DALTON
FULL PAPER

The nature of the normal modes of $[Mo_2(CN)_8]^{4-}$

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Received 25th May 2000, Accepted 4th July 2000
Published on the Web 2nd August 2000

The $^1(\delta \longrightarrow \delta^*)$ resonance-Raman and infrared spectra of $[NEt_4]_4[Mo_2(^{13}CN)_8]$ have been determined and are compared with those previously reported for the natural-abundance isotopomer. The three totally symmetric resonance-enhanced Raman fundamentals of the ^{12}C compound in the 300–415 cm^{-1} region shift to lower wavenumbers (as, of course, do the $\nu(CN)$ bands at *ca.* 2100 cm^{-1}) and change in relative intensity upon ^{13}C substitution. Normal-coordinate calculations on the two isotopomers of the $[Mo_2(CN)_8]^{4-}$ ion reveal that the three modes responsible for the resonance-enhanced Raman bands are strongly mixed and of $\nu(MoMo)$, $\nu(MoC)$, and $\lambda_{op}(MoCN)$ parentage, and that their intensities roughly scale with the amount of $\nu(MoMo)$ character in the modes.

Many studies of the resonance-Raman spectra of quadruply metal–metal bonded complexes have been reported over the past 25 years.[1] Under resonance with the $^1(\delta \longrightarrow \delta^*)$ electronic transition, the overwhelming majority of these molecules show dominant enhancement of a single band (and its overtones) attributable to the metal–metal stretch, $\nu(MM)$. Indeed, the ease with which this band can be detected has led to the metal–metal stretching frequency being used as a fingerprint parameter for characterizing the quadruple bond.[2–9] With one exception, normal-coordinate calculations performed on these complexes[10,11] together with the metal-isotope shifts[12,13] of $\nu(MM)$ and the modest dependence of the latter upon the nature of the ligands[1] have strongly supported the interpretation of the resonance-Raman active mode as being nearly pure metal–metal stretching in character.

Recently, the Clark group reported resonance-Raman spectra of the quadruply metal–metal bonded compound $[NEt_4]_4[Mo_2(CN)_8]$ with excitation into an electronic absorption band that is clearly attributable to the $^1(\delta \longrightarrow \delta^*)$ transition.[14] A prior crystal-structure determination on the related salt $[NBu^n_4]_4[Mo_2(CN)_8]$ revealed the anion to possess the typical D_{4h} structure;[15] it was thus surprising that, in the $\nu(MM)$ region, three bands (at 411, 383, and 309 cm^{-1}) rather than one exhibited significant resonance enhancement in the Raman spectrum. The most intense of these bands, at 411 cm^{-1}, was plausibly assigned to the $\nu(MoMo)$ stretching mode on the basis of the ample precedent provided by earlier studies. Moreover, the comparatively high wavenumber of this mode, as compared with those (335–355 cm^{-1})[1] typically found for quadruply bonded Mo_2L_8 compounds that lack bridging ligands, is consistent with the fact that the metal–metal bond length of the $[Mo_2(CN)_8]^{4-}$ ion (2.122(2) Å)[15] is unusually short for compounds of this type (*ca.* 2.130–2.135 Å).[1]

Following this publication, the Hopkins group reported[11] the molecular structures and vibrational spectra of quadruply metal–metal bonded dimetallotetrayne compounds of the type $M_2(C{\equiv}CR)_4(PMe_3)_4$ (M = Mo or W).[16–21] Like $[Mo_2(CN)_8]^{4-}$, the compound $Mo_2(C{\equiv}CSiMe_3)_4(PMe_3)_4$ was found to exhibit a three-band pattern (397, 362, 254 cm^{-1}) in the resonance-Raman spectrum upon $^1(\delta \longrightarrow \delta^*)$ excitation. The resonance-Raman spectra of isotopomeric derivatives ($^{13}C{\equiv}^{13}CSiMe_3$, $C{\equiv}CSiMe_3$-d_9) display wavenumber shifts and changes in intensities of all three bands relative to those of their natural-abundance counterparts, which strongly imply that the three modes giving rise to these bands are of mixed parentage. This interpretation was supported by normal-coordinate calculations, which showed the three modes each to possess significant contributions from the $\nu(MoMo)$ and $\nu(MoC)$ stretching and $\lambda(MoCC)$ bending coordinates. Thus, the assignment of any one of these bands to $\nu(MoMo)$ is simplistic.

