Raman Spectra and Vibrational Analysis of Molybdenum Cluster Compounds

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THE octa-μ_3-chlorohexamolybdenum(II) cation, $(Mo_6Cl_8)^{4+}$, forms several complexes[1] of the type $[(Mo_6Cl_8)X_6]^{2-}$, which has a structure[2] consisting of two concentric octahedra of Mo and X atoms, the former being enclosed by a cube of Cl atoms. The molecular point group is O_h. We have obtained the Raman spectra of the acids, $H_2[(Mo_6Cl_8)X_6],8H_2O$ where X = Cl, Br, or I, in methanol solution by means of helium (5876 and 6678 Å) and helium–neon laser (6328 Å) excitation, and the infrared spectra (700—50 cm.$^{-1}$) of the solid salts, with the results shown in the Table. Here we describe the results of a preliminary normal co-ordinate analysis based on these data, and point out some of the unusual vibrational properties of these rigid, heavy-atom clusters.

TABLE

Raman and infrared spectra of $[(Mo_6Cl_8)X_6]^{2-}$ *in cm.*$^{-1}$

X = Cl	X = Br	X = I	Assignment
	Raman (solution)		
92s, dep	60ms, dep	44s	t_{2g}
179ms, dep	134m, dep	109ms	e_g
195w, dep	195w	184mw	t_{2g}
215w, dep	216m, dep	215mw	e_g
225w		150w	?t_{2g}
236s, pol	160s, pol	117s	a_{1g}
247s, dep	249s, dep	247m	t_{2g}
310w, dep	279w, dep	247?	e_g
318vs, pol	318vs, pol	318s	a_{1g}
402vw?	356w	318?	a_{1g}
	Infrared (solid)		
221m	167s	132s	t_{1u}
247ms	232m	229m	
330s, bd	305s, bd	295m	
351m	360m, bd	357w	
232w, sh	226w, sh	325vw, sh	other features
294w, sh			

w, weak; m, medium; s, strong; sh, shoulder, bd, broad; dep, depolarized; pol, polarized.

The normal modes of the $[(Mo_6Cl_8)X_6]^{2-}$ ion span the representation in O_h:

$$3A_{1g} + 3E_g + 2T_{1g} + 4T_{2g} + A_{2u} + E_u + 5T_{1u} + 3T_{2u}.$$

Ten of these are permitted as fundamentals in the Raman spectrum ($3a_{1g} + 3e_g + 4t_{2g}$) and five in the infrared ($5t_{1u}$); the seven remaining normal modes are totally inactive. The number of observed Raman lines agrees well with the prediction and suggests that in these species the Mo–X bonds have appreciable covalent character. The infrared data agree substantially with those of other workers;[3-6] the weak supernumerary infrared features may be attributed to solid-state effects.

In view of the comparable masses of the constituent atoms, the close spacing of the vibrational energy terms, and the likely similarity of the bond-force constants, it seems probable that the symmetry co-ordinate representations will be extensively mixed in the normal modes of vibration, particularly those which are infrared active and therefore all belong to the same symmetry class (t_{1u}). For this reason we prefer to avoid the concept of "group frequencies" in these compounds and (with the exception of the very low Mo–X deformations) make no assumptions about the character of the normal modes. Our normal co-ordinate analysis justified this view.

Two of the three totally symmetric a_{1g} fundamentals (ν_1 and ν_2) are identified in the Raman spectra by their total polarization, but the third (ν_3) can only be attributed to one of the very weak lines whose states of polarization could not be determined. A rough force-constant calculation assists the assignment. A minimum of three force constants is needed to define the potential energy; these are conveniently chosen to correspond with the shortest internuclear distances in the cluster: f_M (between adjacent Mo atoms), f_C (between adjacent Mo and cage Cl atoms), and f_X (between Mo and the attached ligand X). A simple calculation by Wilson's G–F matrix method shows that one of the a_{1g} normal modes is approximately orthogonal to the other two (the relevant off-diagonal G elements being zero) and corresponds to an almost pure breathing motion of the Cl_8 cube. Accordingly, it may be identified with the polarized Raman line at 318 cm.$^{-1}$ (ν_1) which is virtually unshifted in all three compounds. The corresponding force constant f_C is 1·1 m.dyn./Å. On comparison with the usual value for *terminal* M–Cl bonds (~ 2 m.dyn./Å) this appears low, but a Cl atom in the cage experiences such a restoring force toward each of *three* equidistant Mo atoms. The bonding may therefore be viewed as a triple bridge or as a donation of an electron pair from the

Cl into a polycentric M.O. formed by the three Mo atoms in an octahedron face.[7] In the latter case the appropriate bond force constant may be found by resolving $3f_C$ in a direction perpendicular to the face centre; the resulting value is 2·1 mdyn./Å. The value of f_C is thus seen to be consistent with either description of the bonding.

The two remaining a_{1g} modes ν_2 and ν_3 are found to be completely 'mixed' vibrations, each involving both Mo–Mo and Mo–X stretching motion, whatever assignment is made for the questionable a_{1g} fundamental ν_3. However, we favour the assignment of ν_3 to a very weak line of high frequency for three reasons:

(i) The force-constant values obtained on this basis (f_M = 1·6, 1·6, and 1·4 mdyn./Å; f_X = 1·8, 1·6, and 1·3 m.dyn./Å, for X = Cl, Br, I respectively) are physically reasonable in the light of established values for metal–metal bonds[8] [f(Hg–Hg) ~2, f(Sn–Sn) ~1, and f(Re–Re) ~ 1·6mdyn./Å] and for terminal metal(II)–halogen bonds [f(M–Cl) ~ 1·8, f(M–Br) ~ 1·6, and f(M–I) ~ 1·2 mdyn./Å].

(ii) Owing to the rigidity and high symmetry of these ions, the three-parameter force field described above suffices also for a calculation of all thirteen spectroscopically active stretching fundamentals. The agreement between observed and calculated frequencies (8% r.m.s. deviation) is remarkably good in view of the crude force field employed. On this basis, the observed bands are assigned to the e_g and t_{2g} symmetry classes in the Table.

(iii) An examination of the a_{1g} normal co-ordinates for a wide range of assumed force constants shows that it is always the ***higher*** of the two 'mixed' a_{1g} vibrations ν_2 and ν_3 that is expected to be ***weak*** in the Raman spectrum. The rough estimate of the relative intensities of ν_2 and ν_3 was made by assuming that Wolkenstein's bond polarizability theory could be applied to these species. If the polarizability derivatives of the Mo–Mo and Mo–X bonds are taken to be approximately the same, then ν_3 is predicted to be about two orders of magnitude weaker than ν_2. The normal co-ordinates show that ν_2 is an in-phase breathing motion of the two octahedra, Mo_6 and X_6; the corresponding polarizability derivative is therefore large, giving an intense Raman line. In contrast, ν_3 is a breathing of the two octahedra *with opposite phase*; there is therefore a tendency to mutual cancellation in forming the overall polarizability change during vibration, with the result that the Raman fundamental is weak. This unusually low intensity may be a common feature of such highly symmetrical cluster compounds; it has previously been remarked[9] in the boron halide cages, $B_nX_n^{2-}$. Details of the normal-co-ordinate analysis of the Mo clusters and infrared data on a number of related compounds will be published.

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