X-Ray Structural and Raman Data, Including Remarkable Resonance Raman Effects, for Quadruple Molybdenum-to-Molybdenum Bonds

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Summary The $Mo_2(SO_4)_4{}^{4-}$ ion has been studied crystallographically and found to have a very short (2·110 Å) Mo–Mo bond; the Raman spectra of this and other $Mo_2{}^{4+}$ complexes exhibit strong bands ("Mo–Mo stretching") in the range 345—406 cm^{-1} with $Mo_2Cl_8{}^{4-}$ compounds showing remarkable resonance Raman enhancements up to the 3rd overtone when irradiated at 4880 Å.

Molybdenum in its lower valence states has an extraordinary tendency to form multiple Mo–Mo bonds, of third[1,2] and fourth order.[3–6] Among the species containing the quadruple bond are the carboxylates $Mo_2(O_2CR)_4$, such as the acetate,[5] the trifluoroacetate,[6a] and the pyridine adduct of the trifluoroacetate,[6b] the $Mo_2Cl_8{}^{4-}$ ion, which occurs in a number of salts,[3] and, presumably, $Mo_2{}^{4+}$ (aq).[7] Several compounds containing quadruple Mo–Mo bonds have previously been found to have strong Raman lines in the range 340—406 cm^{-1}, depending on the compound and its state[6b,8] and this seems diagnostic of the strong metal–metal bond.

An intermediate in the preparation of $Mo_2{}^{4+}$ (aq) from $Mo_2Cl_8{}^{4-}$, namely, $K_4Mo_2(SO_4)_4$, has been reported.[7] The compound was unsuitable for crystallographic investigation. Useful single crystals were obtained by dissolving $K_4Mo_2(SO_4)_4$ in 0·1M-H_2SO_4 and allowing this solution to mix by diffusion through a glass frit with a saturated solution of K_2SO_4 in 0·1M-H_2SO_4.

Table

Frequencies of "Mo-Mo *stretching*" *bands*[a]

Compound	Frequency/cm^{-1}		Mo–Mo Distance	
$Mo_2(O_2CCH_3)_4$	406		2·11(1)	
$Mo_2(O_2CCF_3)_4$	397		2·090(4)	
$Mo_2(O_2CCF_3)_4$·2py	367[b]		2·129(2)	
$K_4Mo_2(SO_4)_4$·$2H_2O$	—		2·110(3)	
$K_4Mo_2(SO_4)_4$	370		—	
$(C_2H_{10}N_2)_2Mo_2Cl_8$·$2H_2O$ ..	350	348 (av.)	2·134(1)	2·141 ±0·006 (av.)
$(NH_4)_5(Mo_2Cl_8)Cl$·H_2O ..	350		2·150(5)	
$K_4Mo_2Cl_8$	345		—	
$K_4Mo_2Cl_8$·$2H_2O$	345[c]		2·139(4)	

[a] For sources of data on distances and frequencies previously reported see ref. 3, 5, and 6. [b] $Mo_2(O_2CCF_3)_4$ dissolved in pyridine has a frequency of 343 cm^{-1}. [c] Sample preparation may have caused dehydration.

The crystals belong to the monoclinic system, space group *C*2/*c*, with $a = 17{\cdot}206(3)$, $b = 10{\cdot}193(2)$, $c = 10{\cdot}061(2)$ Å, $\beta = 94{\cdot}92(2)°$ and $Z = 4$. The structure has been refined using counter-diffractometer data (1217 reflections) to $R_1 = 0{\cdot}034$ and $R_2 = 0{\cdot}043$.

The $Mo_2(SO_4)_4^{4-}$ group lies at a $\bar{1}$ special position and has a structure quite similar to that of $Mo_2(O_2CR)_4$ molecules[5,6] with bridging SO_4 groups. The $Mo_2(SO_4)_4^{4-}$ units are linked through oxygen atoms of some sulphate ligands, as shown in Figure 1. The water molecules are co-ordinated to K^+ ions. The Mo_2O_2S rings are non-planar, having an average dihedral bend of 20° across the $O \cdots\cdots O$ line. These bends are so oriented that the idealized symmetry of the $Mo_2(SO_4)_4^{4-}$ unit is C_{4h}. The values of some important structural parameters, averaged according to C_{4h} symmetry are: Mo–Mo, 2·110(3); Mo–OS, 2·136; MoO–S, 1·510; S–O, 1·440; S–O($\cdots\cdots$Mo), 1·463; $O \cdots\cdots Mo$, 2·593 Å; $\angle$Mo–Mo–O, 94·2°.