Despite their different compositions and point symmetries, the $[Mo_2(CN)_8]^{4-}$ ion and the $Mo_2(C{\equiv}CR)_4(PMe_3)_4$ compounds share several qualitatively similar valence vibrational coordinates involving the $Mo_2(C{\equiv}E)_n$ (E = N or CR) skeletons, including the MoMo, MoC, and CE stretches and the MoMoC and MoCE bends. In view of these similarities, the three-band pattern exhibited by the resonance-Raman spectra of the $[Mo_2(CN)_8]^{4-}$ ion as its ^{13}C isotopomer has been investigated and normal-coordinate calculations on both this compound and its natural-abundance isotopomer have been carried out.

Experimental

General procedures

The compound $[NEt_4]_4[Mo_2(^{13}CN)_8]$ was prepared by the route for the natural-abundance isotopomer[15] using $[NEt_4][^{13}CN]$ prepared from the reaction between $[NEt_4]Cl$ and $Na^{13}CN$ (99% ^{13}C, Cambridge Isotope Laboratories) in place of the natural-abundance reagent.

Infrared spectra were recorded with a Nicolet 750 Fourier-transform spectrometer on samples dispersed in either KCl (4000–650 cm^{-1}) or paraffin wax (600–50 cm^{-1}). Raman spectra were recorded on a Spex 1401 double-grating spectrometer and detected with a Burle C31034 photomultiplier. Dilute (*ca.* 10 mmol dm^{-3}) solutions in methanol were held in a spinning cell with 90° scattering geometry and excited at 568.2 nm (Coherent I301 Kr^+ laser, 40–45 mW). Wavenumber calibration with emission lines from Hg or Ne gave an estimated accuracy for the Raman bands of ±0.5–1 cm^{-1}, depending on the bandwidth. Band intensities were obtained by fitting Lorentzian functions to the observed band profiles, after correcting the

DOI: 10.1039/b004186f

Table 1 F matrix and definitions of symmetry force constants for the a_{1g} symmetry modes of $[Mo(CN)_8]^{4-}$

$$\begin{array}{ccccc}
F_{11} & & & & \\
F_{12} & F_{22} & & & \\
0 & F_{23} & F_{33} & & \\
F_{14} & 0 & 0 & F_{44} & \\
0 & F_{25} & 0 & 0 & F_{55}
\end{array}$$

$F_{11} = f(\mathrm{MoMo})$; $F_{22} = f(\mathrm{MoC}) + f^{trans}(\mathrm{MoC},(\mathrm{MoC})') + 2f^{cis}(\mathrm{MoC},(\mathrm{MoC})')$; $F_{33} = f(\mathrm{CN}) + f^{trans}(\mathrm{CN},(\mathrm{CN})') + 2f^{cis}(\mathrm{CN},(\mathrm{CN})')$; $F_{44} = f(\mathrm{MoMoC})$; $F_{55} = f(\mathrm{MoCN})$; $F_{12} = (8)^{1/2}f(\mathrm{MoMo,MoC})$; $F_{23} = f(\mathrm{MoC,CN})$; $F_{14} = (8)^{1/2}f(\mathrm{MoMo,MoMoC})$; $F_{25} = f(\mathrm{MoC,MoCN})$.

spectra for the wavelength dependence of the throughput of the spectrometer and for the ν^4 dependence of the intensity of scattered radiation.

Normal-coordinate calculations

We have performed force-field calculations on $[Mo_2(CN)_8]^{4-}$ using the Schachtschneider formulation,[22,23] following procedures outlined in our earlier work.[11] The geometry of the ion was taken from the crystal structure of $[NBu^n_4]_4[Mo_2(CN)_8]\cdot 8CHCl_3$[15] and averaged to D_{4h} symmetry, the small observed deviation (6°) of the MoCN units from linearity being neglected. The calculations we report are restricted to the a_{1g} symmetry modes. No experimental band wavenumbers are available for the non-totally symmetric gerade modes. While six infrared band wavenumbers are available for each of the two isotopomers studied, these comprise too small a subset of the ten infrared-active ($4a_{2u} + 6e_u$) fundamentals to allow meaningful force-field refinement, particularly because we cannot experimentally distinguish between modes of a_{2u} and e_u symmetry.

