Raman and Resonance-Raman Studies of Platinum Group Tetrathiomolybdates and Tetrathiotungstates

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The Raman and resonance-Raman spectra of the ions $[M'(MS_4)_2]^{2-}$ (M' = Ni, Pd, or Pt; M = Mo or W) at *ca.* 80 K have been studied with excitation lines ranging from 647.1 to 337.5 nm. The bands assigned to the $\nu(M\text{-}S_b)$, $\nu(M\text{-}S_t)$, and $\nu(M'\text{-}S)$ (b = bridging, t = terminal) fundamentals all show resonance enhancement, and overtone progressions are observed in the resonance-Raman spectra. The nature of these progressions depends on the line used to excite the Raman spectrum. From excitation profile studies, assignments are suggested for the resonant electronic absorption bands.

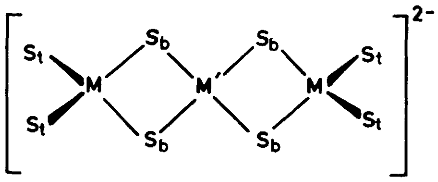
There has been considerable interest[1-4] in the properties of heterometal complexes of the tetrathiomolybdate and tetrathiotungstate ligands, $[MS_4]^{2-}$, since they were first prepared by Müller and Diemann.[5] The $[MS_4]^{2-}$ ions show versatile co-ordination behaviour and, as a result of their having low-lying unoccupied orbitals, form complexes with unusual electronic properties.[1] Furthermore, many of the complexes show interesting and reversible redox processes.[6] Thiomolybdate complexes are of biochemical significance in the nitrogenase problem and in Cu–Mo antagonism.[7-9]

Although i.r. spectra of ions of the type $[M'(MS_4)_2]^{2-}$ (M' = Ni, Pd, or Pt; M = Mo or W) have been studied extensively,[10] only fragmentary studies of the Raman spectra have been reported.[2] A normal co-ordinate analysis[11-14] of the ions (square planar, D_{2h} symmetry) treats only the i.r.-active modes. In the present study the Raman spectra of the tetrathiomolybdate and -tungstate complexes of nickel, palladium, and platinum have been studied and, in particular, the information made available from resonance-Raman (r.R.) studies[15] on the ions has been examined.

No molecular orbital (m.o.) treatment of the square-planar tetrathiotungstate and tetrathiomolybdate complexes is available. The electronic structure of the related 1,2-dithiolenes has been much discussed, *cf.* the m.o. schemes of Gray and coworkers[16] and Schrauzer and Mayweg,[17] and the ordering of the levels has been shown to depend critically on the central atom and on its oxidation state.[18] It is apparent that, on the basis of the information currently available, the ordering of levels in many of these complexes is uncertain. However, both m.o. schemes of refs. 16 and 17 predict a highest occupied molecular orbital (h.o.m.o.) of predominantly ligand and a lowest unoccupied molecular orbital (l.u.m.o.) of predominantly metal character.

On the basis of electrochemical studies, Callahan and Piliero[6] have suggested that, in the case of the nickel complexes, the l.u.m.o. is nickel based and of a_g symmetry. The gap between the l.u.m.o. and a ligand-based orbital of b_{1g} symmetry reduces on going to the analogous palladium complexes, whilst for the analogous platinum complexes, the two levels are of nearly equal energy. This is similar to the situation for the maleonitriledithiolate complexes of nickel, palladium, and platinum as discussed by Geiger *et al.*[19]

However, a recent e.s.r. study of electrochemically reduced $[Ni(MoS_4)_2]^{2-}$, $[Ni(WS_4)_2]^{2-}$, $[Pd(MoS_4)_2]^{2-}$, and $[Pd(WS_4)_2]^{2-}$ by Bowmaker *et al.*[20] indicates that, for the nickel complexes, the one-electron reduction is based on the molybdenum or tungsten atoms whereas for the palladium complexes it is palladium based. X_α Calculations on $[Ni(MoS_4)_2]^{2-}$ and $[Ni(MoS_4)_2]^{3-}$ also suggest that for $[Ni(MoS_4)_2]^{2-}$ the l.u.m.o. is not the expected nickel d_{xy} orbital but composed principally of low-lying molybdenum or tungsten $d_{x^2-y^2}$ and d_{z^2} orbitals.



