Structural and Vibrational Characteristics of the Tetrasulfatodimolybdenum Ions with Mo–Mo Bond Orders of 3.5 and 4.0

AVI BINO, F. ALBERT COTTON*, DAVID O. MARLER

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A & M University, College Station, Tex. 77843, U.S.A.

STUART FARQUHARSON

Dow Chemical Company, Engineering and Analytical Sciences Laboratory, Texas Operations, Freeport, Tex., U.S.A.

BENNETT HUTCHINSON, BILLY SPENCER

Department of Chemistry, Abilene Christian University, Abilene, Tex. 79699, U.S.A.

and JAMES KINCAID

Department of Chemistry, Marquette University, Milwaukee, Wis. 53233, U.S.A.

(Received February 16, 1987)

Abstract

The compound $K_4[Mo_2(SO_4)_4]Br\cdot4H_2O$ has been made and its crystal structure determined. Space group *P4/mnc*; unit cell dimensions, $a = 11.903(2)$, $c = 8.021(1)$ Å, $V = 1136(1)$ Å^3. The compound is isomorphous with the analogous chloride whose structure has been reported. The Mo–Mo and Mo–Br distances are 2.169(2) and 2.926(1) Å, respectively and the $[Mo_2(SO_4)_4]^{3-}$ ions reside on crystallographic special positions with *4/m* symmetry. The Raman spectra of both the bromo and chloro compounds have been measured and the Mo–Mo stretching frequency is 370 ± 1.5 cm^{-1} in each, for the compounds containing the natural isotopic distribution of molybdenum. The chloro compound has been prepared containing the pure isotope ^{92}Mo as well, and the Raman spectra recorded. The ν(Mo–Mo) band is shifted by 6.8 ± 0.5 cm^{-1}. The compound $K_4[Mo_2(SO_4)_4]\cdot2H_2O$ has also been prepared with Mo at natural abundance and with the pure isotope ^{100}Mo, whereby a shift of 8.5 ± 0.5 cm^{-1} was found. These and other results will be discussed with regard to the similarity of the Raman spectra of the $Mo_2(SO_4)_4{}^{3-}$ and $Mo_2(SO_4)_4{}^{4-}$ species.

Introduction

The $[Mo_2(SO_4)_4]^{3-}$ ion was the first complex containing a metal–metal bond of order 3.5 to be discovered [1]. The increase in the Mo–Mo distance from 2.111(1) Å in the quadruply-bonded $[Mo_2(SO_4)_4]^{4-}$ ion to 2.164(2) Å in the $[Mo_2(SO_4)_4]^{3-}$ ion indicates a small but significant weakening of the Mo–Mo bond. This bond weakening is a result of both a reduction in the bond order and an increase in the effective charge on the metal atoms, as has recently been discussed in detail [2].

The weakening of the Mo–Mo bond should manifest itself in other ways besides the increase in bond length. One of the more obvious additional effects of lowering the bond strength should be a decrease in the force constant of the Mo–Mo bond and this might be expected to reveal itself in the Raman spectrum, where bands for M–M stretching are characteristically seen in compounds with M–M multiple bonds. In 1973 it was reported [3] that the Raman spectrum of $K_4[Mo_2(SO_4)_4]$ has a strong band at 370 ± 1 cm^{-1}, which was assigned to ν(Mo–Mo). In 1976 Loewenschuss *et al.* [4] examined the Raman spectra of $K_4[Mo_2(SO_4)_4]\cdot2H_2O$ and $K_3[Mo_2(SO_4)_4]\cdot3.5H_2O$, confirming the presence of a strong band at 371 cm^{-1} in the former but finding a rather complex spectrum for the latter. Bands that they suggested assigning to ν(Mo–Mo) were found at 373 and 386 cm^{-1}, and the doubling was attributed to the presence of two crystallographically non-equivalent ions in the unit cell of $K_3[Mo_2(SO_4)_4]\cdot3.5H_2O$ [1].