For the a_{1g} block the F matrix was defined as set out in Table 1; the F_{ij}'s are symmetry force constants, while f's are valence force constants. There are five totally symmetric modes, as set out in Table 1 of the earlier work:[14] ν(MoMo), ν(MoC), ν(CN), δ(MoMoC), and λ_{op}(MoCN). Note that in this work the terminology λ_{op} and λ_{ip} is used for the bending modes that were denoted $\delta(\mathrm{MoCN})_{ax}$ and $\delta(\mathrm{MoCN})_{eq}$, respectively, in the earlier report;[14] the ip and op subscripts refer to bending motions in and out of the approximate MoC_4 planes. The label λ for the bending mode of a linear ABC triatomic molecule goes back to the early days of vibrational spectroscopy. It is useful to identify linear or nearly linear ABC bends of metal complexes by this label because such modes are generally of much higher wavenumber than other types of bending mode involving metal atoms.

Given a full set of coordinates sufficient to describe all of the vibrations of the molecule, there is a redundancy in the a_{1g} block because one of the coordinates can also be generated from CMoC bending coordinates. We have chosen to delete the δ(CMoC) coordinate from the a_{1g} F and G matrices, which causes no loss of mathematical generality (although δ(CMoC) is a necessary coordinate in some other symmetry blocks). The expressions given for the symmetry force constants in terms of valence force constants neglect the interaction force constants between the two $Mo(CN)_4$ halves of the molecule, as these force constants are expected to be very small. This is actually mathematically irrelevant to the calculation because the inclusion of this type of interaction force constant simply results in the diagonal force constants having additive or subtractive terms involving the interaction constants. We cannot rigorously extract the valence force constants from the symmetry force constants in the absence of refined force constants for other symmetry blocks.

Because the a_{1g} F matrix contains a total of 15 possible force constants whereas we possess only eight experimentally determined band wavenumbers, several assumptions must be made. The force constant F_{35} was set to zero on the basis that the analogous force constants are small for well studied metal–cyanide complexes such as $[Au(CN)_4]^-$ and $[Fe(CN)_6]^{3-}$.[24–26] F_{13} was set to zero on the plausible basis that there are no shared atoms involving the two motions. F_{45} was neglected because bending/bending interaction force constants are usually negligible. F_{34} was neglected because the bending motion shares only one atom with the stretching motion, a situation that generally results in small interaction force constants. Our neglect of F_{24} and F_{15} is somewhat arbitrary, although a tenuous analogy can be made to F_{35}. Some attempts were made to refine a value for F_{15}; these did not converge well (multiple minima were observed, so the number of parameters had evidently outmatched the number of experimental data), but did support the idea that the value of this parameter was small. The somewhat analogous force constant F_{14} was included in the force field because previous work[11,27–30] had indicated it to have a significant effect on the wavenumber of the nominal metal–metal stretching mode.

Initial estimates for F_{22}, F_{23}, F_{33}, F_{25}, and F_{55} were obtained from the literature force fields of metal–cyanide complexes. An initial estimate for F_{11} of 4.08 mdyn $Å^{-1}$ † was calculated from Woodruff's bond-distance/force constant correlation,[31] while f(MoMo,MoC) was arbitrarily set initially at 0.1 mdyn $Å^{-1}$ (hence $F_{12} = (0.1)(8)^{1/2} = 0.282843$ mdyn $Å^{-1}$). F_{44} and F_{14} were problematic: we initially set them to values of 1.0 mdyn Å rad^{-2} and 0.282843 mdyn rad^{-1}, respectively, guided in part by early force fields on dinuclear complexes.[10] The observed ν(CN) values were corrected for anharmonicity as recommended by Jones *et al.*;[24] thus, the ν(CN) values of 2113 (^{12}C) and 2070 cm^{-1} (^{13}C) were converted into harmonic ω(CN) values of 2133 (^{12}C) and 2090 cm^{-1} (^{13}C). This correction has little effect on any part of calculated force fields other than F_{33}. Jones' work suggests that anharmonicity corrections for vibrations <500 cm^{-1} are unlikely to be significant. All calculations simultaneously fit the ^{12}C and ^{13}C data.

