COMPARATIVE QUANTUM CHEMICAL STUDY OF THE BINUCLEAR CLUSTERS OF Tc AND Mo

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The comparative studies of $[Tc_2Cl_8]^{n-}$ (n=2,3,4) clusters with D_{4h} and D_{4d} symmetry and $[Mo_2Cl_8]^{m-}$ (m=4,5) clusters with D_{4d} symmetry in approximation of X_α -scattered waves method have been carried out. Despite the results being present in literature for a long time, for example [1-3], and review [4], the necessity of these calculations is called by contradictory interpretation of Tc-Tc bond shortening for lower Tc oxidation states, on one hand, and by the absence of the experimental proofs about existence of similar Mo complexes, on the other hand.

The peculiarity of our calculations in comparison with above mentioned [1,2] is the choice of atomic spheres' radii. We considered these complexes from the point of view of fragments $[MCl_4]^{q-}$ (M=Tc,Mo) interaction. Extensive practice of such mononuclear fragments [5,6] studies has shown satisfactory results in the model of touching atomic spheres with radii, which minimized the change of electronic potential at spherical bound. We have kept this criterion in binuclear model in relation to the touching spheres of metal and ligand atoms, thus the overlapping of metal atoms spheres was defined by the length of M-M bond. The radii satisfying these conditions appeared to be: R_{Tc}=0.127-0.131nm, R_{Cl}=0.108-0.104nm for Tc clusters and R_{Mo}=0.127-0.131nm, R_{Cl}=0.108-0.104nm for Mo clusters. Test calculations with different atomic spheres radii ratio have shown, that the correct behavior of the nonbonding quasiatomic energy levels of Cl during the variation of the M-M bond length is found only with our radii set. The shift of these levels did not exceed 0,1 eV from average value and corresponded to the redistribution of electronic density.

Our calculations agreed fully with the results [1-3] for the same cluster geometry. In D_{4h} clusters additional electrons (n>2, m>4) occupied antibonding (δ-type orbital, however, in D_{4d} clusters under the same conditions HOMO does not participate in formation of M-M bond.

In this work the length of M-M bond was varied to evaluate its influence on the electronic structure characteristics. In connection with unsatisfactory quantitative evaluation of the total energy in the scattered waves method and simultaneously with the exact calculation of the energy spectrum, we used the model of interatomic interaction potential curve as the sum of one-electron energies of the occupied valence states. Furthermore, the use of the orbital force characteristics of MO, defined as the ratio of MO energy change to M-M bond length change, seems to be rather reliable (Table 1).

Table 1. The summary of total orbital forces (mdyne) for studied clusters

n	$[Tc_2Cl_8]^{n-}$ D_{4h}	$[Tc_2Cl_8]^{n-}$ D_{4d}	m	$[Mo_2Cl_8]^{m-}$ D_{4h}
2	8.24	8.03	4	4.32
3	7.01	6.74	5	2.98
4	4.86	6.00		