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Normal Coordinate Analysis of Metal-Metal Quadruple Bonds Using a More Complete Force Field

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Abstract

Normal coordinate analyses have been performed for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2\text{Cl}_8^{4-}$, $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and $\text{Re}_2\text{Cl}_8^{2-}$ by treating each compound as an isolated molecule with $4/mmm$ (D_{4h}) symmetry and also using the positions found in their respective crystal structures. In all cases the molecules were modelled as flexible structures with the acetate methyl groups taken as point masses. Calculated and experimental frequencies are reported along with valence bond and angle force constants. The normal modes for the $4/mmm$ models are shown and discussed for the bands observed in the experimental IR and Raman spectra of the Mo compounds. As a consequence of considering the bridging ring systems and partial Coulombic charges in the calculations for the isolated molecules and ions, values of 2.0, 2.0, 1.1 and 1.9 N m^{-1} , respectively, are obtained for the $M \equiv M$ force constants. When the intermolecular interactions in the solids are considered, somewhat lower values, 1.8, 1.7, 1.0 and 1.9 N m^{-1} , respectively, are obtained.

Introduction

Normal coordinate analyses have been performed for polycyclic inorganic compounds but little has been

done with systems having both multiple metal-metal bonds and bridging ring systems. An early analysis was performed on $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ by Costa, Pauluzzi & Puxeddu (1957) to determine the force constants in the acetate groups but only the C-C and C-O stretching force constants were considered; the metal-metal bond and metal-ligand interactions were ignored. Vibrational analyses for compounds with bridging acetates have recently been published, but no normal coordinate calculations were carried out and the compounds did not have metal-metal bonds (Johnson, Cannon & Powell, 1981, 1982). The vibrational spectrum of $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ has been examined, but again no normal coordinate analysis was done and the Cu-Cu interaction is considered to be nonbonding (Shriver, Mathey & Greig, 1982). The compounds to be examined here were previously subjected to normal coordinate analysis (Bratton, Cotton, Debeau & Walton, 1971; Ketteringham, Oldham & Peacock, 1976), but only the M_2X_8 portion of the molecules was used and the effects of the bridging rings and residual charges were ignored. We have chosen to do a more complete vibrational analysis of these compounds to explore the effects of the acetate bridges and residual charges on their molecular vibrations with a view toward obtaining a more accurate picture of the multiple metal-metal bond. Although we were able to obtain all the spectra needed for this study from the literature, there were conflicting Raman spectra for

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$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (Bratton *et al.*, 1971; San Filippo & Sniadoch, 1973). Thus, we remeasured both the IR and Raman spectra of this compound.

Experimental

The sample of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ was prepared by previously published methods (Cotton & Brignole, 1972). As this compound is somewhat air and moisture sensitive all manipulations were carried out in a drybox. IR spectra were obtained from KBr pellets ($3000\text{--}600\text{ cm}^{-1}$) and Nujol mulls between polyethylene plates ($600\text{--}300\text{ cm}^{-1}$) on a Nicolet MX-1 Fourier-transform infrared spectrometer. The KBr and Nujol were carefully dried before use. Raman spectra were obtained from powdered samples enclosed in sealed glass tubes. The spinning sample technique was used to prevent burning of the samples by the laser beam. The Raman instrument is a Spex model 1402 which has been extensively modified. The 6471 \AA line of a Spectra Physics 165 krypton laser was used as the excitation source to minimize sample absorption.

Calculations

All calculations were performed on an IBM 3081 computer using the program *WMIN* (Busing, 1980). Although the principal purpose of *WMIN* is to model structures by using potential-energy functions, it will do normal coordinate calculations based on structural data, bond and angle force constants, Coulombic charges and nonbonded interatomic interaction potentials (Gilbert, 1968). The more commonly used normal coordinate analysis programs (*e.g.*, Schachtschneider, 1965), express all the interaction effects as force constants *via* a Urey-Bradley formalism even though most interactions are nonbonding. Moreover, the force constant for each unique interaction is treated separately even though the same interatomic potential function could be applied to many different interatomic interactions. As a result, most analyses using this type of calculation have many of the interaction force constants arbitrarily set to zero in order to reduce the parameterization to match the number of available spectral lines. Because it uses a more generalized set of interatomic potentials, *WMIN* can describe a vibrational model with fewer parameters, all of which can be related more closely to physical quantities such as Coulombic charge and nonbonded radii. However, it is unable to refine these coefficients by matching the calculated vibrational energies to the observed IR and Raman spectra, thus we were required to use trial and error procedures to obtain our best estimates of the force constants and other coefficients.