Initial test calculations (which did not involve force-constant optimization) immediately indicated that the three ^{13}C-sensitive bands in the 300–420 cm^{-1} region are attributable to ν(MoMo), ν(MoC), and λ_{op}(MoCN) modes, and that these three modes are quite strongly mixed. An additional mode, calculated to occur at *ca.* 80 cm^{-1}, had fairly pure (80%) δ(MoMoC) character. Placing this mode in the 300–420 cm^{-1} region would require absurdly high values of F_{44}; for example, increasing F_{44} to 3 mdyn Å rad^{-2} increases the calculated wavenumber of the lowest-wavenumber mode only to 114 cm^{-1}, although it must be cautioned that this effect is in part due to increased mixing with the λ_{op}(MoCN) mode as F_{44} increases. An effort to locate this Raman fundamental experimentally was unsuccessful, but this is consistent with the fact that the resonance-Raman intensity of this band should be very weak (see below).

Consideration of literature calculations on $[MM'(CO)_{10}]^{n-}$ complexes,[27–30] which have an analogous bending mode, suggests that a lower value for F_{44} than our initial estimate is more likely to be correct. We ultimately adopted 0.4 mdyn Å rad^{-2} as a fixed value; there is no hope of refining F_{44} without experimental values for the low-wavenumber mode. Attempts to refine F_{14} also proved to be ill behaved so it was set equal to 0.282843 mdyn rad^{-1}, the same value as in our original assumptions. We have, however, performed a number of calculations in which the values of F_{44} and/or F_{14} were fixed at different values, and some discussion of these will be presented.

Results and discussion

Resonance-Raman assignments

Resonance-Raman spectra of $[Mo_2(^{12}CN)_8]^{4-}$ and $[Mo_2(^{13}CN)_8]^{4-}$ are shown in Fig. 1, and band wavenumbers and

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† 1 mdyn $Å^{-1} = 10^2$ N m^{-1}.

Table 2 Resonance-Raman data and assignments for $[Mo_2(^{12}CN)_8]^{4-}$ and $[Mo_2(^{13}CN)_8]^{4-}$ [a]

$[Mo_2(^{12}CN)_8]^{4-}$		$[Mo_2(^{13}CN)_8]^{4-}$				
Wavenumber [b]/cm^{-1}	I [c]	Wavenumber/cm^{-1}	I [c]	Isotope shift/cm^{-1}	Assignment [b]	Mode number [d]
309	18	303	11	6	λ_{op}(MoCN) [e]	ν_4
383	6	374	3	9	ν(MoC)	ν_3
411	34	406	34	5	ν(MoMo)	ν_2
619	5	604	5	12	$2\lambda_{op}$(MoCN) [e]	$2\nu_4$
719	16	707	13	12	ν(MoMo) + λ_{op}(MoCN) [e]	$\nu_2 + \nu_4$
≈790	3	[f]	—	—	ν(MoC) + ν(MoMo)	$\nu_3 + \nu_2$
822	16	812	14	10	2ν(MoMo)	$2\nu_2$
1130	(10) [g]	1111	—	19	2ν(MoMo) + λ_{op}(MoCN) [e]	$2\nu_2 + \nu_4$
1231	(4) [g]	[h]	—	—	3ν(MoMo)	$3\nu_2$
2113	2	2070	1	43	ν(CN)	ν_1

[a] Recorded in methanol solution; λ_{ex} = 562.8 nm. [b] From ref. 14. [c] Intensities scaled so that $I[\nu$(MoMo)] is the same for both isotopomers. [d] The PEDs of these modes, as determined by normal-coordinate calculations, are set out in Table 4. [e] On the basis of normal-coordinate calculations this mode is better described as λ_{op}(MoCN) than as δ(MoMoC) (the assignment given in ref. 14). [f] Overlapped by 812 cm^{-1} band. [g] Values in parentheses were evaluated using band subtraction techniques on account of solvent interference. [h] Overlapped by MeOH band.

