Raman, Resonance Raman, and Infrared Spectroscopic Study of Complexes containing Copper(I)–Tetrathio-molybdate(VI) and -tungstate(VI) Anions

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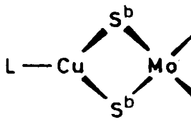
Raman, resonance Raman at *ca.* 80 K, and infrared spectra of thirteen ions of the type [MS$_4$(CuL)$_n$]$^{2-}$ (M = Mo or W; L = CN, SPh, SC$_6$H$_4$Me-4, Cl, or Br; n = 1—4) are reported. Totally symmetric ν(Mo–S) and ν(W–S) stretches are easily identified as giving rise to the most intense bands in the Raman and particularly resonance Raman spectra of the complexes. The pattern (*i.e.* the number of bands, their wavenumbers and relative intensities) observed in the ν(Mo–S) region (415—496 cm^{-1}) is distinctive for the number of Cu$^{\rm I}$ ions co-ordinated to [MoS$_4$]$^{2-}$.

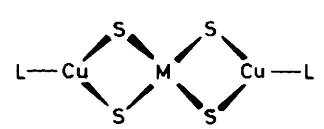
Although the tetrathiometallate(VI) ions [MS$_4$]$^{2-}$ (M = Mo or W) were first isolated in the 1880s,[1] their interesting ability to co-ordinate metal ions was not recognised until almost a hundred years later when, for example, Müller *et al.*[2] prepared [Ni(WS$_4$)$_2$]$^{2-}$. The ions are extremely versatile ligands and have been shown to function as bidentate chelates to a wide variety of metal ions[3,4] including copper(I).[5–14] Syntheses employing these [MS$_4$]$^{2-}$ ions can lead to the formation of M′$_3$MS$_4$ cubane-like clusters which have been characterised by *X*-ray crystallography for M′ = Fe;[15] related cubane-like M′$_3$MS$_3$Cl and M′$_4$M$_2$S$_6$ cages have been identified for M′ = Cu and Ag.[3,16] Such complexes, which involve extensive electron delocalisation over the metal–sulphur cores, are of considerable chemical and biochemical interest. Indeed, the Fe$_3$MoS$_4$ cubane-like clusters[15] currently serve as the best available models for the molybdenum centre of the FeMo cofactor of the nitrogenases. Cu–Mo–S clusters are of special interest because their formation may represent one mechanism for the biological antagonism between copper and molybdenum, which leads to copper deficiency in ruminant animals.[13,17]

Detailed structural and spectroscopic characterisation of chemical systems involving metal–sulphur clusters is important. The results not only strengthen and extend the inherent chemical interest in these systems but also aid the interpretation of corresponding data for the metal–sulphur clusters of more complicated biological systems.[3,4,15,18] There have been several vibrational spectroscopic studies on complexes involving co-ordinated [MS$_4$]$^{2-}$ ions. The majority of these have related to [S$_2$MS$_2$M′S$_2$MS$_2$]$^{n-}$ complexes.[3,4,19–24] Also, and of more relevance to the results reported herein, infrared[3,4,9,25] and Raman[3,4,9,25–29] spectra have been recorded for some (M′L$_x$)$_n$MS$_4$ complexes in which the tetrathiometallate(VI) moiety acts as a bidentate ligand to one or more metal atoms. Bands attributed to Mo–S and W–S stretching vibrations have been found in the region 422—516 cm^{-1}.

The present investigation is concerned with Raman (R), resonance Raman (r.R.), and infrared (i.r.) spectroscopy of thirteen discrete complexes which contain [MS$_4$]$^{2-}$ co-ordinated as a bidentate ligand to one, two, three, or four copper(I) ions (Figure 1). These complexes possess characteristic electronic absorption spectra, the bands of which clearly relate to those of the parent [MS$_4$]$^{2-}$ ion,[3,7,9,13] that of lowest energy being assigned to a sulphur-to-metal charge-transfer transition.[3,27,30–32] Excitation using laser lines within the contour of this absorption band produces enhancement to the intensity of particular Raman bands. In general *A*-term scattering is most important and, if the symmetry of the molecule remains unchanged on excitation, only totally symmetric vibrational modes give rise to intense bands in a r.R. spectrum.[33,34] Moreover, strong enhancement is only observed for those Raman bands which involve the chromophore, *i.e.* that part of the molecule in which significant changes in bond length occur upon electronic excitation. The results complement earlier ^{95}Mo n.m.r. work aimed at providing a spectroscopic basis for distinguishing the number of Cu$^{\rm I}$ ions co-ordinated to [MoS$_4$]$^{2-}$.[35]



(I)



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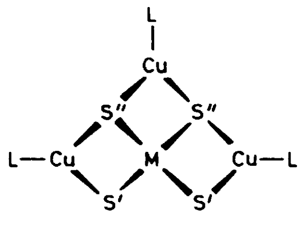

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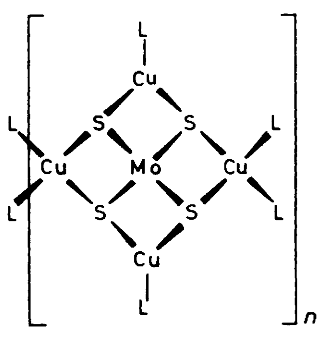

(IV)

Figure 1. Diagrammatic representation of the structures identified for discrete complexes in which [MS$_4$]$^{2-}$ (M = Mo or W) served as a bidentate ligand to one, two, three, or four copper(I) ions, each with trigonal planar or distorted tetrahedral co-ordination

Experimental

Analytically pure samples of the complexes [NPr$^n_4$]$_2$[MoS$_4${Cu(CN)}],[7] [NPr$^n_4$]$_2$[MoS$_4${Cu(^{13}CN)}],[7] [NPr$^n_4$]$_2$[MoS$_4${Cu(SPh)}],[9] [NPr$^n_4$]$_2$[MoS$_4${Cu(SC$_6$H$_4$Me-4)}],[9] [NPr$^n_4$]$_2$[MoS$_4${Cu(CN)}$_2$],[7] [NPr$^n_4$]$_2$[MS$_4${Cu(SPh)}$_2$][9] (M = Mo or W), [PPh$_4$]$_2$[MoS$_4$(CuL)$_2$][14] (L = Cl or Br), [PPh$_4$]$_2$[MoS$_4$(CuL)$_3$]·MeCN,[10] [PPh$_4$]$_2$[WS$_4$(CuBr)$_3$],[14] and [PPh$_4$]$_2$[MoS$_4$(CuL)$_4$]·Me$_2$CO[11] were prepared as described elsewhere.