For this study two vibrational models were examined for each compound. One model consisted

of an isolated molecule with the idealized point group D_{4h} and Cartesian atomic coordinates obtained in each case by averaging the molecular geometries obtained from the crystal structures of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (Cotton, Mester & Webb, 1974), $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ (Kosmin, Surazhskaya, Larina, Kotelnikova & Misailova, 1980), $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ (Brencic & Cotton, 1969), and $[(n\text{-Bu})_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ (Cotton, Frenz, Stults & Webb, 1976). The other model used the real crystallographic symmetry for each solid compound. For the first two compounds the methyl groups were considered to be point masses ($M = 15.01\text{ a.m.u.}$) to maintain $4/mmm$ symmetry for the isolated molecules and because the hydrogen atoms were not located in their crystal structures. Thus the calculated vibrational modes do not include hydrogen motion.

The potential-energy functions for these calculations used bond and angle force constants (K) for the bonded interatomic interactions, Coulombic charges (q_i) where necessary, and nonbonded interaction coefficients (a_i , b_i and p_i). The functions were of the form

$$V = \sum \frac{K}{2} (d - d_0)^2 + \sum \frac{K}{2} (\theta - \theta_0)^2 + \frac{1}{2} \sum q_i q_j / r_{ij} \\ + \sum f(b_i + b_j) \exp[(a_i + a_j - r_{ij}) / (b_i + b_j)] \\ - \frac{1}{2} \sum p_i p_j / r_{ij}^6$$

where f scales the repulsion term to give the appropriate potential-energy units. For the isolated molecule the summations were performed over the entire molecule and for the crystal an accelerated convergence Ewald sum over the lattice was performed. The equilibrium distances, d_0 , and angles, θ_0 , were those found in the crystal structures. The bond and angle force constants (Tables 1 and 2) involving the metal atoms were obtained by trial and error fitting of the calculated vibrational energies to the observed IR and Raman spectra. They will be discussed below. Initial values for other bond and angle force constants (Table 1) were set at reasonable values and subsequently adjusted by trial and error; torsional force constants were ignored. In the case of the two $\text{M}_2\text{Cl}_8^{n-}$ anions, the excess negative charge was distributed equally among the eight Cl atoms, and the counter ions for the crystal calculations were placed as point charges. The nonbonded interaction coefficients (Table 3) are nonbonded radii (a_i), repulsion coefficients (b_i) and softness coefficients (p_i). The nonbonded radii for C, O and methyl are from Bondi (1964) and Pauling (1960), and those for Mo and Re are from Slater (1964). The repulsion coefficients and the nonbonded radius of Cl are those of Busing (1980) with the values for the metals estimated from other known values. The softness coefficients for C and O were taken from Busing (1980) and the others were

Table 1. Force constants for the acetates (N m^{-1} or $\text{J rad}^{-2} \times 10^{18}$)

Linkage	$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$		$\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$	
	Crystal	Molecule	Crystal	Molecule
$K(MM)$	1.8	2.0	1.0	1.1
$K(MO)$	1.6	1.7	2.2	2.2
$K(OC)$	4.9	4.9	4.9	4.9
$K(CMe)$	1.25	1.25	1.25	1.25
$K(MCl)$	—	—	0.45	0.45
$K(OCO)$	3.0	2.9	1.7	1.7
$K(OCMe)$	0.46	0.46	0.46	0.46
$K(MOC)$	2.5	2.5	3.0	3.0
$K(OMM)$	4.9	5.1	0.94	0.94
$K(OMO)_{cis}$	13.0	12.9	9.0	9.0
$K(OMO)_{trans}$	2.6	2.3	3.9	3.9
$K(OMCl)$	—	—	3.5	3.5
$K(MMCl)$	—	—	7.6	7.6

