Vibrational Studies of Compounds with Multiple Molybdenum–Molybdenum and Rhenium–Rhenium Bonds

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A detailed study of the possible force fields for M_2X_8 anions (M = Mo or Re; X = halide or carboxylate) has shown a definite difference in metal–metal stretching force constant between the molybdenum halides (F_{MM} *ca.* 3.5 mdyn Å^{-1}) and the other molecules (F_{MM} *ca.* 4.5 mdyn Å^{-1}). This suggests that δ bonds play a significant part in the metal–metal bond strength for the rhenium compounds and for the molybdenum carboxylates, but probably not for the molybdenum halides.

RAMAN spectroscopy has proved extremely useful in the detection and characterisation of systems containing both homonuclear [1] and heteronuclear [2] metal–metal bonds, in particular, in the study of binuclear species with multiple metal–metal bonds.[3] Generally, the frequency of the most intense line (usually assumed to arise from the metal–metal fundamental stretching frequency) is relatively constant for a series of closely related species,[4] *e.g.* rhenium(III) halides $[Re_2X_8]^{2-}$ (X = Cl or Br) and carboxylates $[Re_2(O_2CR)_4]$.

However, in the case of some binuclear molybdenum(II) complexes the position of the most intense Raman lines varies considerably.[5,6] This apparent range of line position is noteworthy as molybdenum is the only system to our knowledge where such a large variation occurs. Thus we desired to know whether this difference is due to a real difference in force constant for the Mo–Mo bond or simply a consequence of coupling effects. An earlier report [7] was also concerned with this problem but practical difficulties only permitted the authors to conclude that both Re–Re and Mo–Mo force constants for complexes of this type fell in the range 3.0—4.5 mdyn Å^{-1}.†

The present work reports the Mo–Mo force constant in $[Mo_2X_8]^{4-}$ (X = Cl or Br) to be *ca.* 3.5 ± 0.3 mdyn Å^{-1}, while in M_2X_8 species (M = Mo, X = O; M = Re, X = O or Cl) the force constant is *ca.* 4.5 ± 0.4 mdyn Å^{-1}, thus permitting the conclusion that in the molybdenum case different ligand types are associated with a variation in Mo–Mo binding.

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† 1 dyn = 10^{-5} N.

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EXPERIMENTAL

From the symmetry of the $[Mo_2Cl_8]^{4-}$ ion (D_{4h}) three totally symmetric (A_{1g}) vibrations are expected, which are Raman active and would be polarised if a spectrum could be obtained from an homogeneous fluid sample. These vibrations are formed from combinations of the Mo–Mo stretch, Mo–Cl stretch, and the Mo–Mo–Cl deformation co-ordinates. The calculation of force constants from the frequencies alone is of necessity inexact as there are only three frequencies but six General Valence Force Field (G.V.F.F.) constants. The approximation used in this calculation was to apply the 'Kupplungstufen Verfahren' of Fadini.[8,9] This has been shown to give a fair approximation to the G.V.F.F. in the few cases where this is known.[10]

TABLE 1

Symmetry co-ordinates used for A_{1g} species of D_{4h} M_2X_8 molecules and ions

$S_1 = \Delta d(\mathrm{MM})$
$S_2 = \Sigma\Delta r_i(\mathrm{MX})$
$S_3 = \Sigma\Delta\alpha_i(\mathrm{MMX}) - a\Sigma\Delta\beta_i(\mathrm{XMX})$
$S_4 = a\Sigma\Delta\alpha_i(\mathrm{MMX}) + \Sigma\Delta\beta_i(\mathrm{XMX}) \equiv 0$ (redundancy)

Sums were taken over all eight bonds or angles (M = Mo or Re; X = Cl, Br, or carboxylate O). $a = -\sin 2\alpha/\sin\beta$; $\beta = \cos^{-1}(\cos^2\alpha)$.

TABLE 2

Frequency assignments used [a]

	ν(MoMo)	$\nu(MoX_4)$	$\delta(MoX_4)$
$[Mo_2Cl_8]^{4-}$	349	319	120
$[Mo_2(O_2CMe)_4]$	406	690	201 or 188 [b]
$[Mo_2(O_2CCF_3)_4]$	397	502 or 518	205 or 191

[a] Taken from ref. 5. Units are cm^{-1}. [b] The alternative values used span clusters of lines in the Raman spectra.

The symmetry co-ordinates used are given in Table 1 and the frequency assignments in Table 2. The geometry used[11] for $[Mo_2Cl_8]^{4-}$ was Mo–Mo 214 pm, Mo–Cl 245 pm, and Mo–Mo–Cl 105°. Until recently,[12] the precise geometry for molybdenum carboxylates was not certain,[13] but Mo–Mo 200—220 pm, Mo–O 195—205 pm, and O–Mo–O 88—92° gave essentially similar results: F_{11} (Table 3) changes by only 0.03 mdyn $Å^{-1}$ over the range. Calculations were also made using the various alternative frequencies given in Table 2, but again no significant change in F_{11} was observed (range 0.02 mdyn $Å^{-1}$). The results of the calculations are given in Table 3.