M = Mo or W
M' = Ni, Pd, or Pt

Experimental

The complexes $[NPr^n_4]_2[M'(MS_4)_2]$ (M' = Ni, Pd, or Pt; M = Mo or W) were prepared by literature methods.[6,13] Electronic spectra were recorded at *ca.* 80 K on a Varian 2390 spectrometer. Raman spectra were recorded using a Spex 14018/R6 spectrometer. Exciting radiation was provided by Coherent Radiation model CR12 argon-ion and 3000K krypton-ion lasers. Samples were prepared as pressed discs in KBr or $K[BF_4]$ and held at liquid-nitrogen temperature, except for the display spectrum of $[NPr^n_4]_2[Ni(MoS_4)_2]$ which was recorded for a sample at *ca.* 45 K using an Air Products Displex cryostat.

At liquid-nitrogen temperature, power levels of <50 mW at the sample caused minimal decomposition except in the case of $[Ni(MoS_4)_2]^{2-}$, for which the need to avoid decomposition restricted the power levels which could be used to <20 mW at the sample. Solution measurements were made using dimethylformamide, in which solvent the complexes show reproducible spectra; however, a gradual decrease in band intensity is apparent over a period of time ($\sim$10% in 10—15 min), particularly for $[NPr^n_4]_2[Ni(MoS_4)_2]$. Excitation profiles were measured relative to the $\nu_1(a_1)$ band of $K[BF_4]$ and corrected for the spectral response of the instrument.

Results

Electronic Spectra.—The electronic spectra of the complexes (Table 1) are dominated by intense ($\varepsilon \sim 1.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) sulphur-to-molybdenum or sulphur-to-tungsten charge-transfer bands which extend into the region where *d–d* transitions would be expected to occur. This restricts the extent to which electronic structural information may be obtained from the electronic spectra. The lowest energy electronic band of

Table 1. Summary of the properties of the complexes $[NPr^n_4]_2[M'(MS_4)_2]$

Ion	Colour	10^{-3} $\nu_{max.}$ of lowest energy electronic band^a/cm^{-1}	Key i.r. band maxima/cm^{-1} and assignments		Redox potential^b E/V *vs.* s.c.e. (CH_3CN-$[NPr^n_4]Br$)
$[Ni(MoS_4)_2]^{2-}$	Red	19.6s	445, 455	$\nu(Mo-S_b)$	−0.55
			490, 510	$\nu(Mo-S_t)$	−1.35
			330	$\nu(Ni-S)$	
$[Pd(MoS_4)_2]^{2-}$	Dark red	20.9s, 21.3s	435, 450	$\nu(Mo-S_b)$	−1.03
			495, 510	$\nu(Mo-S_t)$	−1.34
			295, 310	$\nu(Pd-S)$	
$[Pt(MoS_4)_2]^{2-}$	Red	21.6s	435, 460	$\nu(Mo-S_b)$	−1.26
			495, 515	$\nu(Mo-S_t)$	
			310, 330, 345	$\nu(Pt-S)$	
$[Ni(WS_4)_2]^{2-}$	Yellow-brown	23.6s, 26.5s	450	$\nu(W-S_b)$	−0.55
			490	$\nu(W-S_t)$	−1.50
			320, 330	$\nu(Ni-S)$	
$[Pd(WS_4)_2]^{2-}$	Yellow-brown	25.1s, 27.6s	440	$\nu(W-S_b)$	−1.03
			490	$\nu(W-S_t)$	−1.40
			290, 310	$\nu(Pd-S)$	
$[Pt(WS_4)_2]^{2-}$	Yellow	23.2 (sh), 24.2s, 31.6s	440, 450	$\nu(W-S_b)$	−1.29^c
			495, 500	$\nu(W-S_t)$	
			300, 350	$\nu(Pt-S)$	

^{a} Recorded by transmission as KBr pellets at 80 K. ^{b} Ref. 6 (s.c.e. = saturated calomel electrode). ^{c} $[NEt_4]ClO_4$.