Table 2. Force constants for the chlorides (N m^{-1} or $\text{J rad}^{-2} \times 10^{18}$)

Linkage	$\text{Mo}_2\text{Cl}_8^{4-}$		$\text{Re}_2\text{Cl}_8^{2-}$	
	Crystal	Free ion	Crystal	Free ion
$K(MM)$	1.7	2.0	1.9	1.9
$K(MCl)$	0.73	0.74	0.92	0.92
$K(MMCl)$	0.50	0.50	0.32	0.32
$K(ClMCl)_{cis}$	2.7	2.7	4.2	4.0
$K(ClMCl)_{trans}$	1.14	1.14	2.4	2.5

estimated by trial and error during this work. These coefficients were used in the isolated-molecule calculations for intramolecular interactions and in the crystal calculations for both intramolecular and intermolecular interactions. For the crystal calculations the surrounding molecules were assumed to be fixed in position and hence the calculations only yield internal molecular modes. In each case a survey of possible values of the unknown force constants was made to determine the sensitivity of the calculated vibrational energies; the range of values tested covered approximately an order of magnitude about their final values. This survey included the commonly accepted values where available from Urey-Bradley calculations (Nakamoto, 1963). Then the values of the force constants were adjusted to their best values by successive calculations until a reasonable agreement between the energy of the observed IR and Raman bands and their calculated values was obtained; the average discrepancy is $\sim 8 \text{ cm}^{-1}$ for the four isolated-molecule calculations. In all cases there was sufficient sensitivity in the calculated vibrational energies to estimate the force constants to 5–10%.

Results and discussion

Our best estimates of the force constants for the bonds and angles in all four compounds, both for isolated molecules and for the solid crystalline structures, are given in Tables 1 and 2. Nonbonded potential coefficients used in these calculations are given in Table 3. As expected, the various values involving

Table 3. Coefficients for interatomic potential functions

	a_i (Å)	b_i (Å)	p_i (Å ³)
O	1.50	0.14	20.5
C	1.70	0.14	16.1
CH_3	2.00	0.14	16.1
Cl	2.43	0.24	18.0
Mo	1.45	0.04	30.0
Re	1.45	0.05	27.0

Nonbonded interaction coefficients: a_i , nonbonded radii; b_i , repulsion coefficients; p_i , softness coefficients.

Table 4. Observed and calculated vibrational modes for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$

Obsd (cm^{-1})†	$P\bar{I}$ calcd (cm^{-1})	D_{4h} calcd (cm^{-1})	Mode		
	1530	A_g	1525	A_{1g}	—
	1521	A_g	1520	B_{1g}	—
1518(I)	1527/1519	$2A_u$	1520	E_u	I
1413(I)	1411	A_u	1411	A_{2u}	II
	1402	A_u	1403	B_{2u}	—
	1391/1387	$2A_g$	1391	E_g	—
	1105	A_g	1098	B_{2g}	—
	1102	A_u	1097	B_{1u}	—
	1030	A_g	1024	A_{1g}	—
	992	A_g	985	B_{1g}	—
948(R)	950/933	$2A_g$	946	E_g	III
937(I)‡	938/930	$2A_u$	933	E_u	IV
	914/903	$2A_u$	912	E_u	—
	752	A_u	752	A_{2u}	—
	731/728	$2A_g$	732	E_g	—
	727	A_u	729	B_{2u}	—
692(R)	703	A_g	703	A_{1g}	V
685(R)	701	A_g	697	B_{1g}	VI
674(I)	698/697	$2A_u$	695	E_u	VII
628(I)	612	A_u	607	A_{2u}	VIII
488(R)	489/482	$2A_g$	491	E_g	IX
	494	A_u	488	B_{2u}	—
413(R)§	411	A_g	413	A_{1g}	X*
406(R)	406	A_g	406	A_{1g}	X
368/337(I)	366/359	$2A_u$	360	E_u	XI
322/315(R)	319/309	$2A_g$	307	E_g	XII
299(R)	306/298	$2A_g$	303/302	B_{1g}/A_{1g}	XIII

† Both IR and Raman active bands are shown and marked accordingly.

