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Vibrational and electronic spectroscopy of the octacyanodimolybdate ion, $[Mo_2(CN)_8]^{4-}$

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The infrared, Raman and resonance-Raman spectra of $[NEt_4]_4[Mo_2(CN)_8]$ have been recorded in solution and the solid state, and the important features of each assigned. The strong, polarised Raman band at 411 cm^{-1} is assigned to ν(MoMo), the highest reported ν(MoMo) value for a quadruply bonded, unbridged dimolybdenum complex. Resonance-Raman studies have shown that ν(MoMo) is coupled to a strong electronic band at 16 580 cm^{-1}. The depolarisation ratio of the band at 411 cm^{-1} is *ca.* $\frac{1}{3}$ at resonance, which indicates that the resonant transition is axially polarised, consistent with its assignment to the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition.

Despite the wide range of quadruply metal–metal bonded dimolybdenum compounds already known,[1] new and relatively simple complexes continue to be discovered.[2] One such complex which has only recently been characterised definitively is the octacyanodimolybdate ion, $[Mo_2(CN)_8]^{4-}$.[3] This was first described, albeit briefly, by Garner and Senior[4] who found that the reaction of $[Mo_2(O_2CCF_3)_4]$ with NEt_4CN gave a bright blue product which could be formulated as $[NEt_4]_4[Mo_2(CN)_8]$ on the basis of elemental analysis; the complex was not however characterised further at that time. A more recent, systematic examination of the substitution of acetate ligands in $[Mo_2(O_2CCH_3)_4]$ by cyanide has led to the isolation of tetraalkylammonium salts of $[Mo_2(CN)_8]^{4-}$, of which the tetra-*n*-butylammonium salt was characterised by X-ray crystallography.[3] The crystal structure of this previously ill defined complex confirmed that it contained a Mo–Mo bond, which is the shortest known (2.122 Å) for an unbridged $[Mo_2L_8]^z$ species. The challenge to relate physical and structural parameters for quadruply metal–metal bonded complexes prompted investigation of the vibrational and electronic spectroscopy of this structurally simple ion.

Experimental

The salt $[NEt_4]_4[Mo_2(CN)_8]$ was prepared as described by Dunbar and co-workers[3] from $[Mo_2(O_2CCH_3)_4]$[5] and NEt_4CN[6] using CH_2Cl_2 freshly distilled from CaH_2. Dry samples were found to be stable in air. Other solvents were of analytical grade and used as received unless stated otherwise.

Solution Raman spectra were recorded by the use of a spinning cell at room temperature, with the 90° scattering geometry, the laser propagation direction being parallel to the spectrometer entrance slit and its polarisation being orthogonal to a line joining the sample and the spectrometer entrance slit. Excitation wavelengths (λ_0) corresponding to the emission lines of Ar^+ and Kr^+ were provided by Coherent I200 and I301 lasers, respectively. Other excitation wavelengths were provided by a CR 599 dye laser employing rhodamine 6G. The radiation power at the sample was typically 50 mW. The scattered light was dispersed by a Spex 1401 double-grating spectrometer and detected with a Burle C31034 photomultiplier. Wavenumber calibration was achieved by superposition of neon emission lines on the sample spectrum. Polarisation measurements involved the use of the sampling arrangement described above, with the addition of an analyser positioned between the collection lens and the polarisation scrambler. Solid-state Raman spectra of samples dispersed in spectroscopic grade KBr were recorded at low temperature (≈90 K) using a purpose-built cryostat cooled with liquid nitrogen. All Raman band intensities were corrected for the spectral response of the instrument. Fourier-transform Raman spectra were recorded with a Nicolet 910 spectrometer, infrared and far-infrared spectra with a Nicolet 750 Fourier-transform spectrometer, the samples being dispersed in spectroscopic grade KBr (mid infrared) and paraffin wax (far infrared). Solution electronic spectra were recorded using a Perkin-Elmer Lambda 16 spectrometer.