the complexes corresponds to the $^1T_2 \longleftarrow {}^1A_1$ ($e \longleftarrow t_1$) transition of the free $[MS_4]^{2-}$ ligand (21 250 and 25 000 cm^{-1} for M = Mo and W respectively). However, the strong metal–ligand interactions characteristic of thiometalate complexes with central atoms possessing open *d* shells give rise to some delocalisation of the valence *d* electrons, and this affects the $^1T_2 \longleftarrow {}^1A_1$ band as follows: in $[Ni(WS_4)_2]^{2-}$ and $[Pd(WS_4)_2]^{2-}$, it is split (by 2 500—3 000 cm^{-1}) into two components of approximately equal intensity whereas for $[Pt(WS_4)_2]^{2-}$ it is shifted to somewhat lower wavenumbers. No comparable splitting is observed for tetrathiomolybdate complexes, apart from a slight amount (*ca.* 400 cm^{-1}) for $[Pd(MoS_4)_2]^{2-}$ as a KBr disc at liquid-nitrogen temperature. However, for $[Ni(MoS_4)_2]^{2-}$ the $^1T_2 \longleftarrow {}^1A_1$ band is shifted to lower wavenumbers by *ca.* 1 700 cm^{-1} from that for $[MoS_4]^{2-}$.

It has been claimed[2] that the close proximity of the S-bridging atoms to one another (seperation *ca.* 2.8 Å) will tend to increase the energy of the occupied non-bonding $3p$(S) ligand orbitals which can interact with the nickel, palladium, or platinum d_{xz} and d_{yz} orbitals, and that such interactions would be particularly strong for $[Ni(MoS_4)_2]^{2-}$.

A summary of the known properties of the complexes is given in Table 1.

Raman Spectra.—1. *Tetrathiomolybdates.* The wavenumbers of the bands observed in the Raman spectra are recorded in Table 2, the dominant features being attributed to the Mo–S stretching fundamentals. The first set of bands occurs around 440 cm^{-1} and is split into two components whereas the second set occurs at around 500 cm^{-1} and is split into three components. The assignments of the bands at 440 cm^{-1} to bridging Mo–S modes and of those at 500 cm^{-1} to terminal Mo–S modes have been made on the basis of a normal co-ordinate analysis in conjunction with ^{58}Ni and ^{92}Mo isotopic substitution.[14] Only one band attributable to $\nu(Mo-S_b)$ and one to $\nu(Mo-S_t)$ display resonance enhancement, where $\nu(Mo-S_t)$ and $\nu(Mo-S_b)$ represent the terminal and bridging Mo–S stretching frequencies, respectively. Each of these bands is polarised (depolarisation ratio, $\rho = \frac{1}{3}$ at resonance with the *ca.* 500 nm electronic band) and is thus attributable to a totally symmetric fundamental.

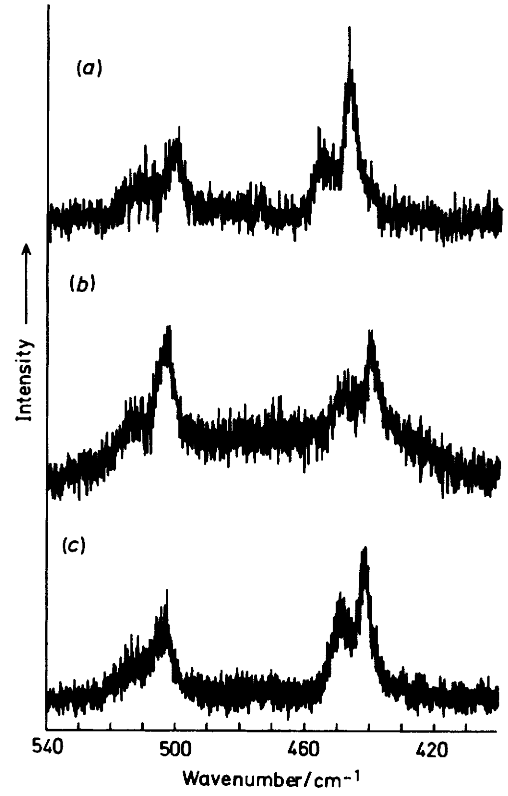


Figure 1. Off-resonance Raman spectra of $[NPr^n_4]_2[M'(MoS_4)_2]$ [M′ = Ni (*a*), Pd (*b*), or Pt (*c*)] at λ_0 = 647.1 nm

When the complexes are excited with 647.1 nm radiation, the spectra of all three complexes are similar to one another and the total $\nu(Mo-S_t)$ band intensity is comparable with that of $\nu(Mo-S_b)$ (see Figure 1). As the tail of the lowest energy electronic transition in these complexes extends into the red, such spectra are, strictly speaking, pre-resonance-Raman spectra. This contrasts with the situation for the thiotungstate complexes[2] (see later) where, off resonance, the intensity of the