‡ This band was not observed by us; however, it was reported by Bratton, Cotton, Debeau & Walton (1971).

§ This band observed for $^{92}\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (Shriver, Cooper, Hutchinson, Morgan & Mathey, 1979).

bonds common to both Mo and Re molecules are usually identical while those involving the metal atoms are quite different. The calculated vibrational frequencies and Mulliken symbols for isolated molecules and crystalline solids of the four compounds are shown in Tables 4–7; the observed values are also given for comparison. Those modes involving principally torsional motion are not listed in the tables. Figs. 1 and 2 show the direction and magnitude of the atomic displacements for the vibrational modes assigned a roman numeral in Tables 4 and 6, respectively. The major axis of each atomic ellipsoid is proportional to the atomic displacement; the minor axes are of arbitrary dimensions. These drawings were made using a locally modified version of ORTEPII (Johnson, 1976). The modes assigned roman numerals in Tables 5 and 7 have similar displacements to those shown in the figures. In most cases the vibrational modes so marked for all four compounds correspond in energy to bands in the observed spectra.

Table 5. Observed and calculated vibrational modes for $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$

Obsd (cm^{-1})*	P_{21}/n calcd (cm^{-1})	D_{4h} calcd (cm^{-1})	Mode
	1439	A_u	1441 A_{2u} II
	1432	A_u	1434 B_{2u} —
	1408	$2B_g$	1408 E_g —
	1396	A_g	1393 A_{1g} —
	1390	A_u	1388 B_{1g} —
1385(I)	1392/1389	$2B_u$	1388 E_u I
	1072	A_g	1076 A_{1g} —
	1043	A_g	1046 B_{1g} —
965(R)	966	A_g	967 B_{2g} —
	971	A_u	964 B_{1u} —
952(I)	953/941	$2B_u$	954 E_u IV
918(R)	913/903	$2B_g$	911 E_g III
	895/887	$2B_u$	894 E_u —
	808	A_u	808 A_{2u} —
	797/792	$2B_g$	793 E_g —
	794	A_g	792 B_{2u} —
721(R)	721	A_u	714 A_{1g} V
704(R)	715	B_g	711 B_{1g} VI
685(I)	716/711	$2B_u$	710 E_u VII
629(I)	624	A_u	626 A_{2u} VIII
	551	A_u	553 B_{2u} —
	509/499	$2B_g$	503 E_g IX
397(R)	405/397	$2B_g$	403 E_g XII
396/390(I)	399/394	$2B_u$	392 E_u —
	355	A_g	346 A_{1g} XIII
356(I)	364/352	$2B_u$	340 E_u XI
	345	A_u	339 B_{1g} —
289(R)	289	A_g	289 A_{1g} X
	250/240	$2B_g$	227 E_g —
220(I)	218	A_u	208 A_{2u} —

* Observed spectra from Bratton, Cotton, Debeau & Walton (1971) and Ketteringham, Oldham & Peacock (1976).

Table 6. Observed and calculated vibrational modes for $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$