Results and Discussion

Raman and infrared spectra

The $[Mo_2(CN)_8]^{4-}$ ion adopts an eclipsed geometry (torsional angle = 0°) in the solid state and is assumed to retain this conformation in solution. It therefore belongs to the D_{4h} point group and has 48 normal modes of vibration, the classification of which is summarised in Table 1. The normal modes are comprised of 23 Raman-active modes ($5a_{1g}$, $4b_{1g}$, $2b_{2g}$ and $6e_g$), six of which are degenerate, 16 infrared-active modes ($6e_u$ and $4a_{2u}$), six of which are degenerate, and nine inactive modes (a_{2g}, $2a_{1u}$, $2b_{1u}$ and $4b_{2u}$). Of the predicted Raman-active modes, four bands are observed that can be attributed to fundamental vibrations (Table 2). For off-resonance excitation [*e.g.* λ_0 = 514.5 nm, Fig. 1(*a*)] a band at 411 cm^{-1} and a broad weaker band at 309 cm^{-1} are observed. There is also a band at 2113 cm^{-1} which, although comparatively weak for resonance excitation, is the most intense feature for λ_0 = 1064 nm. A further band that can be attributed to a fundamental vibration is located at 383 cm^{-1}, but this can only be observed under resonance conditions. Polarisation measurements show that the bands at 411 and 309 cm^{-1} are each polarised, with ρ = 0.32 (0.05) and 0.3 (0.1) respectively (λ_0 = 514.5 nm), hence each of these bands arises from an a_{1g} mode.

The polarised band at 411 cm^{-1} is assigned to ν(MoMo) which is frequently the most intense feature in the Raman spectra of quadruply metal–metal bonded complexes of the type $[M_2L_8]^z$;[7,8] ν(MoC) may also be anticipated to occur in this region of the spectrum,[9] but ν(MC) Raman bands are often very weak and not observed directly.[10] The band at 383 cm^{-1}, which is more readily observed under resonance conditions, is assigned to ν(MoC). This must be the a_{1g} mode, in order for it to couple with ν(MoMo) and give rise to the combination band at ≈790 cm^{-1}, detectable when λ_0 lies in the range 568.2–647.1 nm (see below). The polarised band at 309 cm^{-1} is then assigned to the a_{1g} δ(MoMoC) bend, given that this mode is also likely to combine with ν(MoMo) on resonance to give rise to the

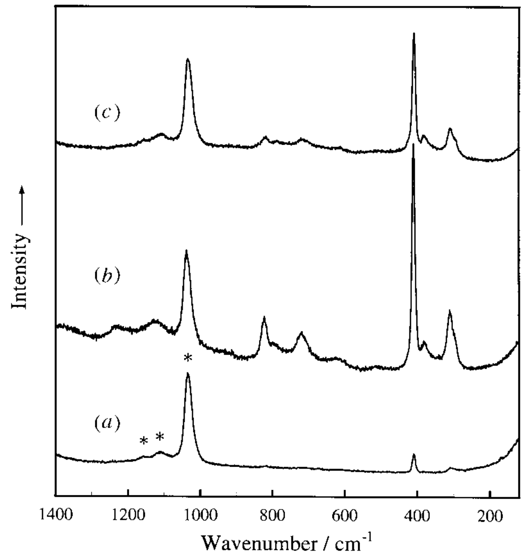

Fig. 1 Raman and resonance-Raman spectra of $[NEt_4]_4[Mo_2(CN)_8]$ in methanol with $\lambda_0 = 514.5$ (*a*), 599.2 (*b*) and 647.1 nm (*c*). The complex concentrations for (*a*) and (*c*) were 4.9 mmol dm^{-3} and for (*b*) 2.2 mmol dm^{-3}. Asterisks locate the solvent bands. Spectra were recorded with a step size of 1 cm^{-1} and an integration time of 4 s