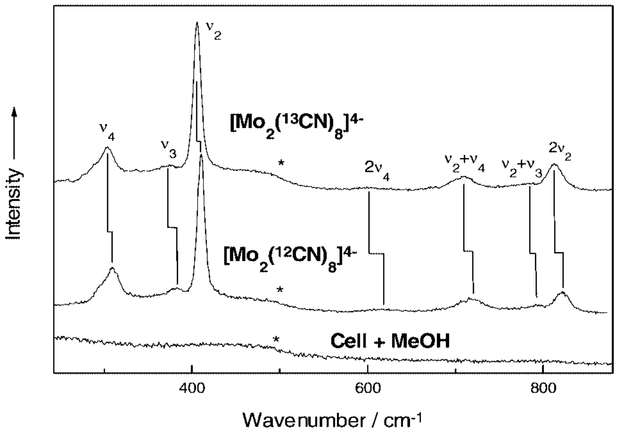

Fig. 1 Resonance-Raman spectra of $[NEt_4]_4[Mo_2(^{12}CN)_8]$ and $[NEt_4]_4[Mo_2(^{13}CN)_8]$ in methanol solution with 568.2 nm excitation over the spectral range 250–900 cm^{-1}. The cell/solvent background is also shown, the features marked with asterisks being due to the cell.

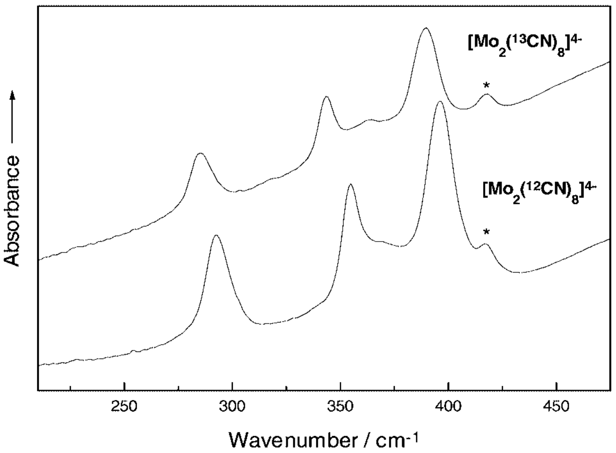

Fig. 2 The FTIR spectra of $[NEt_4]_4[Mo_2(^{12}CN)_8]$ and $[NEt_4]_4[Mo_2(^{13}CN)_8]$ as paraffin wax discs at 20 °C over the spectral range 210–475 cm^{-1}. The asterisks mark bands due to $[NEt_4]^+$.

intensities are set out in Table 2. The three prominent vibrational bands in the 300–420 cm^{-1} region are clearly attributable to totally symmetric modes, as expected from theoretical considerations for resonance-Raman enhancement.[32] Specifically, the bands at 411 and 309 cm^{-1} (values for ^{12}C isotopomer) are polarized, with depolarization ratios close to the expected value of 1/3 for totally symmetric modes resonance enhanced *via* a single-axis polarized electronic transition. While the band at 383 cm^{-1} is too weak to allow measurement of its depolarization ratio, observation of a combination band with the 411 cm^{-1} fundamental confirms the assignment of this band to a totally symmetric mode. The nominal assignments of these bands can be expected to include ν(MoMo) (by comparison to resonance-Raman spectra of other dimolybdenum(II) complexes)[1–4,6,9] as well as ν(MoC) and λ_{op}(MoCN) modes (by comparison to other metal–cyanide complexes).[24,25,33] However, the fact that all three bands exhibit substantial shifts for the ^{13}C isotopomer indicates that mixing among the zero-order vibrational modes is large and that assignments of these bands to simple modes are inappropriate. This is supported by force-field calculations presented later on in this paper.

The $\nu(^{12}CN)$ band observed at 2113 cm^{-1} is extremely weak relative to the low-wavenumber bands in the resonance Raman spectrum, and it is possible, in fact, that its observed intensity might not be enhanced by resonance with the $^1(\delta \longrightarrow \delta^*)$ transition. The totally symmetric ν(CN) mode of metal–cyanide complexes usually gives rise to the most intense band observed in non-resonance-Raman spectra. Since the 2113 cm^{-1} band is the most intense feature in the non-resonance-Raman spectrum of $[Mo_2(CN)_8]^{4-}$ (λ_{ex} = 1064 nm)[14] it follows that it should be assigned to the a_{1g} symmetry ν(CN) mode. Thus, wavenumbers are in hand for four out of the total of five (according to group theory)[14] a_{1g} symmetry fundamentals.