Obsd (cm^{-1})*	P_{bam} calcd (cm^{-1})	D_{4h} calcd (cm^{-1})	Mode
346(R)	352	A_g	359 A_{1g} I
	342	B_{1g}	341 B_{2g} —
	341	A_u	331 B_{1u} —
315(R)	317/312	B_{3g}/B_{2g}	314 E_g II
307(I)	310/309	B_{3u}/B_{2u}	306 E_u III
277(R)	303	A_g	276 A_{1g} IV
275(I)	283	B_{1u}	276 A_{2u} V
	264/262	B_{3u}/B_{2u}	263 E_u —
	262	A_u	255 A_{2u} —
277/253(R)	269/259	B_{2g}/B_{3g}	252 E_g VI
	227	A_g	215 A_{1g} —
	214	A_g	214 B_{1g} —
191(R)	193	A_g	172 B_{1g} VII
182(I)	209	B_{1u}	174 B_{2u} VIII
182/160(I)	174/163	B_{2u}/B_{3u}	168 E_u IX
	111/94	B_{2g}/B_{3g}	109 E_g —
130(I)	109	B_{1u}	106 B_{2u} X

* Observed spectra from Clark & Franks (1975).

Table 7. Observed and calculated vibrational modes for $[(n\text{-Bu})_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$

Obsd (cm^{-1})*	P_{21}/c calcd (cm^{-1})	D_{4h} calcd (cm^{-1})	Mode
	431	A_g	437 B_{2g} —
	423	A_u	429 B_{1u} —
356(R)	359	A_g	369 A_{1g} I
346/338(I)	342/341	$2B_u$	339 E_u III
332(I)	307	A_u	320 A_{2u} V
327/310(R)	335/334	$2B_g$	332 E_g II
295(R)	308	A_g	318 A_{1g} IV
296(I)	296	A_u	306 A_{2u} —
296(I)	290/288	$2B_u$	293 E_u —
271(R)	277/276	$2B_g$	281 E_g VI
255(R)	266	A_g	266 B_{1g} —
	200	B_u	202 B_{2u} VIII
	202	A_g	198 A_{1g} —
184(R)	198	A_g	200 B_{1g} VII
165(I)	175	B_u	181 B_{2u} X
155(I)	179/178	$2B_u$	169 E_u IX

* Observed spectra from Clark & Franks (1976).