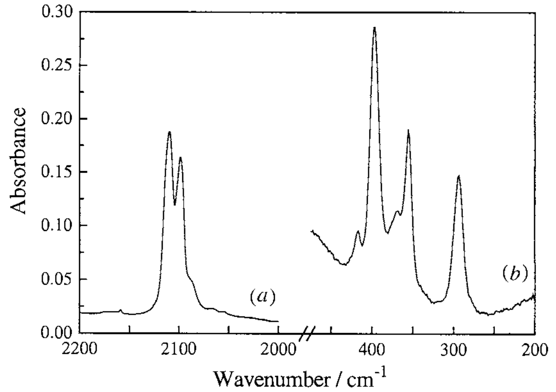

Fig. 2 Infrared spectra of $[NEt_4]_4[Mo_2(CN)_8]$: (*a*) ν(CN) region of the mid-infrared spectrum (KBr disc) and (*b*) far-infrared spectrum (paraffin-wax disc)

observed combination bands at 719 and 1130 cm^{-1} (see below). The remaining band at 2113 cm^{-1} arises from a ν(CN) mode, probably that of a_{1g} symmetry; however this could not be established with certainty since its weakness precluded measurement of the depolarisation ratio.

The important features of the infrared spectrum are shown in Fig. 2 and the band wavenumbers are summarised in Table 3. In the ν(CN) stretching region [Fig. 2(*a*)] the two bands expected (Table 1) are observed at 2110 and 2099 cm^{-1}. The ν(CN) values relative to that of free cyanide in aqueous solution (2080 cm^{-1})[11] indicate that there is little π-back bonding from the molybdenum d_π orbitals to the π* orbitals of the cyanide and hence that the cyanide ligands are behaving predominantly as σ donors. The low-wavenumber region [Fig. 2(*b*)] is more difficult to assign definitively, in the absence of isotopic labelling studies. The two bands at highest wavenumber, 418 and 397 cm^{-1}, are assigned to ν(MoC) whilst the remaining bands, at 370, 356 and 294 cm^{-1}, are attributed to δ(MoMoC) and δ(MoCN) modes. These assignments are however tentative, since there is considerable debate as to the ordering of ν(MC) and δ(MCN) for simple monomeric complexes such as the square-planar $[M(CN)_4]^{2-}$ systems, M = Ni, Pd or Pt.[12] In addition there is a notable lack of detailed vibrational studies on homoleptic divalent molybdenum cyanide complexes to help in the assignment of such bands. The salt $K_4[Mo(CN)_6]$ has been reported, but is only poorly characterised and infrared data are limited to ν(CN) values.[13]

Table 1 Distribution of normal modes of vibration of the $[Mo_2(CN)_8]^{4-}$ ion

	Distribution^a (D_{4h} molecular symmetry)									
Mode	a_{1g}	a_{2g}	b_{1g}	b_{2g}	e_g	a_{1u}	a_{2u}	b_{1u}	b_{2u}	e_u
ν(MoMo)	1									
ν(MoC)	1		1		1		1		1	1
ν(CN)	1		1		1		1		1	1
$\delta(MoMoC)_{ax}{}^b$	1		1		1		1		1	1
$\delta(MoCN)_{ax}{}^b$	1		1		1		1		1	1
$\delta(CMoC)_{eq}{}^b$				1	1			1		1
$\delta(MoCN)_{eq}{}^b$		1		1	1	1		1		1
MoMo torsion						1				
Total	5	1	4	2	6	2	4	2	4	6

^{a} Raman active: $5a_{1g} + 4b_{1g} + 2b_{2g} + 6e_g$. Infrared active: $4a_{2u} + 6e_u$. Inactive: $a_{2g} + 2a_{1u} + 2b_{1u} + 4b_{2u}$. ^{b} ax = Axial, eq = equatorial.