TABLE 3

Force constants,[a] frequencies,[b] and contributions to normal co-ordinates from symmetry co-ordinates, Q [c]

	M [d]	X [d]	d_{MM} (pm)	r_{MX} (pm)	α(MMX)/°	ν_1	ν_2	ν_3	F_{11}	F_{12}	F_{13}	F_{22}	F_{23}	F_{33}	Q_1			Q_2			Q_3		
															S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3
(*a*)	Mo	Cl	214	245	105	349	319	120	3.53	0.57	0.53	2.21	−0.06	1.50	1	−0.59	−0.15	0.89	1	−0.13	0.66	0.01	1
(*b*)	Mo	Cl	214	245	105	319	349	120	3.39	0.55	0.49	2.27	−0.07	1.51	0.92	1	−0.17	1	−0.90	−0.17	0.67	0.01	1
(*c*)	Mo	Cl	214	245	105	417	300	112	3.53	0	0	2.21	0	1.50	1	−0.58	−0.29	0.77	1	0.24	0.70	0.0	1
(*d*)	Mo	Cl	214	245	90	349	319	120	3.53	0	0.63	2.13	0	1.87	1	0	−0.16	0	1	0	0.61	0.0	1
(*e*)	Mo	Cl	214	245	90	380	326	102	3.53	0	0	2.21	0	1.50	1	0	−0.27	0	1	0	0.63	0.00	1
(*f*)	Re	Cl	214	245	105	245	327	120	3.53	0.57	0.53	2.21	−0.06	1.50	1	0.08	−0.17	0.15	1	0.02	0.71	0.01	1
(*g*)	Mo	O	214	245	105	342	486	178	3.53	0.57	0.53	2.21	−0.06	1.50	1	0.06	−0.18	0.17	1	0.02	0.73	0.01	1
(*h*)	Mo	Br	214	245	105	342	216	80	3.53	0.57	0.53	2.21	−0.06	1.50	1	−0.11	−0.14	0.39	1	−0.05	0.64	0.01	1
(*i*)	Mo	$MeCO_2$	211	200	88	406	690	201	4.57	0.01	0.56	4.48	0	1.62	1	−0.03	−0.20	0.03	1	−0.00	0.82	−0.00	1
(*j*)	Mo	CF_3CO_2	211	200	88	397	502	205	4.38	0.02	0.60	2.37	0	1.69	1	−0.06	−0.21	−0.09	1	−0.17	0.85	−0.00	1
(*k*)	Mo	Cl	211	200	88	397	338	139	4.38	0.02	0.60	2.37	0	1.69	1	−0.13	−0.17	0.18	1	−0.03	0.76	−0.00	1
(*l*)	Re	CF_3CO_2	211	200	88	290	501	202	4.38	0.02	0.60	2.37	0	1.69	1	−0.02	−0.34	0.03	1	−0.00	0.90	−0.00	1
(*m*)	Re	Cl	214	245	105	265	357	127	4.38	0.02	0.60	2.37	0	1.69	1	0.34	−0.15	−0.52	1	0.25	0.70	0.01	1

[a] Stretching constants in mdyn A^{-1}, bending (F_{33}) in mdyn A rad^{-2}, and interaction (F_{23}) in mdyn rad^{-1}. [b] Assigned to ν(MM), ν(MCl), and δ(MCl) respectively. [c] From the inverse to eigenvector matrix L^{-1}, where $Q = L^{-1}S$; scaled so the major contributer to the normal co-ordinate has the value unity. [d] Masses used: M=Mo 96, Re 186, X=O 16, Cl 35, Br 80.