It has also been shown that photochemical oxidation of $[Mo_2(SO_4)_4]^{4-}$ to $[Mo_2(SO_4)_4]^{3-}$ in aqueous solution with evolution of H_2 can be effected by near ultraviolet radiation (254 nm), and a very weak absorption band ($\epsilon \sim 143$) at about 7100 cm^{-1}, assignable to the $\delta \rightarrow \delta^*$ transition in $[Mo_2(SO_4)_4]^{3-}$ has been observed [5]. A vibrational progression with a 340 cm^{-1} spacing was observed for this band using a solid sample of $K_3[Mo_2(SO_4)_4]\cdot3.5H_2O$ at 15 K [5]. An earlier low-temperature study of the crystal spectrum of $K_4[Mo_2(SO_4)_4]\cdot2H_2O$ at 15 K showed no vibrational structure [6].

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*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

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In an effort to understand better the properties of the $[Mo_2(SO_4)_4]^{n-}$ ions, especially their Raman spectra, we prepared two compounds containing the $[Mo_2(SO_4)_4]^{3-}$ ion in a crystallographically simpler environment. Previously, we reported the preparation and structure of $K_4[Mo_2(SO_4)_4]Cl \cdot 4H_2O$ [7] in which the dinuclear anion was found in only one kind of crystallographic site, that being one of high symmetry, $4/m$. However, in this compound there are infinite chains of the type ···Mo–Mo···Cl···Mo–Mo···Cl··· along the c axis and, even though the Mo···Cl interactions appear to be weak, we were concerned that the frequency of the Mo–Mo stretching vibration might be appreciably perturbed by interaction with the Mo···Cl stretching mode. To determine if this effect is important, the corresponding bromide was made, and its crystal structure determined, to see if the Mo–Mo distance showed any dependence upon the replacement of Cl^- by Br^-.

In addition we examined the Raman spectra of the $K_4[Mo_2(SO_4)_4X] \cdot 4H_2O$ compounds. Upon finding that both of them display sharp, strong Raman bands at essentially the same frequency (thus indicating that Mo···X interactions are not of major importance) we prepared the chloro compound with pure ^{100}Mo isotope and recorded its Raman spectrum. For comparison with these results we also prepared $K_4[Mo_2(SO_4)_4] \cdot 2H_2O$ with the pure ^{92}Mo isotope and recorded its Raman spectrum. The purpose of these experiments was to determine how much the modes ordinarily described as ν(Mo–Mo) may in fact deviate from that character as a result of mixing with other A_{1g} modes. A similar study was reported several years ago [8] for $Mo_2(O_2CCH_3)_4$, where the isotopic shift suggested that the qualitative description was essentially correct. However, there are structural features of the sulfato-bridged species that might alter the situations significantly, and we also had in mind the puzzling similarity of the frequencies in the $[Mo_2(SO_4)_4]^{4-}$ and $[Mo_2(SO_4)_4]^{3-}$ ions alluded to above.

Experimental

Preparation of $K_4[Mo_2(SO_4)_4]Br \cdot 4H_2O$

A solution of $K_4[Mo_2Cl_8]$ (0.05 g), prepared by a literature method [9] in 5 ml* of 2 M H_2SO_4 and 0.5 M HBr was made under an atmosphere of argon. To this was added, dropwise with frequent agitation between additions, 3.0 ml of H_2O_2 (0.025 M). The color of the solution turned from deep red to grey–blue. KBr (0.05 g) was then added and the solution was stirred at 0 °C for 30 min. The blue precipitate was filtered, washed with acetone and ether, and dried in vacuum. Yield: 50 mg.

Single crystals were obtained by a process of slow interdiffusion, through a glass frit, of the solution containing $[Mo_2(SO_4)_4]^{3-}$ species and a solution of 0.1 M KBr.

X-ray Crystallography

A crystal of dimensions 0.08 × 0.08 × 0.1 mm was attached to the end of a glass fiber and mounted on a Syntex P$\bar{1}$ four-circle diffractometer. Mo Kα (λ = 0.710730 Å) radiation, with a graphite crystal monochromator in the incident beam, was used.