Electronic and resonance-Raman spectra

The electronic absorption spectrum of a dilute solution of the $[Mo_2(CN)_8]^{4-}$ ion is shown in Fig. 3, the dominant feature being a symmetric, moderately intense band ($\varepsilon = 2700$ dm^3 mol^{-1} cm^{-1}) centred at 16 580 cm^{-1}, and thus responsible for the deep blue colour of the sample. It has been suggested that this band should be assigned to the electric dipole-allowed $^1A_{2u} \longleftarrow {}^1A_{1g}$ $[(\delta^*)(\delta) \longleftarrow (\delta)^2]$ transition.[3] Resonance-Raman spectra, where λ_0 falls within the contour of the absorption band in the visible region ($\lambda_0 = 568.2$–647.1 nm), show significant enhancement to the intensity of the band attributed to ν(MoMo) (Table 2). In particular, the excitation profile for ν(MoMo), superimposed on the electronic absorption spectrum in Fig. 3, approximately matches the contour of the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition. The resonance-Raman spectrum for $\lambda_0 = 599.2$ nm is shown in Fig. 1(*b*). A short progression in ν(MoMo) is observed, up to 3ν(MoMo), for which the overtone bands show the expected decrease in intensity and increase in bandwidth which typically accompany an increase in vibrational quantum number. These results are consistent with the assignment of the visible absorption band to the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition, since the principal structural change associated with such a transition is anticipated to occur along the Mo–Mo coordinate. Resonance-Raman studies of other quadruply metal–metal bonded $[M_2X_8]^z$ complexes have shown intensification to the band assigned to ν(MM) and long progressions in ν(MM) when λ_0 is coincident with the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition.[14–16] The band attributed to ν(MoMo) is polarised with a depolarisation ratio (ρ) at resonance ($\lambda_0 = 599.2$ nm) of $\rho = 0.29$ (0.05), consistent with that expected ($\frac{1}{3}$) for a totally symmetric vibration coupled to an electronic transition between non-degenerate states.[17] This result confirms the axial polarisation of the resonant transition.

Other features of the resonance-Raman spectrum shown in Fig. 1(*b*) include an overtone of δ(MoMoC) at 619 cm^{-1} and combination bands at 719 [ν(MoMo) + δ(MoMoC)] and 1130 cm^{-1} [2ν(MoMo) + δ(MoMoC)]. The weak, secondary progression is clearly evident in the solid-state spectrum where interference from solvent absorption bands is absent. The solid-state resonance-Raman and electronic spectra of $[NEt_4]_4[Mo_2(CN)_8]$ dispersed in KBr were recorded at *ca.* 90 K. The spectra for the region <1300 cm^{-1} were generally similar to those obtained from solution measurements, with some minor splittings of bands and small shifts in peak wavenumbers. Strong fluorescence was observed at Stokes shifts >1300 cm^{-1}. The low-temperature electronic spectrum revealed some struc-

Table 2 Raman band wavenumbers, assignments and relative intensities

Wavenumber[a]/cm^{-1}	Assignment	Relative integrated band intensities[b] at various λ_0/nm						
		514.5	568.2	586.0	599.2	621.7	647.1	676.5
309[c]	δ(MoMoC)	2	22	33	66	45	23	2
383	ν(MoC)	—	10	15	41	35	17	1
411[c]	ν(MoMo)	6	34	61	100	74	37	6
619	2 δ(MoMoC)	—	6	21	35	11	8	—
719	ν(MoMo) + δ(MoMoC)	—	19	30	66	46	22	—
≈790	ν(MoC) + ν(MoMo)	—	6	16	43	28	8	—
822	2 ν(MoMo)	—	10	19	26	18	7	—
1130	2 ν(MoMo) + δ(MoMoC)	—	(10)	(8)	(27)	(38)	(5)	—
1231	3 ν(MoMo)	—	(4)	(15)	(19)	(15)	(1)	—
2113	ν(CN)	*d*	2	*d*	*d*	*d*	2	*d*

[a] Recorded in methanol. [b] The ν(MoMo) band at 411 cm^{-1} (λ_0 = 599.2 nm) was assigned an arbitrary intensity of 100 and all other intensities were measured relative to this band. Bands marked — have relative intensities of <1, whilst those in parentheses were evaluated using band-subtraction techniques on account of the solvent interference. Such intensities are therefore less reliable, and particularly so for the band at 1130 cm^{-1}. [c] Polarised. [d] Spectrum not measured in this region.