RESULTS AND DISCUSSION

Use of the assignments $\bar{\nu}$(Mo–Mo) 349 cm^{-1} and $\bar{\nu}$(Mo–Cl) 319 cm^{-1} gave normal co-ordinates composed of mixtures of the symmetry co-ordinates [see Table 3(*a*)]. Reversing the assignments gave much higher coupling in the co-ordinate corresponding to ν_1 although did not change F_{11} very much [Table 3(*b*)]. The coupling is due to the size of the off-diagonal elements in the *G* matrix, for setting the off-diagonal *F* elements to zero still resulted in the normal co-ordinates being considerable mixtures [Table 3(*c*)]. Indeed this mixture is such that there is no real, purely diagonal, force field fitting the experimental frequencies: a positive value of F_{13} is needed to obtain a real solution. Changing the Mo–Mo–Cl bond angle to 90° removed F_{12} and F_{23} but kept F_{13} large and still maintained the coupling between symmetry co-ordinates S_1 and S_3 [Table 3(*d*)]. Removing F_{13} raised ν_3 and lowered ν_1 by 20 and 10% respectively [Table 3(*e*)]. It is thus possible to dissect the vibrational analysis of the A_{1g} class of $[Mo_2Cl_8]^{4-}$ to determine the various contributions. The Mo–Mo force constant stays the same (within 10%) no matter whether one considers as nearly diagonal a force field as possible, one off-diagonal element, the Fadini method result, or bond angles of 105 or 90°. The normal co-ordinates are combinations of the symmetry co-ordinates, the amount of mixing being governed by the size of the off-diagonal *G* matrix elements (mass coupling) not by the force constants. It thus seems that, notwithstanding the high mass coupling, the Mo–Mo force constant in $[Mo_2Cl_8]^{4-}$ is *ca.* 3.5 mdyn $Å^{-1}$, with a possible 10% error if the method has badly overestimated F_{13}.

The coupling between S_1 and S_2 in normal co-ordinates Q_1 and Q_2 is determined by the Mo–Mo–Cl angle or by the relative masses. Calculations were made using the same set of force constants, the Fadini set for the assignment ν_1 at 349 cm^{-1} [Table 3(*a*)], and varying the atom

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masses. When the mass of molybdenum was increased to 186 (*i.e.* the mass of rhenium) then ν_1 and ν_2 went to 245 and 327 cm^{-1} respectively (*cf.* experimental values for $[Re_2Cl_8]^{2-}$ of 275 and 330 cm^{-1}) and the coupling of S_1 and S_2 became very small [Table 3(*f*)]. Similarly, when the mass of chlorine was decreased to 16 (*i.e.* the mass of oxygen) then ν_1 and ν_2 were at 342 and 486 cm^{-1} [*cf.* experimental values for rhenium carboxylates of 400 and 500—700 cm^{-1} depending on the carboxylate, Table 3(*g*). Normal co-ordinates Q_1 and Q_2 again approximate to the symmetry co-ordinates. When the mass of chlorine was increased to 80 (*i.e.* mass of bromine) then Q_1 became really pure S_1 but Q_2 stayed as a mixture of S_1 and S_2 [Table 3(*h*)]. The calculated wavenumbers become 342 and 216 cm^{-1} (*cf.* experimental values of 335 and 223, 251 cm^{-1}).

It thus seems that the $[Mo_2Cl_8]^{4-}$ force field, while predicting well the frequencies for the other molybdenum–halogen compounds, is less successful for rhenium compounds and the molybdenum carboxylates. Similar calculations for $[Mo_2(O_2CR)_4]$ compounds show why. Two sets of frequencies based on R = Me and R = CF_3 were used [Table 3(*i*) and 3(*j*)]. As expected there was little mixing of the symmetry co-ordinates in the normal co-ordinates Q_1 and Q_2 although Q_3 was still a 2 : 3 mixture of $S_1 : S_3$. When the mass of oxygen was increased to 35 (chlorine) using these force fields, too high a value of ν_1 was predicted: 397 cm^{-1} using the trifluoroacetate force field or 403 cm^{-1} using the acetate force field [Table 3(*k*)], *cf.* the experimental value of 349 cm^{-1} for $[Mo_2Cl_8]^{4-}$. However, when the mass of molybdenum was increased to that of rhenium (186) then ν_1 was at 290 cm^{-1} (based on CF_3CO_2) and 296 cm^{-1} (based on $MeCO_2$) [Table 3(*e*)], *cf.* an experimental range of 275—285 cm^{-1}. Even better agreement was obtained when the mass of molybdenum was increased to 186 (rhenium), that of oxygen to 35 (chlorine), and the geometry changed to that of $[Re_2Cl_8]^{2-}$ [Table 3(*m*)]. Calculated values of 265 and 271 cm^{-1} are in good agreement with the experimental value of 275 cm^{-1}. Considerable mixing was again observed as the bond angle now differs considerably from 90°.

In conclusion it appears that there are two distinct force fields, and even by changing masses, angles, and bond lengths it is not possible to find one force field to cover all M_2X_8 species considered here. The observed frequency difference between ν(Mo–Mo) in the carboxylate and halide complexes seem to arise from real differences in force constants, the metal–metal stretch force constant in $[Mo_2X_8]^{4-}$ (X = Cl or Br) being *ca.* 3.5 mdyn Å^{-1}, while in M_2X_8 species (M = Mo, X = O; M = Re, X = O or Cl) the force constant is *ca.* 4.5 mdyn Å^{-1}. As this difference is associated with different ligand types, some part of the explanation may well be found in the ligand-induced eclipsed arrangement of the carboxylates, allowing a favourable situation for δ bond formation.

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