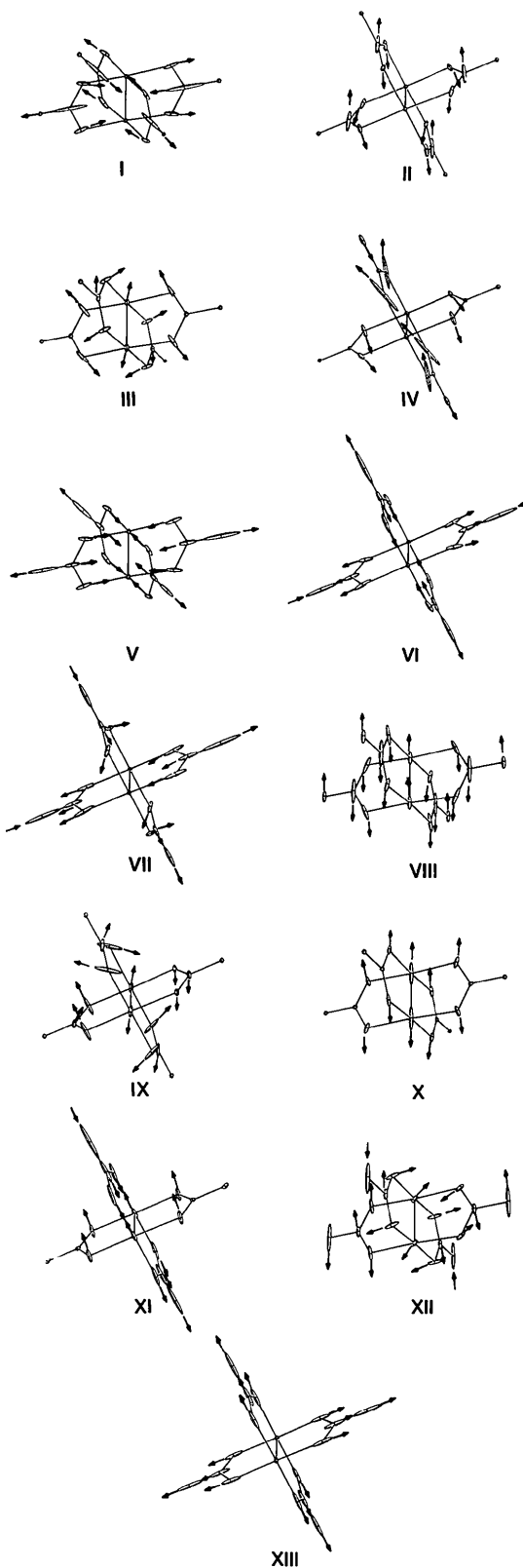


Fig. 1. Thirteen molecular vibrational modes calculated for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. The major axis of each ellipsoid indicates the magnitude and direction of the atom displacement and the arrows indicate the collective atom motion.

A comparison of our calculated vibrational energies and the observed IR and Raman bands for all compounds shows quite good agreement for both the isolated molecule and the crystal calculations. However, in some cases the specific assignments for the observed bands in the crystal are different from those for the molecule. In particular, the Raman modes at 277 and 253 cm^{-1} for $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ are assigned to the molecular modes IV (A_{1g}) and

VI (E_g), respectively, with very good agreement with the calculated values. In the crystal, however, the $\text{Mo}_2\text{Cl}_8^{4-}$ ion is strongly perturbed by two K^+ ions positioned on opposite sides of the $\text{Mo}=\text{Mo}$ bond. As a consequence the molecular E_g mode is split into B_{2g} and B_{3g} modes with calculated values of 269 and 259 cm^{-1} , respectively. Although the agreement is not as good as for the isolated-molecule calculation we prefer to assign both observed Raman modes to this split E_g mode. Inclusion of interaction terms for K^+ would probably increase the splitting and improve the match with the observed bands, but appropriate coefficients for K^+ are not available. Similarly the two IR bands at 182 and 160 cm^{-1} for this compound are assigned to the B_{2u} and B_{3u} modes arising from a split E_u molecular mode (IX).

The poorest fit was obtained for $[(n\text{-Bu})_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ and is most apparent in the low-energy region where the calculated vibrational energies are all higher than the observed values. This is probably due to our neglect of all the structural features and their appropriate interaction terms for the two $(n\text{-Bu})_4\text{N}^+$ ions. This probably has an effect on our estimates of some of the force constants for this compound, but we expect that $K(\text{ReRe})$ is unaffected because it only contributes to two higher energy modes, I and IV.

The most striking effect of our inclusion of more contributions to the force-field model is that our best values for the $M=M$ stretching force constants are considerably lower than those reported previously. For example, our value for $K(\text{MoMo})$ is 1.7–2.0 N m^{-1} as compared to a value of 3.8 N m^{-1} previously given for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ by Bratton *et al.* (1971) and values of 3.5 and 4.5 N m^{-1} for $[\text{Mo}_2\text{Cl}_8]^{4-}$ and $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, respectively, reported by Kettingham *et al.* (1976). Similarly our values for $K(\text{ReRe})$ are markedly different from previously quoted values. Bratton *et al.* give $K(\text{ReRe})$ values of 3.77 N m^{-1} for $\text{Re}_2\text{Cl}_8^{2-}$ and 4.47 N m^{-1} for $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$; while Kettingham *et al.* report values of $\sim 4.5 \text{ N m}^{-1}$ for both compounds. Our values are 1.9 and 1.0 N m^{-1} , respectively, for these two compounds and indicate that the $\text{Re}=\text{Re}$ bond is considerably weaker in the latter molecule than in the former. Some support for this conclusion can be seen in an examination of the molecular-orbital diagrams for M_2L_8 and $M_2L_8X_2$ molecules (Cotton & Wilkinson, 1980). In addition, our values of $K(M\equiv M)$ of $\sim 2.0 \text{ N m}^{-1}$ are more in line with those for $K(M-M)$ and $K(M=M)$, 0.5 and 1.0 N m^{-1} , respectively (Shriver & Cooper, 1980). Moreover, the $\text{Re}\equiv\text{Re}$ and $\text{Mo}\equiv\text{Mo}$ bonds in the two octachlorides probably have very similar strengths as would be expected from their bond order. As a test of our force-field model we substituted ^{92}Mo into our calculations for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and reproduced exactly the shift in the $\text{Mo}\equiv\text{Mo}$ stretch observed by Shriver,