Table 3 Infrared band wavenumbers and assignments

Wavenumber/cm^{-1}	Assignment
294[a]	*b*
356[a]	*b*
370[a]	*b*
397[a]	ν(MoC)
418[a]	ν(MoC)
2099[c]	ν(CN)
2110[c]	ν(CN)

[a] Measured as a paraffin-wax disc. [b] Assigned as either δ(MoMoC) or δ(MoCN). [c] Measured as a KBr disc. A solution spectrum (methanol) also revealed two bands in the ν(CN) region, at 2123 and 2115 cm^{-1} respectively.

ture on the (δ*)(δ) ⟵ (δ)^2 band, although this was not sufficient to permit Franck–Condon analysis.[18]

The electronic spectra of concentrated solutions of the $[Mo_2(CN)_8]^{4-}$ ion show additional weak bands at 20 660 cm^{-1} (ε = 160 dm^3 mol^{-1} cm^{-1}), 27 170 cm^{-1} (100 dm^3 mol^{-1} cm^{-1}) and a shoulder at ≈30 300 cm^{-1}. Spectra of other $[Mo_2X_8]^{4-}$ ions reveal similar features to higher wavenumber of the (δ*)(δ) ⟵ (δ)^2 band and these are thought to arise from electric dipole-forbidden transitions, *e.g.* (δ*)(π)^3 ⟵ (π)^4 and (π*)(δ) ⟵ (δ)^2.[18,19] The bands of $[Mo_2(CN)_8]^{4-}$ could be assigned in a similar manner, but this would be speculative given that the character and arrangement of the unoccupied orbitals lying to higher energy of the δ* orbital may be significantly different from those of $[Mo_2X_8]^{4-}$ (X = Cl or Br), on account of the different π-bonding characteristics of chloride *versus* cyanide. The presence of relatively low-lying ligand-based π* orbitals cannot be ruled out. A further intense band in the electronic spectrum is observed at 36 500 cm^{-1} (ε = 3970 dm^3 mol^{-1} cm^{-1}). Resonance-Raman studies with λ_0 in the vicinity of this band were not carried out due to the lack of suitable excitation lines.

Comparison with other $[Mo_2L_8]^z$ ions

The influence of the ligands L on the structural and spectroscopic parameters associated with the quadruple metal–metal bond is demonstrated by the range of values observed for these parameters in the $[Mo_2L_8]^z$ complexes (Table 4).[1–3,14,15,20–26] The high value of ν(MoMo) for $[Mo_2(CN)_8]^{4-}$ as compared with that for other $[Mo_2L_8]^z$ complexes reflects the nature of the metal–ligand bonding, *i.e.* the strong σ-donor ability of the cyanide ligand and the unimportance of Mo(d$_\pi$) to cyanide(π*) back bonding act so as to increase the electron density on the molybdenum centres and thus to promote strong Mo–Mo interaction, as is also made evident by the relatively short Mo–Mo bond distance in $[Mo_2(CN)_8]^{4-}$. Although a high value for ν(MoMo) would be expected, the actual value (411 cm^{-1}) is in the region more typical of that for carboxylate-bridged complexes, $[Mo_2(O_2CR)_4]$;[*][25–27] it is also significantly higher than that for $[Mo_2Br_4(PMe_3)_4]$ (353 cm^{-1}),[28,29] which has a nearly identical *d*(MoMo) of 2.125 Å.[28] In consequence the MoMo force constant for the former must be considerably larger than that for the latter. Assuming that the diatomic approximation is valid,[30] $k = (5.89 \times 10^{-7})\mu\nu^2$, where *k* is the force constant in mdyn Å^{-1}, μ is the reduced mass in u and ν is the MoMo stretch in cm^{-1}, then $k\{[Mo_2(CN)_8]^{4-}\}$ = 4.77 mdyn Å^{-1} and $k\{[Mo_2Br_4(PMe_3)_4]\}$ = 3.51 mdyn Å^{-1} (1 mdyn Å^{-1} = 10^2 N m^{-1}).