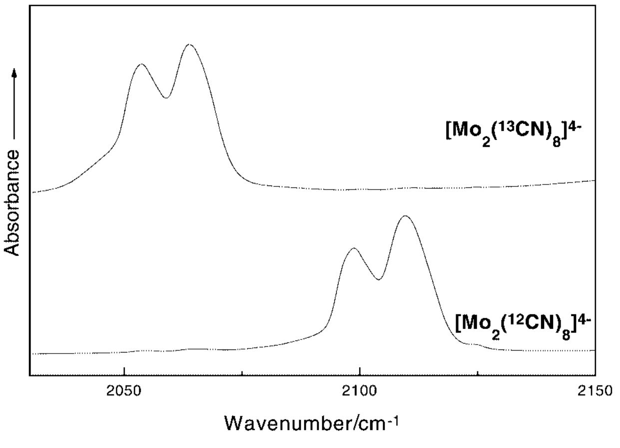

Fig. 3 The FTIR spectra of $[NEt_4]_4[Mo_2(^{12}CN)_8]$ and $[NEt_4]_4[Mo_2(^{13}CN)_8]$ as KCl discs at 20 °C over the spectral range 2030–2150 cm^{-1}.

Infrared assignments

The wavenumbers of the bands observed in the IR spectra of $[NEt_4]_4[Mo_2(^{12}CN)_8]$ and $[NEt_4]_4[Mo_2(^{13}CN)_8]$ are set out in Table 3 and illustrated in Figs. 2 and 3. For solid samples there are two distinct bands in the ν(CN) stretching region, at 2110 and 2099 cm^{-1} for the ^{12}C isotopomer and 2065 and 2053 cm^{-1}

Table 3 Infrared spectroscopic data and assignments for $[NEt_4]_4[Mo_2(^{12}CN)_8]$ and $[NEt_4]_4[Mo_2(^{13}CN)_8]$[a]

Wavenumber/cm^{-1}		Isotope shift/ cm^{-1}	Assignment
$[Mo_2(^{12}CN)_8]^{4-}$ [b]	$[Mo_2(^{13}CN)_8]^{4-}$		
294m	287m	7	λ_{op}(MoCN)
356m	344m	12	e_u ν(MoC)[c]
370w	365w	5	a_{2u} ν(MoC)[c]
397s	390s	7	λ_{ip}(MoCN)[c]
418w	418w	0	$[NEt_4]^+$ [c]
2099m	2053m	46	ν(CN)
2110s	2065s	45	ν(CN)

[a] Solid samples dispersed in KCl (4000–650 cm^{-1}) or paraffin wax (600–50 cm^{-1}). [b] Data from Ref. 14. [c] Assignment revised from Ref. 14.

for the ^{13}C isotopomer. Under D_{4h} symmetry these are expected to arise from e_u and a_{2u} symmetry modes; the stronger and higher-wavenumber of the two bands is assigned to the e_u symmetry mode on the basis of a simple dipole-addition model for their intensities, which predicts a substantially higher intensity for the e_u mode than for the a_{2u} mode because the Mo–Mo–C angle (103.7°) is close to 90°. For the ^{12}C isotopomer in methanol solution these bands are shifted to 2123 and 2115 cm^{-1}; the shifts are attributable to hydrogen bonding between the cyanide ligands and the methanol solvent. The close similarity in wavenumber between the IR band (MeOH solution) at 2115 cm^{-1} and the Raman band (MeOH solution) of a_{1g} symmetry at 2113 cm^{-1} is consistent with the expectation that there should be little coupling between CN oscillators across the metal–metal bond; that is, the wavenumbers should be identical in the absence of such coupling. However, the sizable shifts between solution and solid-state values highlight the dangers involved in comparing vibrational data obtained for cyanide complexes in different media.

The low-wavenumber bands are more difficult to assign. A feature observed at 418 cm^{-1} does not shift upon ^{13}C substitution of the anion and, moreover, coincides with the strongest band of $[NEt_4]Br$ in this spectral region. The prior assignment of this band to a ν(MoC) mode[14] must, therefore, be withdrawn. The remaining four bands in the 250–400 cm^{-1} region are all ^{13}C sensitive and, by analogy to the literature,[24,33] assignments are suggested as follows: 350–380 cm^{-1}, ν(MoC) (a_{2u} and e_u); *ca.* 290 cm^{-1}, λ_{op}(MoCN) (a_{2u} and e_u); *ca.* 390 cm^{-1}, λ_{ip}(MoCN) (e_u). The more intense of the two bands in the 350–380 cm^{-1} region (356 cm^{-1} for the ^{12}C isotopomer) is suggested to be the e_u symmetry ν(MoC) mode, once again on the basis of a dipole-addition intensity model. The high wavenumber of the λ_{ip}(MoCN) mode relative to that of the λ_{op}(MoCN) mode is expected by comparison with square-planar $[M(CN)_4]^{n-}$ complexes, for which the in-plane MCN bending force constants are found to be substantially larger than the out-of-plane ones; this has been attributed to repulsive interactions for in-plane bending that contribute to the restoring forces.[25] The situation for $[Mo_2(CN)_8]^{4-}$ is, plausibly, similar because of the near-planar geometry of the $Mo(CN)_4$ units.