Raman and r.R. spectra at *ca.* 80 K were obtained using a liquid-nitrogen-cooled cell for each complex, the latter being compressed into a KBr disc. Spectra were recorded on a Spex 14018 (Ramalog 6) spectrometer equipped with 1 800 line mm^{-1} holographic gratings in conjunction with Coherent Radiation models CR 500 K and CR 3000 K krypton-ion, CR 12 argon-ion, and CR 490 dye lasers (rhodamine 6G) using excitation lines ranging in wavelength from 406.7 to 676.4 nm. As most of the molybdenum compounds show strong luminescence with 647.1-nm excitation, either the 568.2- or 676.4-nm lines were preferred, or a dye laser line. To avoid thermal decomposition, the laser power at the sample was held at < 100 mW for Raman and < 30 mW for r.R. experiments. The scattered radiation was detected using standard photon-counting techniques employing an RCA C31034 photomultiplier. Wavenumbers were measured from the attenuated Rayleigh line.

I.r. spectra in the range 30—660 cm^{-1} were recorded at ambient temperature on a Bruker IFS 113 V interferometer. The samples were finely dispersed in molten paraffin wax (m.p. ~49 °C) and pressed into discs.

Results and Discussion

Type (**I**) *Complexes.*—The point symmetry of the $[S^t_2MoS^b_2\{Cu(CN)\}]^{2-}$ anion is C_{2v}.[7,8] The stretching modes (ν) group as $5a_1$(R, i.r.) + $2b_1$(R, i.r.) + b_2(R, i.r.). Two of the bending modes (δ) have a_1 symmetry. Six Raman bands (but none in the 2 100 cm^{-1} region) show strong resonance enhancement (Figure

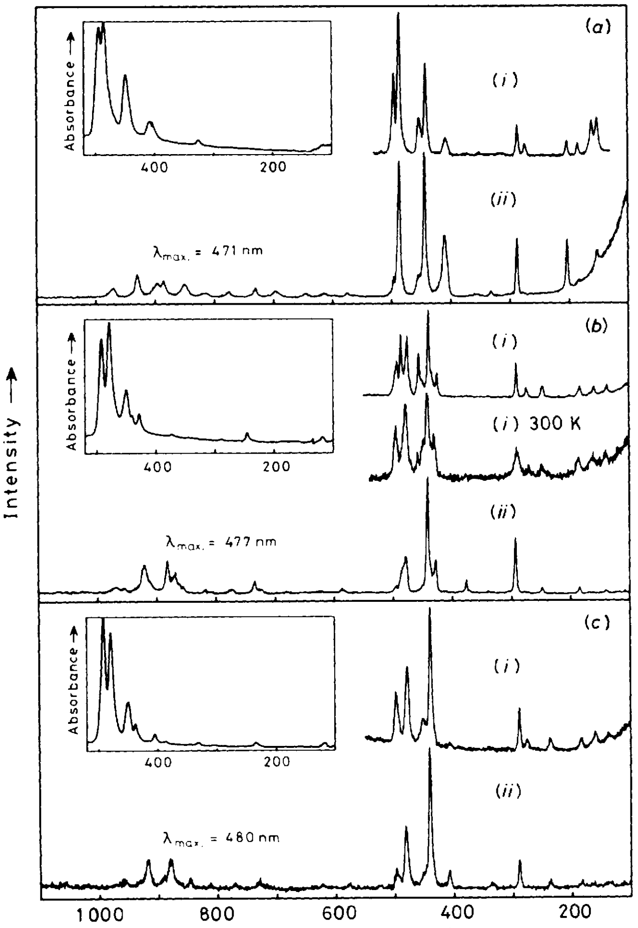

Figure 2. Raman (100—550 cm^{-1}), resonance Raman (100—1 100 cm^{-1}), and infrared (100—520 cm^{-1}, inset) spectra of (*a*) $[NPr^n_4]_2[MoS_4\{Cu(CN)\}]$, λ_0 = 583.5 (*i*) and 476.5 nm (*ii*); (*b*) $[NPr^n_4]_2[MoS_4\{Cu(SPh)\}]$, λ_0 = 568.2 (*i*) and 488.0 nm (*ii*); (*c*) $[NPr^n_4]_2[MoS_4\{Cu(SC_6H_4Me-4)\}]$, λ_0 = 568.2 (*i*) and 476.5 nm (*ii*)