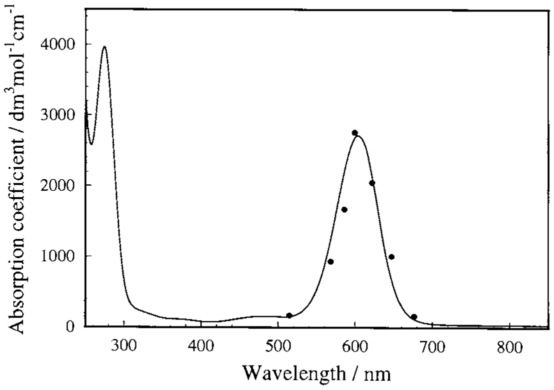

Fig. 3 Solution electronic absorption spectrum of $[NEt_4]_4[Mo_2(CN)_8]$ in methanol. The excitation profile for ν(MoMo) (●) is superimposed on the absorption spectrum

The wavenumber and intensity of the (δ*)(δ) ⟵ (δ)^2 band for $[Mo_2(CN)_8]^{4-}$ are generally consistent with a pattern previ-

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[*] The carboxylate-bridged complexes are also known to co-ordinate to neutral ligands in the axial positions collinear with the metal–metal bond. In the case of $[Mo_2(O_2CR)_4]$, ν(MoMo) typically shifts to lower wavenumber by 30–40 cm^{-1} upon axial ligation of neutral donor ligands such as pyridine.[26] For the present complex ν(MoMo) appears to be essentially solvent independent, although this has not been explored in any detail since $[NEt_4]_4[Mo_2(CN)_8]$ has only limited solubility in many typical non-aqueous solvents, whilst other solvents react with the complex as shown by a change in colour of the solution. For example aqueous solutions of $[Mo_2(CN)_8]^{4-}$ become green quite rapidly, and these colour changes cannot be suppressed by the addition of an excess of cyanide. The nature of the species formed under these conditions has not been investigated. The complex is however sufficiently soluble in acetonitrile for Raman measurements to be carried out, and the solutions appear to be stable. Under these conditions ν(MoMo) occurs at 408 cm^{-1} suggesting that axial ligation does not occur. The (δ*)(δ) ⟵ (δ)^2 transition is also relatively insensitive to the effect of solvent, supporting the conclusion based on Raman data that axial ligation is unimportant in the case of the $[Mo_2(CN)_8]^{4-}$ ion.

Table 4 Bond distances [*d*(Mo–Mo)], MoMo stretch [ν(MoMo)] and $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition wavenumbers and absorption coefficients (ε) for some quadruply bonded dimolybdenum complexes

Complex	*d*(Mo–Mo)/ Å	$\tilde{\nu}$(MoMo)^{a,b}/ cm^{-1}	$(\delta^*)(\delta) \longleftarrow (\delta)^{2\,a,b}$/ cm^{-1}	ε/ dm^3 mol^{-1} cm^{-1}
$K_4[Mo_2Cl_8]$	2.139^c	346^{a,d}	19 000^{a,d}	1 050^e
$[NH_4]_4[Mo_2Br_8]$	2.135^c	336^{a,f}	18 000^{a,f}	1 170^e
$[NH_4]_4[Mo_2(NCS)_8]\cdot 4H_2O$	2.162^{c,g}	—	14 500^{b,h}	2 600^h
$[NBu^n{}_4]_4[Mo_2(CN)_8]\cdot 8CHCl_3$	2.122^i	411^{b,j}	16 580^{b,j}	2 700^j
$[Mo_2(NH_3)_8][CF_3SO_3]_4$	—	—	20 000^k	—
$[Mo_2(NCCH_3)_8(NCCH_3)_2][BF_4]_4\cdot 2NCCH_3$	2.187^c	—	16 750^{b,l}	1 130^l
$[Mo_2(OH_2)_8]^{4+}$	—	—	19 840^{b,m}	340^m
$Li_4[Mo_2(CH_3)_8]\cdot 4thf^n$	2.148^c	336^{b,o}	19 500^{b,o}	1 500^o
$[Mo_2(O_2CCH_3)_4]$	2.093^c	404^{a,p}	22 700^{b,e}	60^e
$[Mo_2(O_2CCF_3)_4]$	2.090^c	397^{b,q}	23 300^{b,q}	120^e
$[Mo_2(O_2CCF_3)_4]\cdot 2py^r$	2.129^c	343^{b,q}	19 700^{b,q}	—