Rotation photographs and ω-scans of several strong reflections indicated that the crystal was of satisfactory quality. Preliminary examination showed that the crystal belonged to the tetragonal system, space group $P4/mnc$. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range $25° < 2\theta < 35°$ giving $a = 11.903(2)$, $c = 8.021(1)$ Å and $V = 1136(1)$ Å^3.

Data were measured by θ–2θ scans. A total of 377 reflections in the range $0° < 2\theta \leqslant 50°$ were collected of which 349 having $I > 3\sigma(I)$ were used to solve and refine the structure. General procedures for data collection have been described elsewhere [10]. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 40.96 cm^{-1}. ψ scans at $\chi = 90°$ for several reflections showed no variation greater than 8%; no absorption correction was applied.

The positions of all atoms were initially set at those found for the isomorphous [7] chloro compound. The structure was refined** in space group $P4/mnc$ to convergence using anisotropic thermal parameters for all the non-hydrogen atoms.

The discrepancy indices,

$$R_1 = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

and

$$R_2 = \frac{[\Sigma w(|F_o| - |F_c|)^2]^{1/2}}{\Sigma w|F_o|^2}$$

had final values of $R_1 = 0.044$, $R_2 = 0.063$ with a goodness of fit parameter equal to 1.44. See also 'Supplementary Material'.

Preparation of Isotopically Substituted Compounds

Both tetrasulfato dimolybdenum compounds were prepared with isotopic molybdenum using ^{92}Mo-

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*Unfortunately, in ref. 8 there is an error in the quantity of 2 M H_2SO_4, which should be 5.0 ml and not 50 ml. The reaction does not work with the large amount.

**All crystallographic computing was done on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Tex., using the Enraf-Nonius structure determination package.

(97.37T) or ^{100}Mo(97.47%) as obtained from Oak Ridge National Laboratories. The isotopic metal was converted to isotopic $Mo(CO)_6$ by oxidizing the metal with nitric acid and then submitting the resulting MoO_3 to a CO pressure of 1000 psi at 350 ℃ in a microreactor [11, 12]. Isotopic $K_4Mo_2Cl_8$ was obtained by reacting the isotopic $Mo(CO)_6$ with acetic acid to yield $Mo_2(O_2CCH_3)_4$ [13] which was converted to the $K_4Mo_2Cl_8$ as previously described [9]. Isotopic $K_4[Mo_2(SO_4)_4]\cdot 2H_2O$ and $K_4[Mo_2(SO_4)_4]Cl\cdot 4H_2O$ were prepared from isotopic $K_4Mo_2Cl_8$ as described for the compounds at natural abundance [1, 7].

Recording of Raman Spectra

Solid samples of the two $K_4[Mo_2(SO_4)_4]X\cdot 4H_2O$ compounds were initially examined using a rotating wheel sample mount and a 4880 Å exciting line (420 mW Ar/Kr laser). The spectra of the two compounds were virtually identical from 200 to 400 cm^{-1}, although many differences were observed in the weak lines above 400 cm^{-1}. In both compounds there was an extremely strong, sharp line at 370 ± 1 cm^{-1}.

The isotopically substituted compounds as well as samples with Mo at the natural abundance distribution of isotopes were then reexamined under conditions allowing greater precision in the measurement of frequencies.

Raman spectra were collected on samples of $K_4[Mo_2(SO_4)_4]Cl\cdot 4H_2O$ with Mo at natural abundance and ^{92}Mo as 5% KBr pellets. The 5145A laser line (500 mW) and a Spex 1403 double monochromator at Purdue University were employed to measure the spectra. Differences in the Raman shifts of the isotopomers were determined from the 521 cm^{-1} plasma line and confirmed by the Rayleigh line. No decomposition was observed in the spectra reported although a weak line at 390 cm^{-1} appeared if the sample remained in the laser beam.

Raman spectra were collected on solid $K_4[Mo_2(SO_4)_4]\cdot 2H_2O$ with Mo at natural abundance and ^{100}Mo. These samples were sealed under inert atmosphere in 5 mm pyrex tubes. The 4579A laser line (15 mW) was employed with Spex 1401 double monochromator Raman instrumentation at Marquette University. Differences in the Raman shifts of the isotopomers were determined from the Rayleigh line. No decomposition of the samples was observed.