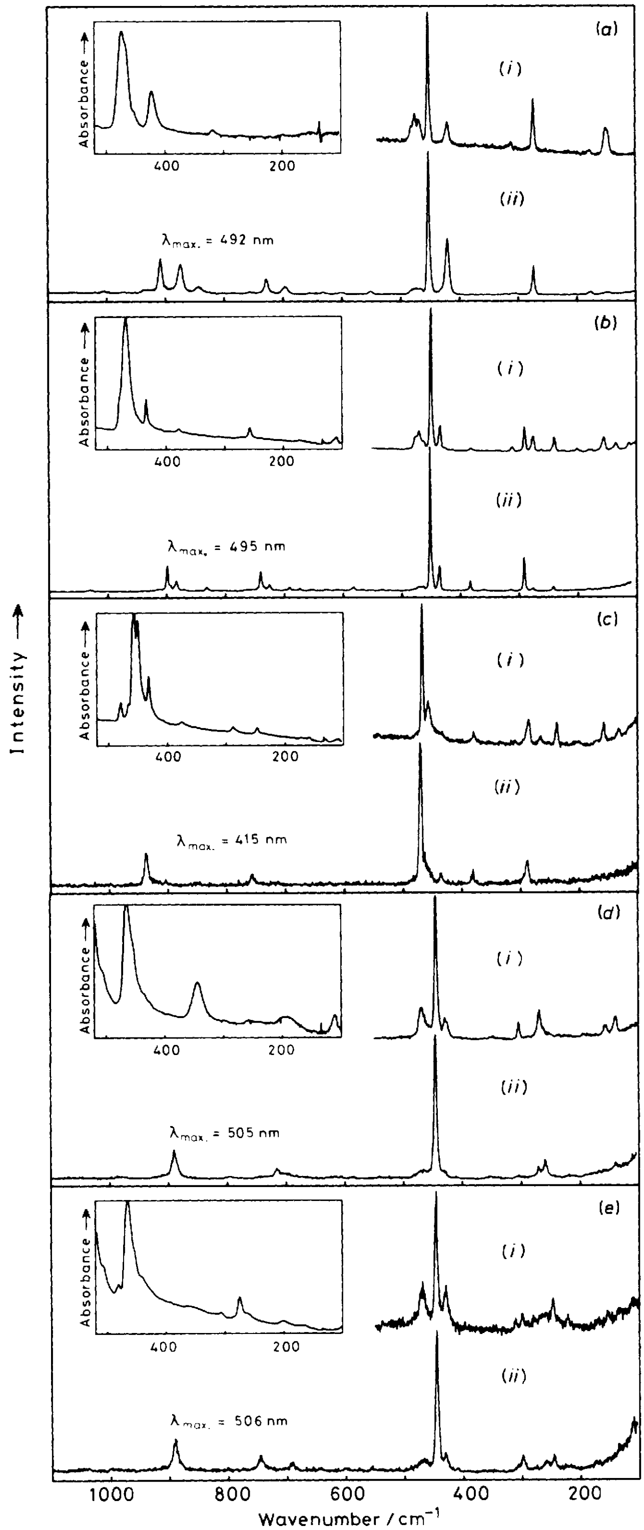

Figure 3. Raman (100—550 cm^{-1}), resonance Raman (100—1 100 cm^{-1}), and infrared (100—520 cm^{-1}, inset) spectra of (*a*) $[NPr^n_4]_2[MoS_4\{Cu(CN)\}_2]$, λ_0 = 568.2 (*i*) and 488.0 nm (*ii*); (*b*) $[NPr^n_4]_2[MoS_4\{Cu(SPh)\}_2]$, λ_0 = 583.5 (*i*) and 514.5 nm (*ii*); (*c*) $[NPr^n_4]_2[WS_4\{Cu(SPh)\}_2]$, λ_0 = 583.5 (*i*) and 406.7 nm (*ii*); (*d*) $[PPh_4]_2[MoS_4(CuCl)_2]$, λ_0 = 583.5 (*i*) and 514.5 nm (*ii*); (*e*) $[PPh_4]_2[MoS_4(CuBr)_2]$, λ_0 = 568.2 (*i*) and 514.5 nm (*ii*)

Table 1. Wavenumbers ($\tilde{\nu}$/cm^{-1}) and assignments of bands observed in the Raman and infrared spectra of the complexes $[NPr^n{}_4]_2[S^t{}_2MoS^b{}_2(CuL)]$ in the range 520—100 cm^{-1}, together with ν(CN)

L = CN		L = SPh		L = SC_6H_4Me-4		
R	i.r.	R	i.r.	R	i.r.	Assignment (C_{2v})
2 118	2 117s					ν(C–N), a_1[a]
496	495s	493	493s	496	492s	$\nu_{asym.}$(Mo–S^t), b_2
		486[b]				
486	486s	475	480s	477	480s	$\nu_{sym.}$(Mo–S^t), a_1
		456[b]				
453	449s	449	450s	451	450s	$\nu_{asym.}$(Mo–S^b), b_1
442		440		439	438m	$\nu_{sym.}$(Mo–S^b), a_1
		426	428m	407	406m	Thiolate
409	408m					ν(Cu–C), a_1[a]
		375	373w		386w	ν(Cu–SPh), a_1
	325m			336	332w	
288		291		288		$\nu_{sym.}$(Cu–S^b), a_1
275		274		276		
		247	245m	236	234m	
204						δ($MoS^t{}_2$), a_1
185		183		184		
161		159		160		
152						δ($MoS^b{}_2$), a_1
		138		137		
	110w		117w		115w	

Overtone and combination bands:

$[MoS_4\{Cu(CN)\}]^{2-}$	356 (204 + 152), 575 (2 × 288), 615 (409 + 204), 646 (442 + 204), 696 (409 + 288), 731 (442 + 288), 776 (486 + 288), 816 (2 × 409), 851 (442 + 409), 886 (2 × 442), 897 (486 + 409), 931 (486 + 442), 971 (2 × 486), 1 218 (486 + 442 + 288), 1 338 (486 + 442 + 409), 1 372 (486 + 2 × 442), 1 382 (2 × 486 + 409), 1 416 (2 × 486 + 442)
$[MoS_4\{Cu(SPh)\}]^{2-}$	583 (2 × 291), 721 (426 + 291), 733 (440 + 291), 771 (480 + 291), 816 (440 + 375), 856 (480 + 375), 869 (440 + 426), 880 (2 × 440), 920 (480 + 420), 954 and 969 (2 × 480), 1 174 (2 × 440 + 291), 1 211 (480 + 420 + 291), 1 260 (2 × 440 + 375), 1 310 (2 × 440 + 426), 1 322 (3 × 440), 1 346 (480 + 440 + 426), 1 360 (480 + 2 × 440), 1 398 (2 × 480 + 440)
$[MoS_4\{Cu(SC_6H_4Me\text{-}4)\}]^{2-}$	729 (440 + 228), 770 (480 + 288), 844 (440 + 407), 877 (2 × 440), 917 (480 + 440), 956 (2 × 480)

[a] ν(C–N) at 2 074 cm^{-1}, ν(Cu–C) at 405 cm^{-1} observed in the Raman and i.r. spectra of the ^{13}C labelled complex. [b] Not observed in a room-temperature spectrum.