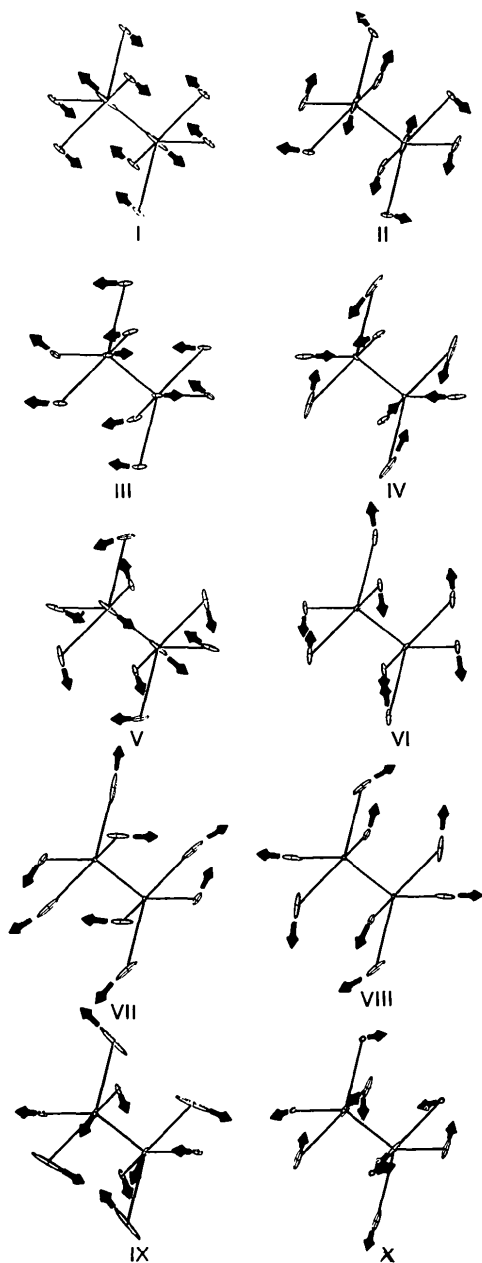


Fig. 2. Ten molecular vibrational modes calculated for $\text{Mo}_2\text{Cl}_8^{4-}$. The major axis of each ellipsoid indicates the magnitude and direction of the atom displacement and the arrows indicate the collective atom motion.

Cooper, Hutchinson, Morgan & Mathey (1979). Furthermore, if the value of $K(MM)$ is set to zero we see a drop of only ~30% in the energy of the $M\equiv M$ stretch, indicating that most of the contribution to the force field at the metal atoms is from elsewhere in the structure. Clearly, the previous workers' neglect of the other contributions to the force field lead to a substantial overestimate of $K(MM)$ as well as an improper ranking of $K(MM)$ values for related compounds. Moreover, the use of a more generalized force field with fewer parameters has given us a vibrational model that is well determined by the available IR and Raman spectra without neglect of any interactions.

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Relation Between Tetrahedron Connections and Composition for Structures with Tetrahedral Anion Complexes*

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Abstract

For the classification of structures with tetrahedral anion complexes such as silicates or phosphates different parameters have been proposed, such as Zoltai's tetrahedral sharing coefficient or Liebau's connectedness and linkedness. Another parameter,

labelled TT , is discussed here, which denotes the average per tetrahedron of the sum (over all four corners of a tetrahedron) of the number of tetrahedra which are connected with one corner of the tetrahedron considered. If there are only isolated or corner-connected tetrahedra in the structure the TT parameter corresponds simply to the average number of tetrahedron-tetrahedron connections per tetrahedron. The TT parameter can be related to Zoltai's sharing coefficient and Liebau's connectedness and linkedness. The particular advantage of the introduction of the TT parameter is that it can be obtained

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