It is possible that the above lines of argument may be flawed because mixing among MoC stretching and MoCN bending coordinates is expected to be very large;[24] this circumstance will lead to modifications to the wavenumbers and intensities of the bands, except for those attributed to the ν(CN) modes, which are energy factored. Accordingly, the assignments for these modes are tentative.

Normal-coordinate calculations

The calculated force field for the a_{1g} symmetry vibrational modes of $[Mo_2(^{12}CN)_8]^{4-}$ and $[Mo_2(^{13}CN)_8]^{4-}$ is presented in Table 4. The modes are denoted in Table 4 as ν_1–ν_5, in order of decreasing wavenumber. The agreement between the calculated and observed band wavenumbers is excellent. The refined force constants in Table 4 are all reasonable by comparison to the literature. Owing to the small range of wavenumbers of the three observed ν(CN) modes, F_{33} should be close to f(CN). However, $f^{trans}(MC,(MC)')$ is usually found to be positive and only about 10–20% as large as f(MC), so F_{22} is likely to be an overestimate of f(MoC).[24,25,34]

The potential energy distributions in Table 4 reveal a similarity between the calculated amounts of MoMo stretching character in the modes and the relative intensities of the observed resonance-Raman bands. This is highlighted in Table 5, where both experimental resonance-Raman intensities and calculated MoMo character are compared for these modes. The δ(MoMoC) mode (ν_5) has very little MoMo character, as indicated by the potential energy distribution (PED), and hence it would be expected to give rise to a band of insufficient intensity to appear above the solvent background.

This pseudo-quantitative correlation can be explained if the $^1(\delta \longrightarrow \delta^*)$ excitation band for which resonance-Raman data were obtained involves an excited-state distortion nearly exclusively along the MoMo internal coordinate. This view is entirely consistent with previous studies of $^1(\delta \longrightarrow \delta^*)$ resonance-Raman spectra; the complication in the case at hand is that there is extensive mixing of the MoMo stretching coordinate into several vibrational modes. This is the same

Table 4 Results of normal-coordinate calculations of the a_{1g} symmetry fundamental vibrations of $[Mo_2(CN)_8]^{4-}$

	Wavenumber/cm^{-1}		Potential energy distribution (%)				
Mode	obs.	calc.	ν(MoMo)	ν(MoC)	ν(CN)	δ(MoMoC)	λ_{op}(MoCN)
$\nu_1(^{12}C)$	2133[a]	2134.8	0.0001	3.61	96.4	0	0
$\nu_1(^{13}C)$	2090[a]	2088.0	0.0001	3.36	96.6	0	0
$\nu_2(^{12}C)$	411	411.1	50.1	2.3	0.001	7.00	40.6
$\nu_2(^{13}C)$	406	406.7	58.4	1.42	0.02	6.50	33.7
$\nu_3(^{12}C)$	383	381.3	18.1	63.1	3.46	0.20	15.2
$\nu_3(^{13}C)$	374	374.4	10.8	64.1	3.11	0.52	20.6
$\nu_4(^{12}C)$	309	308.2	32.3	42.2	0.43	0.32	24.8
$\nu_4(^{13}C)$	303	302.5	29.8	41.8	0.40	0.40	27.5
$\nu_5(^{12}C)$	—	54.0	0.98	0.53	0	91.8	6.7
$\nu_5(^{13}C)$	—	53.5	0.95	0.51	0	92.1	6.47

Symmetry force constants[b]: $F_{11} = 4.606$ mdyn $Å^{-1}$; $F_{12} = 1.091$ mdyn $Å^{-1}$; $F_{22} = 2.056$ mdyn $Å^{-1}$; $F_{23} = 0.0642$ mdyn $Å^{-1}$; $F_{33} = 16.819$ mdyn $Å^{-1}$; $F_{14} = [0.282843$ mdyn $rad^{-1}]$[c]; $F_{44} = [0.4$ mdyn Å $rad^{-2}]$[c]; $F_{25} = -0.1228$ mdyn rad^{-1}; $F_{55} = 0.3667$ mdyn Å rad^{-2}.