2) and are thus attributed to totally symmetric modes (Table 1). Of these, the bands at 486 and 442 cm^{-1} are assigned to $\nu_{sym.}$(Mo–S^t) and $\nu_{sym.}$(Mo–S^b), respectively, the relative order being decided upon the basis that the terminal Mo–S bonds are shorter than the bridging ones.[7,8] The band at 409 cm^{-1} is shifted to 405 cm^{-1} upon ^{13}C labelling; it is thus attributed to the ν(Cu–C) mode because no other fundamentals, except ν(C–N) (which shifts from 2 118 to 2 074 cm^{-1}), show any significant ^{13}C isotopic shift. The bands at 288, 204, and 152 cm^{-1} are attributed to the other a_1 modes $\nu_{sym.}$(Cu–S^b), δ(Mo–S^t), and δ(Mo–S^b), respectively. Bands attributed to $\nu_{asym.}$(Mo–S^t) (b_2) and $\nu_{asym.}$(Mo–S^b) (b_1) can be observed in the normal Raman spectrum of the complex, 10—12 cm^{-1} above those attributed to the corresponding symmetric modes. A clear assignment of the other bands to $\nu_{asym.}$(Cu–S^b) and to non-totally symmetric bending modes cannot be made. The r.R. spectrum also shows overtone and combination bands involving all the totally symmetric fundamentals except ν(C–N), which itself gives rise to a Raman band (at 2 118 cm^{-1}) showing no resonance enhancement. This leads to the conclusion that excitation within the envelope of the electronic transition with $\lambda_{max.}$ = 471 nm affects bond distances in the S_2MoS_2CuC moiety but to no significant extent the C–N bond length; this is consistent with the fact that the resonant transition is essentially S→Mo in character.

Our assignment of the band at 442 cm^{-1} to $\nu_{sym.}$(Mo–S^b) is in clear contrast to previous ones by Müller *et al.*[3,29] and Sarkar and Mishra[13] who assigned a band at 416 and 418 cm^{-1} in their r.R. and i.r. spectra, respectively, of this species to $\nu_{sym.}$(Mo–S^b) and the intense Raman band at 447 cm^{-1} to $[MoS_4]^{2-}$ impurity. The occurrence of many combination bands involving this mode (442 cm^{-1} in our r.R. spectrum, Figure 2, Table 1) demonstrates clearly that all these a_1 modes belong to the same molecule since, if $[MoS_4]^{2-}$ impurity were responsible for the band at 442 cm^{-1}, overtone progressions but not combination bands involving this mode would be observed. We have found no shifts in band wavenumbers with change in temperature. Compared to the 80-K r.R. spectrum the room-temperature r.R. spectrum (spinning KBr disc, 488.0-nm excitation) of $[NPr^n{}_4]_2[MoS_4\{Cu(CN)\}]$ shows broader bands (full-width at half-maximum for fundamentals ~8 cm^{-1}) and more intense overtone and combination bands.

In the $[NPr^n{}_4]_2[MoS_4\{Cu(SPh)\}]$ structure[9] the symmetry of the anion is lowered to C_1 by the phenylthiolate ligand. However, the symmetry of the $S^t{}_2MoS^b{}_2CuS'$ core deviates only very little from C_{2v}. Comparison of the Raman and r.R. spectra (Figure 1) of $[MoS_4\{Cu(SPh)\}]^{2-}$ and $[MoS_4\{Cu(SC_6H_4Me\text{-}4)\}]^{2-}$ with that of $[MoS_4\{Cu(CN)\}]^{2-}$ demonstrates the close structural relationship between the chromophores of these complexes. The four ν(Mo–S) modes and the $\nu_{sym.}$(Cu–S^b) mode (Table 1) are found within 10 cm^{-1} of their values for the cyano

Table 2. Wavenumbers ($\tilde{\nu}$/cm^{-1}) and assignments of bands observed in the Raman and infrared spectra of the complexes $[(LCu)S_2MS_2(CuL)]^{2-}$ in the range 520—100 cm^{-1}, together with ν(CN)

L = CN, M = Mo[a]		L = SPh, M = Mo[a]		L = SPh, M = W[a]		L = Cl, M = Mo[b]		L = Br, M = Mo[b]		
R	i.r.	R	i.r.	R	i.r.	R	i.r.	R	i.r.	Assignment (D_{2d})
2 130	2 127s									ν(C–N)
482		476	480 (sh)		480m				481w	$\nu_{asym.}$(M–S)
475	474s	471	468s	458	457s	468	465s	468	465s	
469	468 (sh)	463			450s		455 (sh)			
452	452 (sh)	450	450 (sh)	468	467w	446		445		$\nu_{sym.}$(M–S), a_1
		434	434m	434	432m	430		428		Thiolate and/or $\nu_{asym.}$(M–S)
420	422m									ν(Cu–C), a_1
		382	378w	380	375w					ν(Cu–SPh)
							341m			ν(Cu–Cl)
311	317w	312								
						305	302w	308	305w	
275		291		287	288w			298		
								278	274m	ν(Cu–Br)
		276				270				
		262	256m		246w	259	257w	264		
		241		238				245		
								218		
		201		202					200w	
		180					190w			
178		176								
									165w	
		156		158	157w	156		154		
149										
		135		132		139		134		
			108w		107w		110m			