[a] Solid-state measurement. [b] Solution measurement. [c] Ref. 1, p. 143. [d] Ref. 14. It should be noted that ν(MoMo) is somewhat dependent on the identity of the cation, as is *d*(Mo–Mo). [e] Ref. 20. [f] Ref. 15. [g] For $[NH_4]_4[Mo_2(NCS)_8]\cdot 6H_2O$, *d*(MoMo) = 2.174 Å. [h] Ref. 21. [i] Ref. 3. [j] This work. [k] Ref. 2. The medium for this measurement was not quoted. [l] Ref. 22. Some decomposition of the complex was noted. [m] Ref. 23. [n] thf = Tetrahydrofuran. [o] Ref. 24. The value of ε given is an upper limit. [p] Ref. 25. [q] Ref. 26. [r] The pyridine (py) ligands occupy the axial co-ordination sites collinear with the Mo–Mo bond.

ously noted for quadruply bonded dimolybdenum complexes, *i.e.* complexes with strong donor ligands tend to display low-energy, high-intensity $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transitions, as compared with those with relatively hard ligands, which have high-energy, low-intensity transitions.[20] Extracting precise information about the nature of the metal–metal interaction, in particular the δ-bond interaction, from the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition energy is however difficult.[20] One parameter which would be of particular interest is the one-electron δ–δ* orbital separation, since this could be compared directly for complexes with different L. Although this term is incorporated in the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition energy it is not readily evaluated owing to the contribution of electron correlation and configuration interaction to the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition energy in d^4d^4 quadruply bonded systems.[31] In the case of the d^4d^3 systems (*i.e.* the one-electron oxidised congeners of $[Mo_2L_8]^z$), which have a doublet $(\delta)^1$ ground state, the wavenumber of the $(\delta^*) \longleftarrow (\delta)$ transition gives a better indication of the δ–δ* orbital separation since the electron-correlation contribution is effectively cancelled out and the metal–metal bond length is not anticipated to alter significantly on removal of a δ electron.[31] Unfortunately the $[Mo_2(CN)_8]^{4-}$ ion can only be oxidised irreversibly, which prevents this information from being obtained.† The high absorption coefficient of the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition for $[Mo_2(CN)_8]^{4-}$ is particularly interesting, being of the same order of magnitude as those for $[Mo_2X_4(PMe_3)_4]$ complexes, for which ε = 3110, 4060 and 5250 dm^3 mol^{-1} cm^{-1} for X = Cl, Br and I respectively. The increase in the value of ε along the series X = Cl, Br, I has been attributed to increased mixing of the halide-to-metal charge-transfer and $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transitions.[28] In the case of the $[Mo_2(CN)_8]^{4-}$ ion, where the latter explanation cannot apply, the high intensity of the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition is likely to arise through efficient δ overlap; this can again be attributed to the ability of the cyanide ligand to lower the effective positive charge on the molybdenum ions and thereby to promote expansion of the metal 4d orbitals.[32]

Conclusion

From the results of Raman, resonance-Raman and electronic absorption spectroscopy on $[NEt_4]_4[Mo_2(CN)_8]$, a self-consistent picture emerges for the assignment of the polarised Raman band at 411 cm^{-1} to ν(MoMo) and of an axially polarised electronic band at 16 580 cm^{-1} to the $(\delta^*)(\delta) \longleftarrow (\delta)^2$ transition, and for the coupling of the former to the latter. The value of 411 cm^{-1} for ν(MoMo) is the highest observed for an $[Mo_2L_8]^z$ complex in which L is a monodentate ligand, and is consistent with the relatively short Mo–Mo bond length.