Table 2. Wavenumbers and assignments of bands observed in the resonance-Raman spectra of $[NPr^n_4]_2[M'(MoS_4)_2]$ (M′ = Ni, Pd, or Pt)[a]

$\tilde{\nu}$/cm^{-1}			
M′ = Ni	M′ = Pd	M′ = Pt	Assignment
	176		
	214		
252	218.5		$\delta(MoS_4)$
		300.5	ν_7
304	310	312	ν_4 } $\nu(M'-S)$
332	318.7	344	ν_1
444.5[b] (p)	437.5[c] (p)	440.6[d] (p)	$\nu_2\ (a_{1g})$ } $\nu(Mo-S_b)$
452	445 (sh)	448	
	465	463	
	497 (sh)	497 (sh)	ν_5
499.3 (p)	501 (p)	502.2 (p)	$\nu_3\ (a_{1g})$ } $\nu(Mo-S_t)$
510	511.7	512	ν_6
		548	
	607		
	611	610	$\nu_4 + \nu_7$
	618	636	$2\nu_4$
	627		$\nu_1 + \nu_4$
	634		$2\nu_1$
		742	
	749	750	
779	756	785	$\nu_1 + \nu_2$
	808		
	821		
891	874	878	$2\nu_2$
		923	
	931	934	$\nu_2 + \nu_5$
940	940	944	$\nu_2 + \nu_3$
	991		$2\nu_5$
		991	$\nu_3 + \nu_5$
	1 003.5	1 005	$2\nu_3$
		1 009	$\nu_5 + \nu_6$
	1 046		$\delta(CCC)$ (?), $[NPr^n_4]^+$
	1 189	1 189	$2\nu_2 + \nu_4$
1 220		1 222	$2\nu_2 + \nu_1$
		1 250	
	1 250	1 295	
1 336	1 311	1 315	$3\nu_2$
	1 370	1 373	$2\nu_2 + \nu_5$
	1 375	1 380	$2\nu_2 + \nu_3$
		1 394	
	1 430	1 435	$\nu_2 + 2\nu_5$ $\nu_2 + 2\nu_3$
	1 449		$2\nu_3 + 445$
	1 484		
	1 492		
	1 499		$3\nu_3$
	1 622	1 625	$3\nu_2 + \nu_4$
	1 630	1 659	$3\nu_2 + \nu_1$
	1 747	1 752	$4\nu_2$
	1 808	1 812	$3\nu_2 + \nu_5$
	1 811	1 818	$3\nu_2 + \nu_3$
		1 830	
	1 871		$2\nu_2 + 2\nu_5$
		1 871	$2\nu_2 + 2\nu_3$
	1 884		
	2 057	2 048	$4\nu_2 + \nu_4$
	2 181	2 184	$5\nu_2$
	2 243	2 242	$4\nu_2 + \nu_5$
	2 247	2 251	$4\nu_2 + \nu_3$
	2 616		$6\nu_2$
	2 682		$5\nu_2 + \nu_3$

[a] sh = Shoulder, p = polarised. [b] $\rho = 0.28$ with 514.5 nm excitation. [c] $\rho = 0.33$ with 488.0 nm excitation. [d] $\rho = 0.36$ with 514.5 nm excitation.