Overtone and combination bands:

$[MoS_4\{Cu(CN)\}_2]^{2-}$	552 (2 × 275), 697 (421 + 275), 729 (452 + 275), 844 (2 × 421), 875 (452 + 421), 908 (2 × 452), 1 151 (452 + 421 + 275), 1 182 (2 × 452 + 275), 1 296 (452 + 2 × 421), 1 328 (2 × 452 + 421), 1 361 (3 × 452)
$[MoS_4\{Cu(SPh)\}_2]^{2-}$	581 (2 × 291), 673 (382 + 291), 691 (450 + 241), 725 (450 + 276, 434 + 291), 741 (450 + 291), 833 (450 + 382), 885 (450 + 434), 900 (2 × 450), 1 031 (450 + 2 × 291), 1 190 (2 × 450 + 291), 1 336 (2 × 450 + 434), 1 350 (3 × 450)
$[WS_4\{Cu(SPh)\}_2]^{2-}$	756 (468 + 287), 937 (2 × 468), 903 (468 + 434), 1 223 (2 × 468 + 287), 1 403 (3 × 468)
$[MoS_4(CuCl)_2]^{2-}$	716 (446 + 270), 891 (2 × 446), 1 160 (2 × 446 + 270), 1 334 (3 × 446)
$[MoS_4(CuBr)_2]^{2-}$	693 (445 + 245), 745 (445 + 298), 890 (2 × 445), 1 133 (2 × 445 + 245), 1 188 (2 × 445 + 298), 1 336 (3 × 445)

[a] $[NPr^n_4]^+$ salt. [b] $[PPh_4]^+$ salt.

compound and the $\nu_{sym.}$ modes also give rise to intense overtone and combination bands in the r.R. spectrum. Additional bands are found at 426 and 375 cm^{-1} for the SPh complex and at 407 and 336 cm^{-1} for the SC_6H_4Me-4 derivative. The apparent shift is indicative of a thiolate-centred mode. Bands near 430 and 380 cm^{-1} are also observed for the $[MS_4\{Cu(SPh)\}_2]^{2-}$ complexes (Figure 3, Table 2).

The features in the region below 280 cm^{-1} are very similar for the two thiolates but different from those of the cyano compounds and a proper assignment seems rather difficult to make.

The Raman spectrum of $[MoS_4\{Cu(SPh)\}]^{2-}$ at *ca.* 80 K shows some unexpected additional sharp bands at 486 and 456 cm^{-1}. These are not observed in the room-temperature spectrum, the ν(Mo–S) region of which resembles closely the spectra of the SC_6H_4Me-4 and CN complexes.

The i.r. spectra (Figure 2, insets) of these type (**I**) complexes correspond well with the Raman data. The ν(Mo–S^t) modes give rise to more intense bands than do the ν(Mo–S^b) ones. No bands attributable to $\nu_{sym.}$(Mo–S^b) can be observed for the cyano complex but a very weak band is observed in the spectra of the thiolates.

Type (**II**) *Complexes*.—Two different crystal structures containing the $[MoS_4\{Cu(CN)\}_2]^{2-}$ anion have been established. With $[AsPh_4]^+$ as counterion [7] discrete anions are found which deviate very little from the maximum possible D_{2d} symmetry, whereas in the $[NMe_4]^+$ structure [8] the anions form infinite zig-zag chains with trigonal-planar S_2CuC and distorted tetrahedral S_2CuC_2 centres. Only one band attributable to a C–N stretching mode is observed in the Raman and i.r. spectra of $[NPr^n_4]_2[MoS_4\{Cu(CN)\}_2]$ and therefore we assume D_{2d} symmetry for the anion. For $[NPr^n_4]_2[MoS_4\{Cu(SPh)\}_2]$ the site symmetry of the anion is C_2,[9] being approximately D_{2d} for the $SCuS_2MoS_2CuS$ core. No crystallographic data are known for the other complexes of this type, so approximate D_{2d} symmetry is assumed for their cores. For the $XCuS_2MoS_2CuX$ moiety (X denoting a single atom) the ten stretching normal co-ordinates (ν) group as $3a_1$(R) + $3b_2$(R, i.r.) + $2e$(R, i.r.) and, of the bending modes (δ), only one is totally symmetric.

The Mo complexes show their strongest Raman band at 449 ± 4 cm^{-1} (Figures 2 and 3), this band being attributed to the a_1 ν(Mo–S) mode. The weaker and broad band at 472 ± 4 cm^{-1} is assigned to the asymmetric (b_2, e) ν(Mo–S) modes. In the spectra of $[WS_4\{Cu(SPh)\}_2]^{2-}$ the intense totally symmetric ν(W–S) mode is at higher wavenumber than the antisymmetric one. This closely resembles the situation for $[NBu_4]_2[MoS_4]$ [$\nu_1(a_1)$ = 451.1, $\nu_3(t_2)$ = 469.9 cm^{-1}][31] and $[NBu_4]_2[WS_4]$ (ν_1 = 477.6, ν_3 = 463.3 cm^{-1}).[32] The modes at *ca.* 434 cm^{-1} in the molybdenum and tungsten phenylthiolate

Table 3. Wavenumbers ($\tilde{\nu}$/cm^{-1}) and assignments of bands observed in the Raman and infrared spectra * of the complexes $[PPh_4]_2[MS_4(CuL)_3]$ in the range 520—100 cm^{-1}