Results and Discussion

Spectroscopic Results

The Raman shifts are listed in Table I. The spectra of the $K_4[Mo_2(SO_4)_4]X\cdot 4H_2O$ compounds are shown in Fig. 1. We note first that the frequencies of the ν(Mo–Mo) vibrations are equal within experimental error (±1.5 cm^{-1}) for the chloro and bromo compounds of type $K_4[Mo_2(SO_4)_4]X\cdot 4H_2O$. This implies that in neither compound does the presence of the axial ligands have any significant effect on the strength or force constant of the Mo–Mo bond. The alternate hypothesis that sizable effects do occur but that they fortuitously turn out to be equal seems unlikely. This is particularly so since the structural results (*vide infra*) show that all dimensions of the Mo_2O_8 core are identical within experimental error in the two compounds and that both the Mo–Cl and Mo–Br bonds are very long and weak.

TABLE I. Observed Raman Shifts (cm^{-1})[a]

$K_4[Mo_2(SO_4)_4]\cdot 2H_2O$		$K_4[Mo_2(SO_4)_4]Cl\cdot 4H_2O$		$K_4[Mo_2(SO_4)_4]Br\cdot 4H_2O$
^{NA}Mo[b]	^{100}Mo	^{NA}Mo	^{92}Mo	^{NA}Mo
246 ± 2	243 ± 2	246 ± 2	248 ± 2	190(sh) ± 10 (?)
274 ± 3	272 ± 3	266 ± 3	267 ± 3	248 ± 3
		318 ± 5	N.O.	317 ± 5
371.3 ± 0.5	362.8 ± 0.5	369.0 ± 0.5	375.8 ± 0.5	370 ± 1
				410 ± 5
		438 ± 2	N.O.	440 ± 10
				482 ± 15
		521 ± 2	521 ± 2	522 ± 5
		600 ± 5		600 ± 10
		630 ± 5		630 ± 5
		828 ± 10		810 ± 15
		912 ± 15		915 ± 10
		925 ± 15		927 ± 15 (?)
		529 ± 5		953 ± 5

[a] Uncertainties are estimated from reproducibility and depend on the sharpness of the band. [b] NA = Natural Abundance (eq. to mass 96); N.O. means not observed; blank entries imply that this region was not recorded.

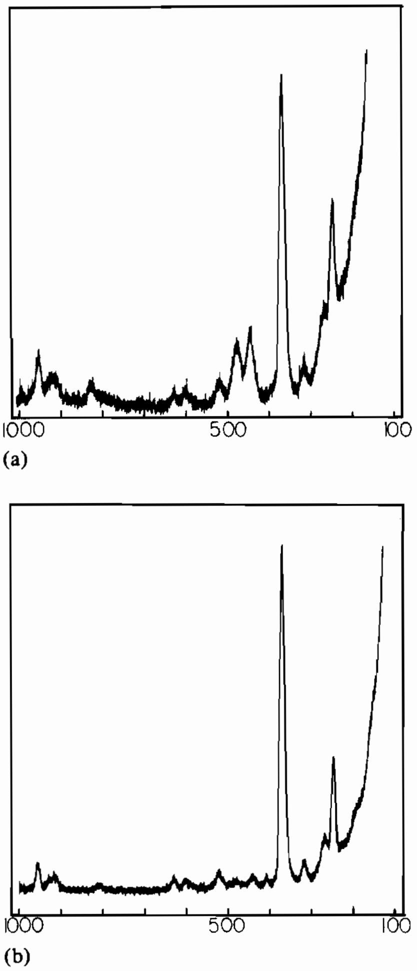

Fig. 1. The Raman spectra of (a) $K_4[Mo_2(SO_4)_4]Cl \cdot 4H_2O$ and (b) $K_4[Mo_2(SO_4)_4]Br \cdot 4H_2O$ recorded with a 4880 A exciting line, using the solid compounds on a rotating wheel type sample holder.

