Electronic Structure of Octachlorodimolybdate(II)

By JOE G. NORMAN, JUN.* and HAROLD J. KOLARI

(*Department of Chemistry, University of Washington, Seattle, Washington* 98195, *U.S.A.*)

Summary The nature of metal–metal and metal–chlorine bonding in $Mo_2Cl_8^{4-}$ as predicted by a first-principles, all-electron, self-consistent-field calculation is discussed.

THE strongest known metal–metal bonds among the transition elements occur in a series of dinuclear chromium(II), molybdenum(II), and rhenium(III) complexes where metal–

metal distances† up to 0·7 Å shorter than expected for single bonds have been found crystallographically.[1] Among the simplest of these molecules structurally are $Mo_2Cl_8{}^{4-}$ and $Re_2Cl_8{}^{2-}$. Symmetry arguments and crude calculations for these and similar species indicate a total metal–metal bond order of four, made up from σ-, two π-, and δ-type overlaps.[2]

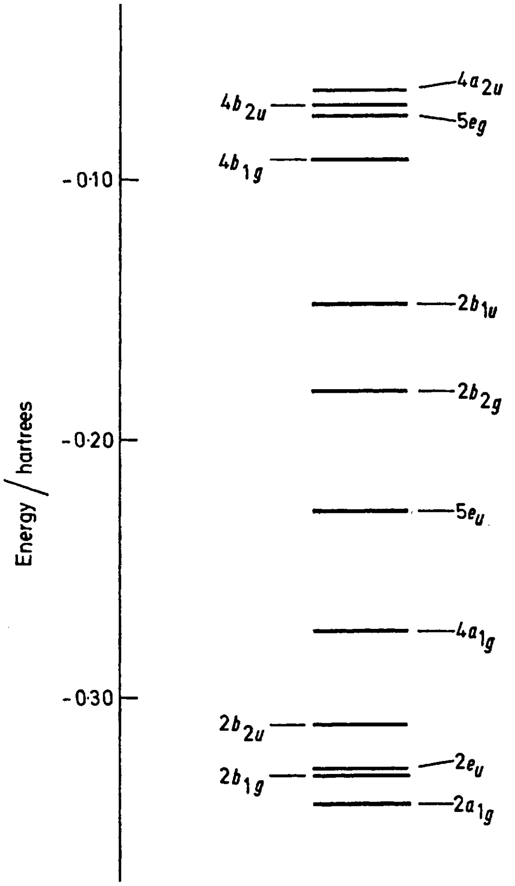

FIGURE. Valence energy levels of $Mo_2Cl_8{}^{4-}$ with appreciable molybdenum character.

We report here a first-principles calculation of the electronic structure of octachlorodimolybdate(II), $Mo_2Cl_8{}^{4-}$, using the Xα scattered-wave (XαSW) method. This method has been thoroughly reviewed;[3–5] briefly, it is a self-consistent-field technique which yields one-electron eigenvalues in quite good agreement with experiment, being equal or superior in this respect to the best *ab initio* calculations, but which requires much less computer time than even minimal-basis set Hartree-Fock treatments when applied to large molecules. $Mo_2Cl_8{}^{4-}$ was calculated in idealized D_{4h} symmetry; the bond parameters Mo–Mo = 2·14 Å, Mo–Cl = 2·45 Å, and $\angle$ (Mo–Mo–Cl) = 105° are averages of crystallographic values.[6] The complete one-electron Schrödinger equation was solved directly for all valence and core eigenvalues by Johnson's scattered-wave technique[3] for a potential made fully self-consistent by iteration and including Slater's Xα approximation to exchange correlation.[7] The potential of a spherical shell of four units positive charge surrounding the anion was included to approximate the stabilizing effect of a crystal lattice.

The resulting valence energy levels having more than 20% molybdenum character are shown in the Figure. The highest occupied level among them, and for the molecule as a whole, is $2b_{2g}$. Not shown are nineteen closely-spaced predominantly chlorine $3p$ levels in the range $-0·26$ to $-0·34$ hartrees (with molybdenum character averaging 4% and never exceeding 14%) and eight nearly pure chlorine $3s$ levels in the range $-0·71$ to $-0·73$ hartrees. The following conclusions can be made from these results.

(1) The levels predominantly associated with metal–metal bonding are occupied $4a_{1g}$, $5e_u$, and $2b_{2g}$ (σ-, π-, and δ-type overlaps, respectively) and their antibonding counterparts, unoccupied $4a_{2u}$, $5e_g$, and $2b_{1u}$. The ordering and location of these levels agrees completely with the original qualitative proposals of Cotton and subsequent semi-empirical calculations[2] on $Re_2Cl_8{}^{2-}$. The only discrepancy with the qualitative picture is the absence here of two non-bonding a_{1g} and a_{2u} levels previously thought to be near $2b_{1u}$ in energy. Such levels would be expected in the valence region only if $5s$ and $5p_z$ functions were important valence orbitals for molybdenum; in fact, $5d$ functions are the most predominant source of molybdenum contribution to every state having appreciable metal character.

(2) The six metal–metal levels average 85% molybdenum character, $5e_u$ having the lowest value of 70%. Mixing between metal–metal and metal–ligand bonding is thus much smaller than predicted by both XαSW[8] and semi-empirical[9] calculations for the weaker metal–metal bond in $Mn_2(CO)_{10}$. The metal character of $4a_{1g}$ and $4a_{2u}$ is about 85% $5d_{z^2}$; of $5e_u$ and $5e_g$, about 95%, $5d_{xz,yz}$; of $2b_{2g}$ and $2b_{1u}$, pure $5d_{xy}$ by symmetry. The minor metal contributors to $4a_{1g}$ and $4a_{2u}$ are $5s$ and $5p_z$, respectively.

(3) The molybdenum $5d_{x^2-y^2}$ orbital is used chiefly in Mo–Cl bonding and contributes heavily to the $2b_{1g}$, $2b_{2u}$, $4b_{1g}$, and $4b_{2u}$ levels, which form two classic metal-ligand bonding–antibonding pairs. The lower two levels have about 70% chlorine and the upper two 75% molybdenum character. The remaining important Mo–Cl bonding levels, $2a_{1g}$ and $2e_u$, average 65% chlorine character.

The increase in metal–metal bond lengths observed in molecules with similar structures to $Mo_2Cl_8{}^{4-}$ as one moves toward the right in a transition-metal row has been explained in terms of the qualitative MO diagram by populating antibonding orbitals and the nonbonding a_{1g} and a_{2u} orbitals absent from our quantitative description.[2,10] We feel that conclusions drawn on this basis are still largely valid, since the $4b_{1g}$ and $4b_{2u}$ orbitals can fill much the same role as the hypothetical a_{1g} and a_{2u} set, in the sense that

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† Units used in this paper, in terms of SI base-units, are 1 Å = 10^{-10} m, 1° = 0·01745 rad, and 1 hartree = $4·359 \times 10^{-18}$ J.

their population should not greatly affect the metal–metal bond strength. Further calculations on dinuclear complexes containing strong metal–metal bonds are in progress to assess the general validity of the energy-level scheme found for $Mo_2Cl_8^{4-}$.

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