L = Cl, M = Mo		L = Br, M = Mo		L = Br, M = W		
R	i.r.	R	i.r.	R	i.r.	Assignment (C_2)
475	476s	478	478s	466	463s	ν(M–S′)
468	468s	469	468s	454	455 (sh)	
444	444m	444	442m			$\nu_{asym.}$(M–S″), *b*
432	432w	429	430w	437	437 (sh)	$\nu_{sym.}$(M–S″), *a*
					432s	
413						
370		360				
352	352s		(350w)			ν(Cu–Cl)
303	300w	312	305w	309	302 (sh)	
298				299		
	294w				293m	
273		280		287		
			276m		268m	ν(Cu–Br)
262		265	263m	259	258m	
		250		252		
239		236		245		
230		224		224		
				219		
				212		
185			200w	201	202w	
				190		
144		168	165w	166	165w	
					148w	
134		132		126		
	105m	108		105		

Overtone and combination bands:

$[MoS_4(CuCl)_3]^{2-}$	568 (433 + 134), 619 (433 + 185), 664 (433 + 230), 698 (433 + 264), 867 (2 × 433), 890 (2 × 444)
$[MoS_4(CuBr)_3]^{2-}$	535 (429 + 108), 562 (429 + 132), 652 (429 + 224), 695 (429 + 265), 858 (2 × 429), 893 (429 + 469)
$[WS_4(CuBr)_3]^{2-}$	562 (438 + 125), 574 (468 + 106), 648 (438 + 212), 682 (468 + 212), 908 (468 + 438), 937 (2 × 468)

* Weak peaks coincident with bands observed for $[PPh_4]Br$ are omitted.

spectra are enhanced under resonance conditions and form some combination bands. Corresponding absorptions are found in the i.r. spectra and also in that of the $[MoS_4\{Cu(SPh)\}]^{2-}$ ion. Therefore these modes are assigned to thiolate modes. The 420 cm^{-1} mode of $[MoS_4\{Cu(CN)\}_2]^{2-}$ is assigned to ν(Cu–C) by similar arguments. By contrast the bands observed at 430 and 428 cm^{-1} in the Raman and r.R. spectra of $[MoS_4(CuL)_2]^{2-}$ (L = Cl or Br) do not form combination bands in the r.R. spectrum and no corresponding i.r. absorptions are found; tentatively, these are assigned to $\nu_{asym.}$(Mo–S). As was found for $[MoS_4\{Cu(SPh)\}]^{2-}$, the Raman, r.R., and i.r. spectra of the molybdenum and tungsten thiolates show a band at *ca.* 380 cm^{-1} which is assigned to a thiolate mode.

The i.r. bands of $[MoS_4(CuL)_2]^{2-}$ (L = Cl or Br) at 341 and 274 cm^{-1} are attributed to ν(Cu–L) modes.

Type (**III**) *Complexes*.—Structural parameters are known for all the $[PPh_4]_2[MS_4(CuL)_3]\cdot CH_3CN$ complexes (M = Mo or W, L = Cl or Br) under investigation.[10,12] The anions have either C_2 site symmetry or structures which deviate only insignificantly from this symmetry. The Mo–S′ bonds are shorter by 0.05 Å than the Mo–S″ ones but no significant differences between the co-ordination geometries of the copper atoms have been detected.

There are 7*a*(R, i.r.) and 6*b*(R, i.r.) stretching modes (ν) for the $[MS_4(CuL)_3]^{2-}$ anion. The most intense band in the Raman and r.R. spectra of the Mo complexes is found at 430 ± 2 cm^{-1} and attributed to $\nu_{sym.}$(Mo–S″) (*a*) while the weaker one at 444 cm^{-1} is attributed to $\nu_{asym.}$(Mo–S″) (*b*) (Table 3, Figure 4). The bands at *ca.* 468 and *ca.* 477 cm^{-1} belong to the $\nu_{sym.}$(Mo–S′) (*a*) and $\nu_{asym.}$(Mo–S′) (*b*) modes but it is not clear why the band attributed to the *a* mode displays only small intensity enhancement under resonance conditions, and no overtone or combination bands. For the tungsten analogue the two strong Raman bands at 437 and 466 cm^{-1} are assigned to $\nu_{sym.}$(W–S″) (*a*) and $\nu_{sym.}$(W–S′) (*a*), respectively. The weak band at 454 cm^{-1} is tentatively attributed to $\nu_{asym.}$(W–S″) (*b*) while $\nu_{asym.}$(W–S′) (*b*) is found at 432 cm^{-1} in the i.r. spectrum only. No useful Ar$^+$- or Kr$^+$-laser excitation line is available near the absorption maximum (434 nm) in the electronic spectrum of this complex. With the 457.9-nm line only a near r.R. spectrum can be obtained ($\varepsilon_{458}/\varepsilon_{434}$ = 0.55), which does not excite strong overtone or combination bands.

As for the type (**I**) complexes, the i.r. bands are more intense for $\nu_{asym.}$(Mo–S) modes than for the corresponding $\nu_{sym.}$ ones. However, this seems not to be the case for $[WS_4(CuBr)_3]^{2-}$. In good agreement with results for the type (**II**) complexes, bands are found in the i.r. spectra which are readily attributable to ν(Cu–Cl) at 352 cm^{-1} and to ν(Cu–Br) in the range 268—276 cm^{-1}.