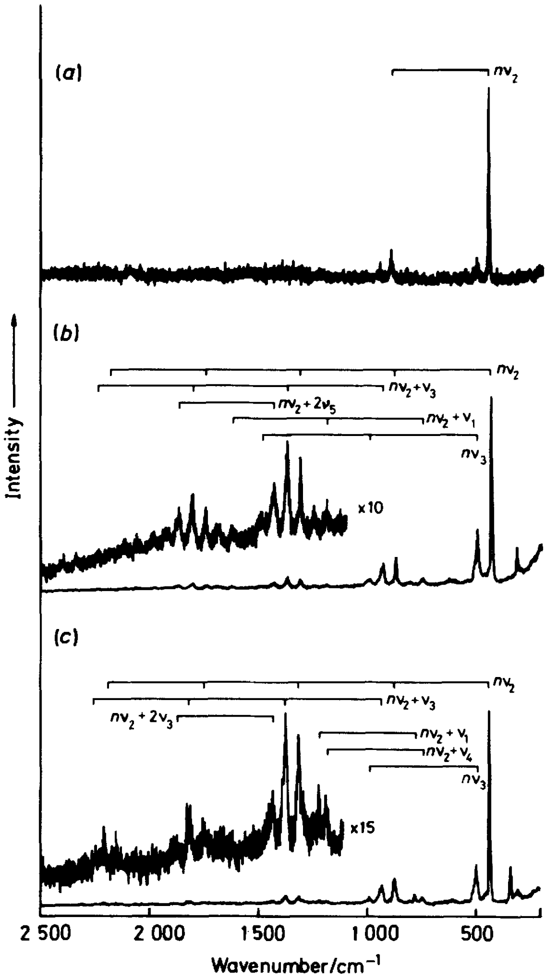


Figure 2. Resonance-Raman spectra of (*a*) $[NPr^n_4]_2[Ni(MoS_4)_2]$ at $\lambda_o = 514.5$, (*b*) $[NPr^n_4]_2[Pd(MoS_4)_2]$ at $\lambda_o = 476.5$, and (*c*) $[NPr^n_4]_2[Pt(MoS_4)_2]$ at $\lambda_o = 496.5$ nm

band attributed to $\nu(W-S_t)$ is very much greater than that attributed to $\nu(W-S_b)$, as would be predicted from the higher π-bond character of its terminal relative to its bridging WS bonds.[2,11,14]

The spectra of all three tetrathiomolybdates show resonance enhancement of the bands attributed to $\nu_2[\nu(Mo-S_b)]$, $\nu_3[\nu(Mo-S_t)]$, and $2\nu_2$, but only those of the palladium and platinum complexes show enhancement of $\nu_1[\nu(M'-S)]$. The r.R. spectra (see Figure 2) are dominated by overtone progressions in ν_2 and $\nu_2 + \nu_a$, where ν_a is ν_1, ν_3, ν_4, or ν_5, *i.e.* other Raman-active bands in the 310—502 cm^{-1} region (Table 2). These progressions extend to $6\nu_2$ and to $5\nu_2 + \nu_a$ for the palladium complex, and to $5\nu_2$ and to $4\nu_2 + \nu_a$ for the platinum complex. There are also weak progressions in ν_3 (to $3\nu_3$). The r.R. spectrum of $[Ni(MoS_4)_2]^{2-}$ only shows weak progressions in ν_2 (to $3\nu_2$) and $\nu_2 + \nu_1$ (to $2\nu_2 + \nu_1$), and the combination band $\nu_2 + \nu_3$. Harmonic band wavenumbers (ω_2) and anharmonicity constants (x_{22}) for all three molybdenum complexes are listed in Table 3.

Excitation profiles were measured for all bands which were sufficiently intense to give reliable data. Interference from other Mo–S$_t$ stretches, especially off resonance, was a particular problem when measuring the intensity of ν_3, which accordingly may contain some contribution from Mo–S$_t$ stretches other than that of a_{1g} symmetry. A similar, though less extensive problem, occurs for the Mo–S$_b$ stretches. Accordingly, the

Table 3. Harmonic band wavenumbers and anharmonicity constants for $[NPr^n_4]_2[M'(MoS_4)_2]$ and $[NPr^n_4]_2[M'(WS_4)_2]$ (M' = Ni, Pd, or Pt)

Ion	ω_2/cm^{-1}	x_{22}/cm^{-1}
$[Ni(MoS_4)_2]^{2-}$	444.5	$\leqslant -0.5$
$[Pd(MoS_4)_2]^{2-}$	438.0	−0.28
$[Pt(MoS_4)_2]^{2-}$	441.9	−0.83
$[Ni(WS_4)_2]^{2-}$	459.5	~0.0
$[Pd(WS_4)_2]^{2-}$ *	448.1	−0.2
$[Pt(WS_4)_2]^{2-}$	452	~ −1

* Also determined: $\omega_1 = 317.5$ cm^{-1}, $x_{11} = -0.23$ cm^{-1}.

