Direct Evidence for the Quadruple Metal–Metal Bond in the Octachlorodimolybdenum(II) Ion, $[Mo_2Cl_8]^{4-}$, using *X*-Ray Emission Spectroscopy

By DEREK E. HAYCOCK and DAVID S. URCH*
(*Chemistry Department, Queen Mary College, Mile End Road, London* E1 4NS)
and C. DAVID GARNER, IAN H. HILLIER, and GEORGE R. MITCHESON
(*Chemistry Department, Manchester University, Manchester* M13 9PL)

Summary Analysis of the $MoL\beta_{2,15}$ ($4d$–$2p$) *X*-ray emission peak from $[Mo_2Cl_8]^{4-}$ shows the presence of three molecular orbital energy levels, contributing to the Mo–Mo quadruple bond, together with a peak at a higher binding energy which is attributed to Mo–Cl bonding orbitals.

X-RAY crystallographic studies have established[1] that the anion of the salt $K_4[Mo_2Cl_8],2H_2O$ consists of an approximately cubic array of eight chlorine atoms, within which a pair of molybdenum atoms are centred along one four-fold axis. The short approach of these metal atoms [2·138(4) Å] together with the eclipsed conformation of this unit, are taken to be indicative of a quadruple $(\delta_{xy})^2$ $(\pi_{xz,yz})^4$ $(\sigma_{z2})^2$ metal–metal bond. Polarised single-crystal absorption spectroscopic studies[3] are consistent with the lowest energy transition for this anion corresponding to a $\delta \rightarrow \delta^*$ promotion. Photoelectron (p.e.) spectroscopy has been successfully applied to probe the electronic structure of several $Mo_2(O_2CR)_4$ compounds[4] and the results are consistent with a $\delta < \pi,\sigma$ binding energy sequence for the metal–metal orbitals.[5]

We have obtained *X*-ray emission spectra,[6] using a Philips PW1410 *X*-ray spectrometer, in which $K_4[Mo_2Cl_8],2H_2O$ was irradiated with *X*-rays from a chromium anode *X*-ray tube. The resolving power of the spectrometer was increased to over 1000 using additional collimation and a silicon (111) defect-free diffracting crystal.[7] The measurement of the $MoL\beta_{2\cdot15}$ emission, which arises from the metal's $4d \rightarrow 2p_{3/2}$ electronic transitions, allows the determination of the relative binding energies of those valence orbitals having substantial molybdenum $4d$ character.[8] The resulting spectrum is shown in the Figure. Each data point represents the number of counts observed during a 700 s period. The experimental line width (principally determined by collimator and core state life-time functions) for the molybdenum $L\alpha_{1,2}$ ($3d \rightarrow 2p_{3/2}$) peak at 2293 eV was found to be 3·1 eV. Since the $MoL\beta_{2,15}$ is of a similar energy, arises from relaxation to the same core state, and is observed under similar experimental conditions, it is reasonable to

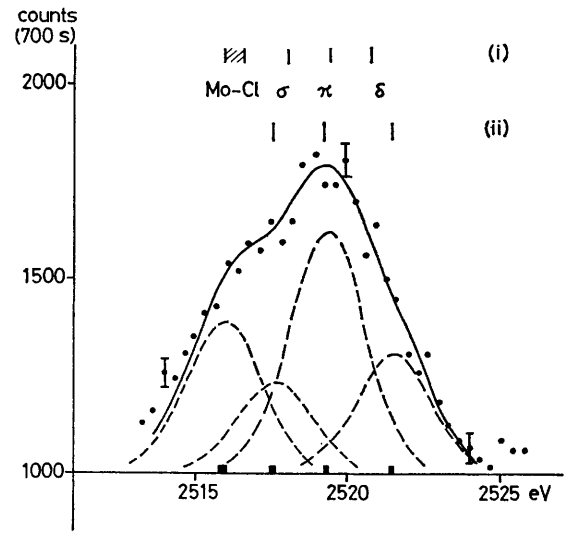

FIGURE. Dots indicate the experimental data for the Mo $L\beta_{2,15}$ *X*-ray emission from $K_4Mo_2Cl_8$. Typical error limits are shown by one standard deviation. The solid line is the summation of the four component Gaussian peaks shown – – –. The centre of each Gaussian is given by a short vertical line on the eV scale. (i) the relative positions of groups of molecular orbitals with considerable Mo $4d$ character as calculated by Norman and Kolari[10] centred on the peak at 2519·3 eV. (ii) relative positions of σ, π, and δ orbitals using the *ab. initio* results reported here for $[Mo_2F_8]^{4-}$.

assume that the line width for this peak should also be *ca.* 3·1 eV. The observed peak has a much greater breadth than this value but can be resolved into four constituent Gaussian peaks (each with a width at half-height of 3·1 eV), as shown in the Figure (relative intensities 1·3 (2521·4 eV) : 2·7 (2519·3 eV) : 1 (2517·6 eV) : 1·7 (2515·9 eV). This spectrum provides the first direct experimental evidence for the ground-state electronic structure of this ion.

The simplest explanation of this result is that the three peaks of highest energy arise from transitions from the orbitals of the quadruple metal–metal bond, namely from the δ, two π, and σ orbitals, respectively. The fourth peak at 2515·9 eV is assigned to a group of molecular orbitals, having significant molybdenum $4d_{x^2-y^2}$ and $4d_{z^2}$ character, contributing to the Mo–Cl bonds. The presence of chlorine $3p$ character in this peak is confirmed by the ClK$\beta_{1,3}$ ($3p \rightarrow 1s$) *X*-ray spectrum, aligned with the MoL$\beta_{2,15}$ spectrum using core electron binding energy measurements.[9]

This assignment of these four peaks is consistent with the eigenvalues and molybdenum character of the respective molecular orbitals, as obtained from an SCF Xα calculation[10] on $[Mo_2Cl_8]^{4-}$. The molybdenum character of the relevant molecular orbitals δ, π, σ, and Mo–Cl bonding, suggests an intensity ratio of 1·1 : 1·8 : 1 : 1·6, respectively, the calculated orbital energy separations from the δ level being 1·4, 2·7, and 4·1—4·9 eV. As a further model of the metal–metal interaction in $[Mo_2Cl_8]^{4-}$, we have performed an *ab initio* SCF-MO calculation in a near minimal basis on the hypothetical ion, $[Mo_2F_8]^{4-}$. The structure of this anion was taken to be the same as that of $[Mo_2Cl_8]^{4-}$, except that the Mo–F bond length was reduced from the Mo–Cl value by the difference between the ionic radii of F^- and Cl^-. Such a calculation yielded the separation of the π and σ orbitals from the δ orbital to be 2·2 and 3·9 eV, respectively. Although such excellent agreement with the experimental values of 2·1 and 3·8 eV is fortuitous, the close correspondence between the experimental and theoretical data suggests that a reasonably accurate description of the metal–metal and, to some extent, the metal–chlorine bonding in $[Mo_2Cl_8]^{4-}$ has now been achieved.

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