Type (**IV**) *Complexes*.—The anions in the structure of $[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$ are linked and form infinite chains.[11] Each anion contains two trigonal planar Cu atoms, the other two being in a distorted tetrahedral co-ordination, forming Cu(μ-Br)$_2$Cu linkages. Whereas the Cu–Br bond length for the trigonal units [mean = 2.281(3) Å] is very close to the value for the $[MS_4(CuBr)_3]^{2-}$ ions, the bond lengths within the $CuBr_4$ units vary as much as from 2.320 to 2.927 Å. However, the differences in Cu–Br bonding hardly affect the MoS_4Cu_4 core, whose structure is close to the maximum possible D_{2d}

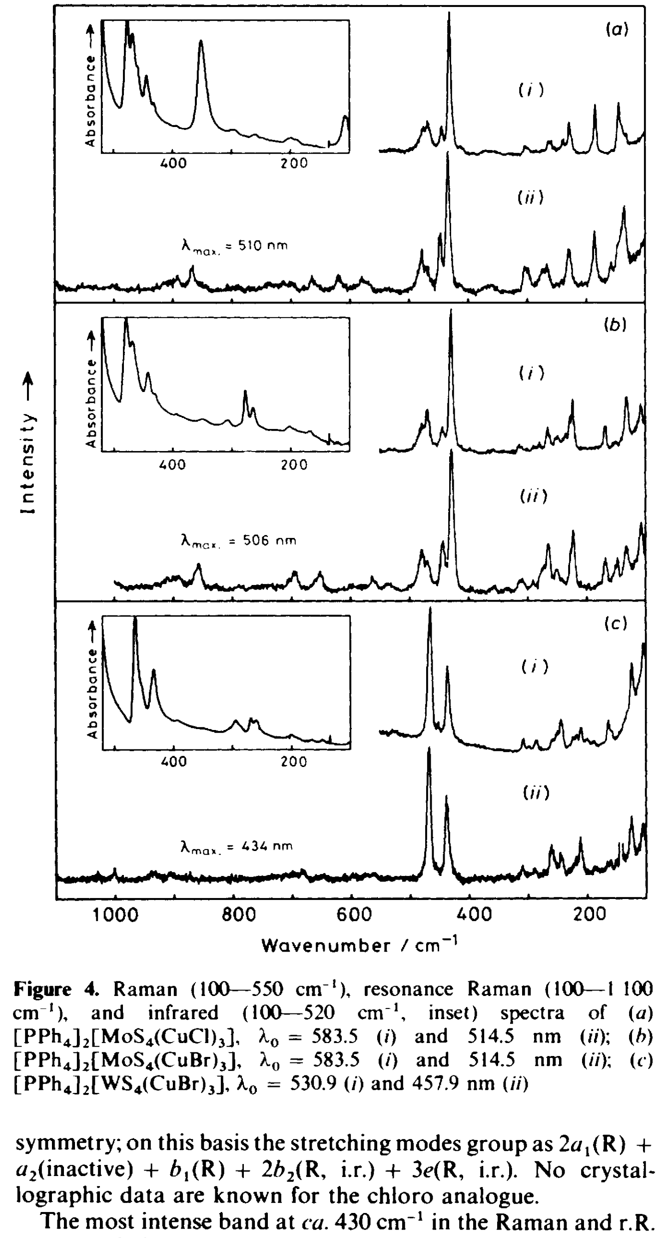

Figure 4. Raman (100—550 cm^{-1}), resonance Raman (100—1 100 cm^{-1}), and infrared (100—520 cm^{-1}, inset) spectra of (*a*) $[PPh_4]_2[MoS_4(CuCl)_3]$, λ_0 = 583.5 (*i*) and 514.5 nm (*ii*); (*b*) $[PPh_4]_2[MoS_4(CuBr)_3]$, λ_0 = 583.5 (*i*) and 514.5 nm (*ii*); (*c*) $[PPh_4]_2[WS_4(CuBr)_3]$, λ_0 = 530.9 (*i*) and 457.9 nm (*ii*)

symmetry; on this basis the stretching modes group as $2a_1(R) + a_2(\text{inactive}) + b_1(R) + 2b_2(R, \text{i.r.}) + 3e(R, \text{i.r.})$. No crystallographic data are known for the chloro analogue.

The most intense band at *ca.* 430 cm^{-1} in the Raman and r.R. spectra of these two complexes is attributed to the totally symmetric ν(Mo–S) (a_1) mode (Figure 5). Bands in the range 451—463 cm^{-1} are attributed to the $\nu_{asym.}$(Mo–S) (*e*) (Table 4) mode but it is unclear whether or not the splitting observed for the chloro compound arises from a bigger structural distortion in this case. The weak band at *ca.* 416 cm^{-1} is attributed to $\nu_{asym.}$(Mo–S) (b_2) by analogy with results found for the type (**II**) complexes. Corresponding i.r. bands are found for the ν(Mo–S) (*e*) modes, the weak absorption at 431 cm^{-1} in the $[MoS_4(CuCl)_4]^{2-}$ spectrum being a further indication of distortion from D_{2d} symmetry. By analogy with type (**II**) and (**III**) complexes, the bands at *ca.* 350 (L = Cl) and *ca.* 270 cm^{-1} (L = Br) are attributed to ν(Cu–L) modes of the trigonal-planar copper centres, whereas weaker features at lower wavenumbers might be assigned to the distorted tetrahedral ones.

$[PPh_4]^+$, $[NPr^n_4]^+$, $[SPh]^-$ *and* $[SC_6H_4Me\text{-}4]^-$ *Modes.*— For $[PPh_4]Br$ the most intense Raman bands (583.5-nm excitation) in the range 120—1 600 cm^{-1} are observed at 1 000 and 1 030 cm^{-1}. Weaker bands are found at 182, 205, 256, 264, 284, 618, 681, 1 100, 1 110, 1 158, and 1 590 cm^{-1}.