[a] Experimental value corrected for anharmonicity. See Experimental section. [b] See Table 1 for definitions of force constants. The number of significant figures given for the force constants is that required to produce the calculated mode wavenumbers and PEDs with precision. The accuracy of the force constants is certainly much lower, perhaps to two significant figures. [c] Values given in brackets were constrained.

Table 5 Resonance-Raman intensities and calculated relative PED content of the MoMo coordinate for a_{1g} symmetry modes of $[Mo_2(CN)_8]^{4-}$

	I^a		Relative content of MoMo stretch in calculated PED ^{b}	
Mode	^{12}C	^{13}C	^{12}C	^{13}C
ν_1	0.06	0.03	2×10^{-6}	2×10^{-6}
ν_2	1	1	1	1
ν_3	0.18	0.09	0.362	0.185
ν_4	0.53	0.32	0.644	0.511
ν_5	^{c}	^{c}	0.0195	0.0163

^{a} Intensities relative to those of the 411 cm^{-1} band (^{12}C) or the 406 cm^{-1} band (^{13}C); data from Table 2. ^{b} Data from Table 4. ^{c} Not observed.

situation that was observed for the $Mo_2(C{\equiv}CR)_4(PMe_3)_4$ complexes.[11]

That the correlation is not better than it is probably reflects deficiencies in the force field. The mixing of the internal coordinates involved in ν_2, ν_3, and ν_4 is very sensitive to the various force constants; indeed, the isotope sensitivity of the relative resonance-Raman intensities is an indication of the delicate balance that is involved.

We tested the possible limitations of the force field by examining the effect of changing the assumptions about the fixed values of F_{14} and F_{44}. The calculated force field is not particularly sensitive to F_{44} as long as the value of the latter is *ca.* <1 mdyn Å rad^{-2}, although the PEDs do show some variation. However, there is a surprisingly large sensitivity of the force field to F_{14}. For example, if the value of F_{14} is fixed to zero the refined force field gives $F_{11} = 4.058$ mdyn Å^{-1}, quite close to the value predicted by Woodruff's correlation[31] (4.08 mdyn Å^{-1}). By contrast, the value in the force field presented here (4.606 mdyn Å^{-1}, Table 4) is surprisingly close to the 'diatomic' value of 4.77 mdyn Å^{-1} based upon an assignment of ν_2 as a pure MoMo stretching mode.[14] Outside of the dramatic change in F_{11} the differences between the two force fields are subtle and distributed over many force constants. This alternative force field is definitely not preferable to the one presented in Table 4; its RMS error in duplication of wavenumbers is over a factor of two worse (concentrated in a poor duplication of ν_4), and the PEDs show much larger mixing of the MoMo stretching coordinate into ν_3 than would be consistent with our explanation of the resonance-Raman intensity effects.

We emphasize that our force field is tentative and that the important MoMo stretching force constant can be (arguably) claimed to be determined only to within 10%. Nonetheless, the vibrational mixing effects that are clearly made evident by the results provide the key to understanding the complicated resonance-Raman spectrum of $[Mo_2(CN)_8]^{4-}$.

Conclusion

We have now established two examples of quadruply metal–metal bonded complexes of the type $M_2(AB)_n$ in which there is strong vibrational coupling among the ν(MM), ν(MA), and λ_{op}(MAB) modes. A key factor for both $[Mo_2(CN)_8]^{4-}$ and $Mo_2(CCR)_4(PMe_3)_4$[11] is that the three active modes have similar wavenumbers. For the λ_{op}(MAB) mode to have such a high wavenumber (for a metal-involved bending mode) the AB force constant must be high, according to our normal-mode calculations, a situation that is achieved for these examples by the AB unit having a triple bond.

The possibility of such coupling should be considered for general classes of metal–metal bonded complexes (including those with M_2 bond orders less than four) in which wavenumber matches similar to those of our examples are present.

Acknowledgements

The support of this research by the National Science Foundation (Grant CHE 9700451 to M. D. H.), the University of London Intercollegiate Research Service and the Engineering and Physical Sciences Research Council (to R. J. H. C.) is gratefully acknowledged.

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