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References

1 F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, Clarendon Press, Oxford, 2nd edn., 1993, pp. 139–231.
2 A. G. Comrie, A. McVitie and R. D. Peacock, *Polyhedron*, 1994, **13**, 193.
3 S. L. Bartley, S. N. Berstein and K. R. Dunbar, *Inorg. Chim. Acta*, 1993, **213**, 213.
4 C. D. Garner and R. G. Senior, *J. Chem. Soc., Dalton Trans.*, 1975, 1171.
5 A. B. Brignole and F. A. Cotton, *Inorg. Synth.*, 1972, **13**, 81.
6 S. Andreades and E. W. Zahnow, *J. Am. Chem. Soc.*, 1969, **91**, 4181.
7 W. K. Bratton, F. A. Cotton, M. Debeau and R. A. Walton, *J. Coord. Chem.*, 1971, **1**, 121.
8 A. P. Ketteringham and C. Oldham, *J. Chem. Soc., Dalton Trans.*, 1973, 1067.
9 D. M. Adams, *Metal–Ligand and Related Vibrations*, Edward Arnold, London, 1967, pp. 111–119, 165–176; A. M. Golub, H. Kohler and V. V. Skopenko, *Chemistry of Pseudohalides, Topics in Inorganic and General Chemistry*, ed. R. J. H. Clark, Elsevier, Amsterdam, 1986, pp. 142–146; W. P. Griffith, *Coord. Chem. Rev.*, 1975, **17**, 177.
10 G. J. Kubas and L. H. Jones, *Inorg. Chem.*, 1974, **13**, 2816.
11 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 3rd edn., 1978, p. 259.
12 L. H. Jones, *Inorganic Vibrational Spectroscopy*, Marcel Dekker, New York, 1971, vol. 1, p. 117.
13 J. Sun Yoo, E. Griswold and J. Kleinburg, *Inorg. Chem.*, 1965, **4**, 365.
14 R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, 1975, **97**, 2691.
15 R. J. H. Clark and N. R. D'Urso, *J. Am. Chem. Soc.*, 1978, **100**, 3088.
16 R. J. H. Clark and M. J. Stead, *Inorg. Chem.*, 1983, **22**, 1214.
17 R. J. H. Clark and B. Stewart, *Struct. Bonding* (*Berlin*), 1979, **36**, 1; R. J. H. Clark and T. J. Dines, *Angew. Chem., Int. Ed. Engl.*, 1985, **25**, 131.

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† Cyclic voltammetry of $[NEt_4]_4[Mo_2(CN)_8]$ in 0.1 mol dm^{-3} $NBu^n{}_4PF_6$–acetonitrile at a platinum working electrode revealed an irreversible oxidation at $E_{pa} = +0.35$ V, *versus* the Ag–AgCl reference electrode against which the ferrocenium–ferrocene couple occurs at +0.55 V.

18 P. E. Fanwick, D. S. Martin, F. A. Cotton and T. R. Webb, *Inorg. Chem.*, 1977, **16**, 2103.

19 J. G. Norman and H. J. Kolari, *J. Am. Chem. Soc.*, 1975, **97**, 33.

20 M. C. Manning and W. C. Trogler, *J. Am. Chem. Soc.*, 1983, **105**, 5311.

21 A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem.*, 1979, **18**, 3558.

22 F. A. Cotton and K. J. Wiesinger, *Inorg. Chem.*, 1991, **30**, 871.

23 A. R. Bowen and H. Taube, *Inorg. Chem.*, 1974, **13**, 2245.

24 A. P. Sattelberger and J. P. Fackler, *J. Am. Chem. Soc.*, 1977, **99**, 1258.

25 R. J. H. Clark, A. J. Hempleman and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1988, 973.

26 F. A. Cotton and J. G. Norman, *J. Am. Chem. Soc.*, 1972, **94**, 5697.

27 W. C. Trogler and H. B. Gray, *Acc. Chem. Res.*, 1978, **11**, 232.

28 M. D. Hopkins, W. P. Schaefer, M. J. Bronikowski, W. H. Woodruff, V. M. Miskowski, R. F. Dallinger and H. B. Gray, *J. Am. Chem. Soc.*, 1987, **109**, 408.

29 C. Svendsen, M. J. Nielsen, O. S. Mortensen, S. J. R. Allers and R. J. H. Clark, *Chem. Phys.*, 1997, **215**, 89.

30 P. D. Harvey, *Coord. Chem. Rev.*, 1996, **153**, 175.

31 M. D. Hopkins, H. B. Gray and V. M. Miskowski, *Polyhedron*, 1987, **6**, 705.

32 D. J. Santure and A. P. Sattelberger, *Inorg. Chem.*, 1985, **24**, 3477.

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