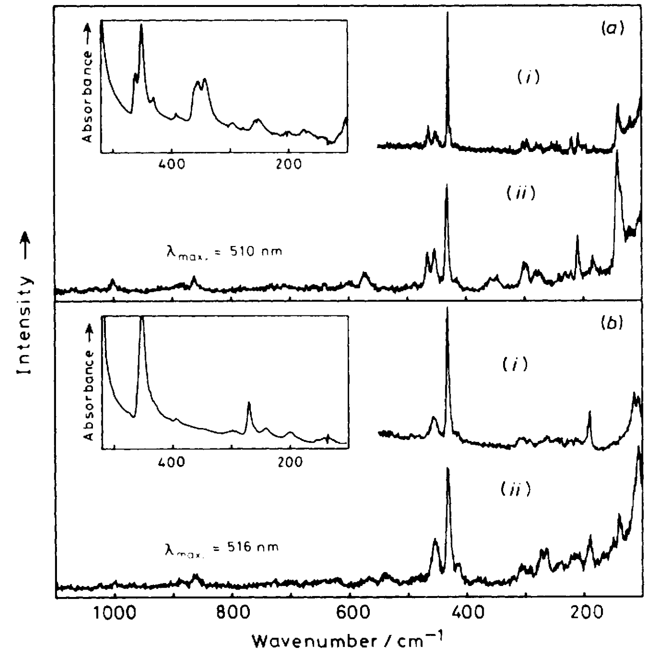

Figure 5. Raman (100—550 cm^{-1}), resonance Raman (100—1 100 cm^{-1}), and infrared (100—520 cm^{-1}, inset) spectra of (*a*) $[PPh_4]_2[MoS_4(CuCl)_4]$, λ_0 = 676.4 (*i*) and 514.5 nm (*ii*); (*b*) $[PPh_4]_2[MoS_4(CuBr)_4]$, λ_0 = 676.4 (*i*) and 514.5 nm (*ii*)

Table 4. Wavenumbers ($\tilde{\nu}/cm^{-1}$) and assignments of bands observed in the Raman and infrared spectra of the complexes $[PPh_4]_2[MoS_4(CuL)_4]$ in the range 520—100 cm^{-1}

L = Cl		L = Br		
R	i.r.	R	i.r.	Assignment (D_{2d})
463	462m			$\nu_{asym.}$(Mo–S), *e*
		455		
452	451s		457s	
430	431w	432		$\nu_{sym.}$(Mo–S), a_1
415		417		$\nu_{asym.}$(Mo–S), b_2
	393w		393w	
	360 (sh)			ν(Cu–Cl)
	355m			
	344m			
302		306		
295	295w	292	297w	
			291w	
280				
272			268m	ν(Cu–Br)
		262		
254	252w			
			240w	
220				
208				
	200w			
182		190	198w	
	175w		153w	
140			137w	
120				
		114		
		107		

Overtone and combination bands:

$[MoS_4(CuCl)_4]^{2-}$	572 (430 + 140), 597 (452 + 140, 463 + 140), 861 (2 × 430)
$[MoS_4(CuBr)_4]^{2-}$	538 (432 + 107), 567 (455 + 107), 621 (432 + 190), 864 (2 × 432)

For [NPr$^n_4$]Br the band at 1 321 cm^{-1} is the strongest, while weaker ones are observed at 130, 159, 318, 337, 358, 376, 763, 792, 850, 938, 972, 1 035, 1 042, 1 066, 1 105, 1 143, 1 164, 1 275, 1 445, 1 451, 1 456, 1 466, 1 472, and 1 482 cm^{-1}.

For the [PPh$_4$]$_2$[MS$_4$(CuL)$_n$] salts the 1 000 and 1 030 cm^{-1} cation modes appear as weak bands in the Raman and near r.R. but not in r.R. spectra because the intensities of cation bands are not enhanced under resonance conditions for the [MS$_4$(CuL)$_n$]$^{2-}$ anion. [NPr$^n_4$]$^+$ is only a very weak scatterer and no cation bands have been observed in Raman and r.R. spectra of [NPr$^n_4$]$_2$[MS$_4$(CuL)$_n$].

The typical aryl ring modes give rise to bands in the range 680—1 100 cm^{-1} in the Raman spectra of the complexes involving thiolate ligands.

Conclusions

The symmetric molybdenum–sulphur stretching modes of the [MoS$_4$(CuL)$_n$]$^{2-}$ ions, n = 1—4, can be identified as giving rise to strong and sharp bands in the Raman spectra of these complexes and particularly in the r.R. spectra of type (**I**) and (**II**) complexes. The wavenumbers of these modes are distinctive: $\nu_{sym.}$(Mo–μ_3-S), $\nu_{sym.}$(Mo–μ-S), and $\nu_{sym.}$(Mo–S^t) are found in the regions 429—432, 439—469, and 475—486 cm^{-1}, respectively. This parallels the change in bond length: d(Mo–μ_3-S) = 2.227—2.242, d(Mo–μ-S) = 2.196—2.245, and d(Mo–S^t) = 2.162—2.163 Å. As the maximum local symmetry of the MoS$_4$Cu$_n$ moiety changes from C_{2v} through D_{2d} and C_2 to D_{2d} (n = 1—4) the pattern (*i.e.* the number of bands, their position and intensity) in the ν(Mo–S) region of the Raman and r.R. spectra is characteristic of the number of copper(I) ions co-ordinated to [MoS$_4$]$^{2-}$. $\nu_{sym.}$(W–S) occurs, for those structurally related tungsten complexes studied, some 5—20 cm^{-1} above $\nu_{sym.}$(Mo–S). Of the complexes studied, the resonance enhancement of bands attributed to ν(Cu–L) modes is rather weak except for the cyano ones. This leads to the conclusion that the changes in bond lengths upon excitation within the contour of the sulphur–molybdenum charge-transfer band are confined to the MoS$_4$Cu$_n$ core. This means that the molecular orbitals involved in the charge-transfer process are mainly centred on that core.

Raman and r.R. spectroscopy thus show promise as sensitive techniques with which to identify co-ordination modes of transition metals to tetrathiomolybdate(VI) anions, a matter of particular interest in respect of the thiomolybdate-containing biological systems.

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