Isotopic shift measurements were made employing $K_4[Mo_2(SO_4)_4] \cdot 2H_2O$ with ^{NA}Mo and ^{100}Mo and $K_4[Mo_2(SO_4)_4]Cl \cdot 4H_2O$ with ^{NA}Mo and ^{92}Mo. We take the effective mass number for ^{NA}Mo (the natural mixture of molybdenum isotopes) to be equivalent to ^{96}Mo, as previously explained [8]. Because of the weakness and small shifts expected for all bands other than the one due primarily to the mode consisting mainly of Mo–Mo stretching, it is only for the latter, which are very strong and sharp (see Figs. 1(a) and 1(b)), that meaningful results were obtained. We believe that we have measured the positions of these bands to within 0.5 cm^{-1} in each isotopomer, which would place an e.s.d. of *ca.* 0.7 cm^{-1} on the shifts. These data along with the shifts calculated for pure Mo–Mo stretching (uncoupled with any other internal modes) are presented in Table II.

In each case, the observed shift is equal, within two e.s.d.s, to the calculated shift for a pure Mo–Mo vibration. From this we conclude that (a) in each compound the strong (probably resonance-enhanced) band at *ca.* 370 cm^{-1} can be described as essentially a Mo–Mo stretching mode, and (b) there may be a little more mixing with other modes in the case of the $[Mo_2(SO_4)_4]^{3-}$ ion (shift of 6.8 ± 0.7 cm^{-1}) than in the case of the $[Mo_2(SO_4)_4]^{4-}$ ion (shift of 8.5 ± 0.7 cm^{-1}), but this is not a required conclusion because of the uncertainties.

TABLE II. Observed and Calculated Isotopic Shifts for ν(Mo–Mo) Modes

Compound	Observed shift (cm^{-1})	Calculated shift (cm^{-1})
$K_4[Mo_2(SO_4)_4] \cdot 2H_2O$	8.5 ± 0.7	7.6
$K_4[Mo_2(SO_4)_4]Cl \cdot 4H_2O$	6.8 ± 0.7	7.9

There is general agreement between our Raman spectra and those reported by Loewenschuss *et al.* [4]. It was these workers who originally raised the question of why the frequency of the ν(Mo–Mo) band is scarcely different in the 3– and 4– ions, even though they differ in bond order (3.5 *versus* 4.0) and bond lengths (2.168 *versus* 2.111 Å). Loewenschuss *et al.*, suggested that this might be because the mode in question involves enough mixing of the Mo–Mo internal coordinate with others such as Mo–O, Mo–Mo–O, and deformation of the entire Mo–O–S–O–Mo ring, at least in one of the two complexes, that the consequences of changing the Mo–Mo force constant are not simply manifested. We were hoping that the isotopic shift data would provide some direct confirmation of this hypothesis. In fact, it does not, although it cannot be said to vitiate it either.

It must be borne in mind that a large difference in ν(Mo–Mo) could not have been expected in any case. By employing the type of empirical relationship that exists between force constants and bond lengths [14]* we can estimate that the difference of *ca.* 0.05 Å in Mo–Mo bond lengths in the two anions corresponds to a difference of about 0.3 md/Å in a force constant in the range of about 4–5 md/Å. This in turn would lead to a frequency difference for 'pure' Mo–Mo oscillators of only about 14 cm^{-1}. Even a small variation in mode mixing from one case to the other, together with other small structural and compositional differences between the species, could obscure such a change.

We thus draw the conclusion that in both $[Mo_2(SO_4)_4]^{n-}$ species, the Raman band at *ca.* 370 cm^{-1} is a virtually pure ν(Mo–Mo) mode and that the explanation for the negligible frequency difference

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*The correlation proposed by these authors is not greatly different from earlier ones and the argument we base upon it is thus not sensitive to the exact correlating function used.

from one of these species to the other is that very small variations in the dynamics of the two vibrating systems could easily obscure the maximum inherent difference of *ca.* 14 cm^{-1}.

Structural Results

The compound $K_4[Mo_2(SO_4)_4]Br \cdot 4H_2O$ is isostructural with its chloride analog [7]. The atomic positional parameters are listed in Table III and the molecular dimensions obtained therefrom are presented in Table IV, along with those for the chloride analog [7] for comparison. The structure of the $[Mo_2(SO_4)_4]^{3-}$ ion, with the adjacent axial Br^- ions is shown in Fig. 2. In both cases the axial interactions are extremely weak (Mo–Cl and Mo–Br distances being ~0.5 Å longer than expected for real single bonds) and thus the $[Mo_2(SO_4)_4]^{3-}$ portions of each structure are essentially identical.