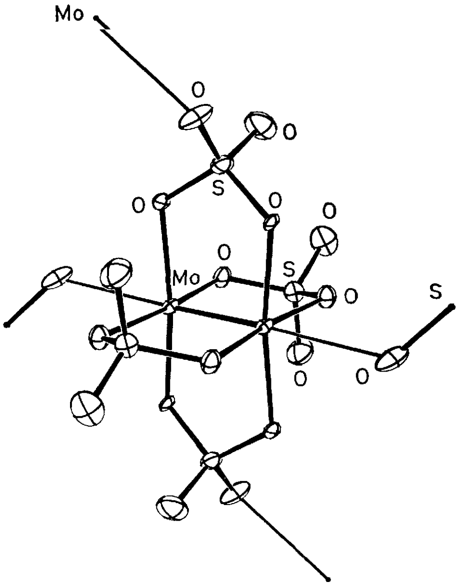

FIGURE 1. *The structure of the* $Mo_2(SO_4)_4^{4-}$ *unit in* $K_4Mo_2(SO_4)_4 \cdot 2H_2O$.

For $K_4Mo_2(SO_4)_4$ (the powder originally described by Bowen and Taube)[7] there is a strong Raman line at 370 cm^{-1} characteristic of a strong Mo–Mo bond and thus indicative of the presence of the $Mo_2(SO_4)_4^{4-}$ ion in this substance. The Raman spectrum of this substance was observable only by using the rotating sample technique.[9] This result prompted us to employ the same technique for various intensely coloured compounds containing the $Mo_2Cl_8^{4-}$ ion, which had previously proved intractable. Spectra were recorded for the four compounds[3] $(NH_4)_5Mo_2Cl_9 \cdot H_2O$, $K_4Mo_2Cl_8$, $K_4Mo_2Cl_8 \cdot 2H_2O$, and $(C_2H_{10}N_2)_2Mo_2Cl_8 \cdot 2H_2O$ using 6471 Å excitation from an argon laser. In each case lines of approximately equal intensity were recorded at *ca.* 300 and *ca.* 350 cm^{-1}, the exact frequencies varying by a few wavenumbers. The former can be assigned to a "Mo–Cl stretching" mode and the latter to the "Mo–Mo stretching" mode.

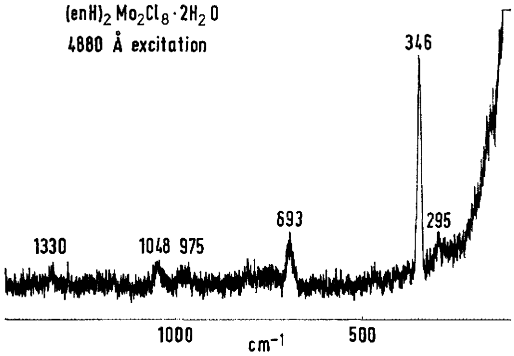

FIGURE 2. *Typical Raman spectrum of a* $Mo_2Cl_8^{4-}$ *compound showing the resonance effect.*

The use of 4880 Å excitation causes a striking manifestation of the resonance Raman effect.[10] Energy of excitation is so strongly channelled into the totally symmetric "Mo–Mo stretching" mode that not only is the fundamental enormously enhanced, but the 1st, 2nd, and, in some spectra, even 3rd overtones are observed, as shown in Figure 2.

The available data on "Mo–Mo stretching" frequencies are summarized in the Table. It is clear that the frequencies correlate only crudely with the Mo–Mo distances. This shows that the normal modes responsible for these strong bands are only roughly approximated by the description "Mo–Mo stretching," though they undoubtedly incorporate a substantial proportion of that particular symmetry coordinate, which is mainly responsible for their very great intensities. A previous, approximate analysis[8] of the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ vibrations indicated that the "Re–Re stretching" modes at *ca.* 275 cm^{-1} consisted of only about 65% of Re–Re stretching. For $Mo_2Cl_8^{4-}$ the mixing of Mo–Mo and Mo–Cl stretching is doubtless also extensive.

As an example of the utility of the Raman spectrum in detecting strong Mo–Mo bonds (which do not always persist in the product even though present in the starting material)[11] we have examined the Raman spectrum of a beautiful, orange microcrystalline product obtained by reaction of $Mo_2(O_2CMe)_4$ with aqueous oxalic acid. A band at 396 cm^{-1} suggests the presence of a quadruple Mo–Mo bond, and thus the effort to characterize the substance more fully should be worthwhile.

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