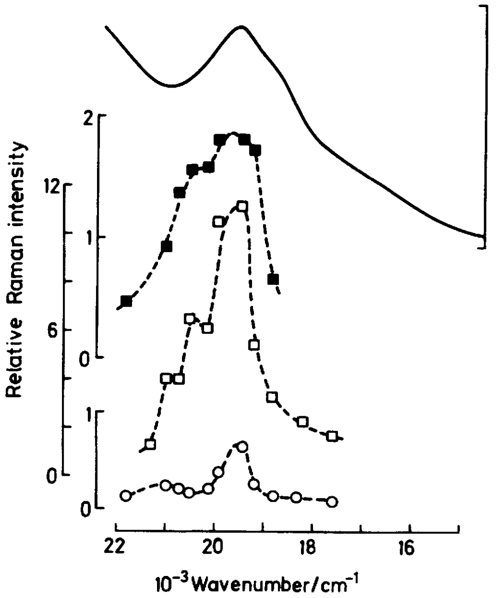


Figure 3. Excitation profiles of the ν_b (□), $2\nu_b$ (■), and ν_t (○) bands of $[Ni(MoS_4)_2]^{2-}$ together with the electronic spectrum

excitation profiles of these bands are labelled as ν_t and ν_b, respectively, in Figures 3—5. For all three complexes, there is structure in the excitation profiles.

2. *Tetrathiotungstates.* The wavenumbers of the bands observed in the Raman spectra are recorded in Tables 4—7 and, as for the tetrathiomolybdates, the dominant features are attributed to the W–S and M'–S stretching fundamentals. The bridging W–S band around 450 cm^{-1} is split into two components and the terminal W–S band around 500 cm^{-1} into three components (Figure 6).

Off resonance (647.1 or 568.2 nm excitation), the band attributed to $\nu(W-S_t)$ completely dominates the spectrum and that attributed to $\nu(W-S_b)$ has very low intensity. This is as predicted from the higher π-bond character of the terminal than the bridging W–S bonds.[2,11,14]

At resonance with the lowest electronic band, the spectra of the tetrathiotungstates are complicated and differ significantly from those of the corresponding tetrathiomolybdates. The bands attributed to $\nu(M'-S)$, $\nu(W-S_b)$, and $\nu(W-S_t)$ all show resonance enhancement [see Figures 7—9, where $\nu(W-S_t)$ denotes any of the three terminal W–S stretches which may contribute]. As for the tetrathiomolybdates, interference from $W-S_t$ and $W-S_b$ stretches other than those of a_{1g} symmetry affected the measurement of the intensities of the ν_3 and ν_2 bands, which are similarly labelled as ν_t and ν_b, respectively, in Figures 10—12.

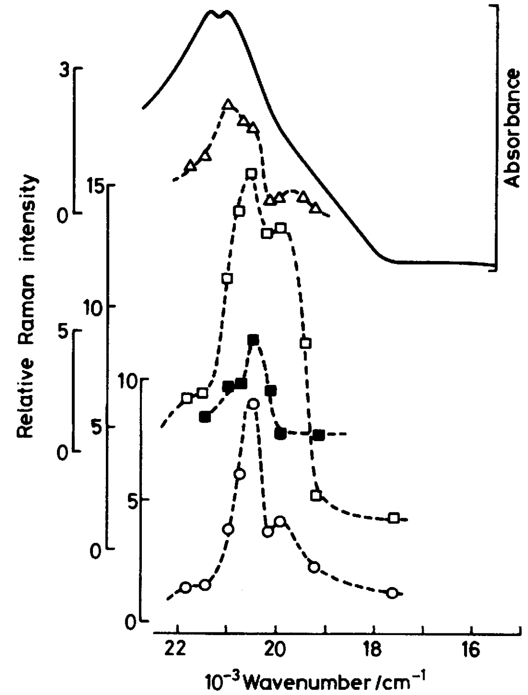


Figure 4. Excitation profiles of the ν_b (□), $2\nu_b$ (■), ν_t (○), and $\nu(Pd-S)$ (△) bands of $[Pd(MoS_4)_2]^{2-}$ together with the electronic spectrum