TABLE III. Atomic Positional Parameters[a]

Atom	*x*	*y*	*z*
Mo(1)	0.0000(0)	0.0000(0)	0.3648(2)
Br	0.0000(0)	0.0000(0)	0.0000(0)
K(1)	0.3338(4)	0.1662(0)	−0.2500(0)
S(1)	0.2707(3)	0.4087(3)	0.0000(0)
O(1)	0.3466(6)	0.4211(6)	0.1517(8)
Ow(1)	0.4800(11)	0.2173(13)	−0.5000(0)
O(2)	0.2249(10)	0.2982(9)	0.0000(0)
O(3)	0.1879(9)	0.4958(11)	0.0000(0)

[a] The form of the anisotropic thermal parameter is: $\exp[-(B(1.1)*h*h + B(2.2)*k*k + B(3.3)*l*l + B(1.2)*h*k + B(1.3)*h*l + B(2.3)*k*l)]$. e.s.d.s are given in parentheses.

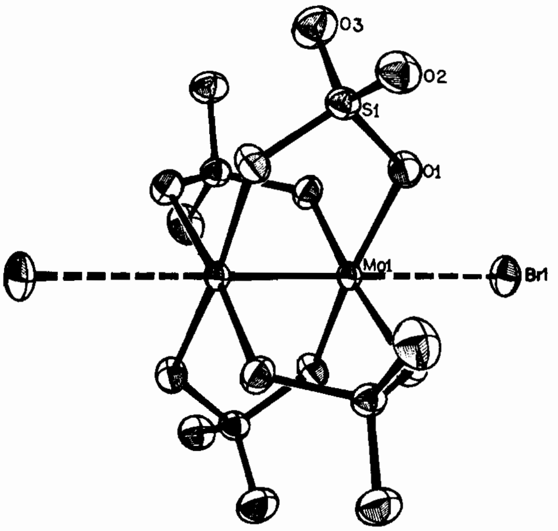

Fig. 2. The structure and atom numbering scheme for the $[Mo_2(SO_4)_4]^{3-}$ ion and its adjacent Br^- ions in $K_4[Mo_2(SO_4)_4]Br \cdot 4H_2O$.

TABLE IV. Bond Distances (Å) and Bond Angles (°) for the $K_4[Mo_2(SO_4)_4X] \cdot 4H_2O$ Compounds with X = Cl[a], Br

	X = Cl	X = Br
Distances		
Mo–Mo′	2.167(2)	2.169(3)
Mo–X	2.881(1)	2.926(1)
Mo–O(1)	2.061(4)	2.058(5)
S(1)–O(1)	1.514(4)	1.522(6)
S(1)–O(2)	1.444(6)	1.424(9)
S(1)–O(3)	1.433(6)	1.430(10)
Angles		
Mo′–Mo–O(1)	93.3(1)	93.7(2)
O(1)–Mo–O(1)′	173.3(2)	172.6(3)
O(1)–Mo–O(1)″	89.81(1)	89.76(2)
Mo–O(1)–S(1)	121.5(2)	121.3(3)
O(1)–S(1)–O(1)‴	105.2(3)	106.1(5)
O(1)–S(1)–O(2)	108.5(2)	108.4(3)
O(1)–S(1)–O(3)	110.0(2)	109.8(4)
O(2)–S(1)–O(3)	114.1(3)	114.0(6)

[a] From ref. 7.

Supplementary Material

A table of observed and calculated structure factors (2 pages) is available from author F.A.C.

Acknowledgements

Financial support by the National Science Foundation at Texas A&M University is gratefully acknowledged. B.H. acknowledges the Robert A. Welch Foundation (Grant #483) and the ACU Research Council for their support. The Raman equipment at Marquette University was purchased under NSF Instrumentation Grant CHE 8413956.

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