valence electrons, deviations from regularity are not expected to decrease the relative total energy; however, this might be the case for a smaller number of electrons. Accordingly, all known Mo_6 clusters with 24 valence electrons were found to be undistorted octahedra, whereas deviations from octahedral symmetry have been observed for clusters with fewer electrons (*20–22*). Among the last-mentioned compounds, however, some show metallic properties and therefore cannot be treated by means of our simple model (*12–14*).

Comparing M_6 clusters from tungsten and rhenium ($n = 5$) leads to a quite similar situation (cf. Table I, Figs. 4a and b) shifted one group to the right (diagonal relationship). The fact that exclusively almost regular diamagnetic Re_6 clusters with 24 valence electrons have been found until today (*1–7, 23*) can easily be understood in terms of our computational results.

Our calculations on W_6 clusters revealed a situation comparable to that for Nb_6 clusters. Here, M_6 units with fewer than 24 valence electrons should be possible. In such compounds moreover, deviations from O_h symmetry can be expected. To our knowledge several structures containing W_6 clusters with 24 electrons have recently been determined at a high level of accuracy (*24, 25*). All were found to consist of almost undistorted tungsten octahedra. On the other hand, only one compound is described in which simple electron counting leads to a number of 22 electrons per cluster ($W_6Br_{16} \mathrel{\hat{=}} [W_6Br_8]Br_4[Br_4]_{2/2}$ (*26*)). In the latter, a deviation from O_h symmetry can be expected. But for a final discussion the structural data of W_6Br_{16} have to be refined.

Although our results are in good agreement with experimental data, it should be mentioned that regarding the symmetry of the highest filled molecular orbital of the M_6 unit they are in conflict with results obtained using other more elaborate methods (*12–14, 27*). This result strongly depends not only on the interatomic distances and angles in the structures under discussion, but on the value of the nd orbital exponent too. So, for example, in (*27*) the value of 1.3 for the Mo $4d$ orbital exponent used by us leads to a HOMO of t_{2u} symmetry for the M_6 unit, too.

A lower limit of 20 electrons per M_6 unit, as assumed in the case of the Chevrel phases, might be in accordance with a highest occupied molecular orbital of e_g symmetry for these units. This limit, however, clearly does not hold for the compounds examined by us (cf. Nb_6I_{11}).

Acknowledgment

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