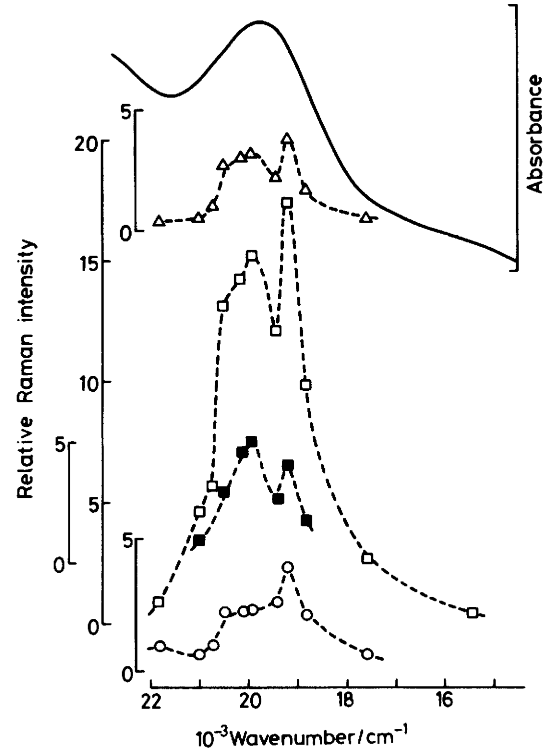


Figure 5. Excitation profiles of the ν_b (□), $2\nu_b$ (■), ν_t (○), and $\nu(Pt-S)$ (△) bands of $[Pt(MoS_4)_2]^{2-}$ together with the electronic spectrum

$[NPr^n_4]_2[Ni(WS_4)_2]$. At resonance with the electronic absorption band at 424 nm, the Raman band assigned to $\nu(W-S_b)$ and that assigned to $\nu(W-S_t)$ are both enhanced, the former being the more enhanced. At resonance with the electronic absorption band at 377 nm, the band assigned to $\nu(W{-}S_t)$ and that assigned to $\nu(Ni{-}S)$ are both enhanced, the latter being the more enhanced.

At resonance with the electronic absorption band at 424 nm, overtone progressions are observed in ν_2 (to $5\nu_2$), ν_3 (to $3\nu_3$),$n\nu_2 + \nu_3$ (to $n = 5$), $n\nu_3 + \nu_2$ (to $n = 3$), $n\nu_2 + 2\nu_3$ (to $n = 4$), $n\nu_2 + 3\nu_3$ (to $n = 3$), and $n\nu_3 + 2\nu_2$ (to $n = 3$).

At resonance with the electronic absorption band at 377 nm, overtone progressions are observed in ν_1 (to $3\nu_1$), ν_3 (to $3\nu_3$), ν_4 (to $2\nu_4$), $n\nu_1 + \nu_2$ and $n\nu_1 + \nu_6$ (to $n = 2$), $n\nu_3 + \nu_2$ (to $n = 3$), and $n\nu_6 + \nu_1$ (to $n = 2$), together with the combination band $\nu_1 + \nu_2 + \nu_3$ (Table 5).

$[NPr^n_4]_2[Pd(WS_4)_2]$. At resonance with the electronic absorption band at 399 nm, the bands attributed to $\nu(W{-}S_b)$ and $\nu(W{-}S_t)$ are both enhanced, the latter being much the more intense. At resonance with the electronic absorption band at 362 nm, the Raman band attributed to $\nu(Pd{-}S)$ is preferentially enhanced and those attributed to $\nu(W{-}S_b)$ and $\nu(W{-}S_t)$ are also enhanced and of about the same intensity. For this complex the band attributed to $\nu(W{-}S_b)$ is never more intense than that attributed to $\nu(W{-}S_t)$.

At resonance with the electronic absorption band at 399 nm, overtone progressions are observed in ν_2 (to $2\nu_2$), ν_4 (to $2\nu_4$), ν_5 (to $4\nu_5$), $n\nu_2 + \nu_6$ (to $n = 2$), $n\nu_4 + \nu_5$ ($n = 2$, 4, or 5), $n\nu_5 + \nu_4$ (to $n = 2$), $n\nu_6 + \nu_4$ ($n = 1$ or 3), $n\nu_6 + \nu_2$ (to $n = 2$), $n\nu_6 + \nu_5$ ($n = 2$ or 3), and $n\nu_6 + \nu_2 + \nu_5$ (to $n = 3$), together with various combination bands (Table 6) such as $2\nu_5 + 2\nu_6$.

At resonance with the electronic absorption band at 362 nm, overtone progressions are observed in ν_1 (to $7\nu_1$), ν_2 (to $2\nu_2$), ν_3 (to $3\nu_3$), ν_6 (to $3\nu_6$), $n\nu_1 + \nu_3$ (to $n = 7$), $n\nu_1 + \nu_2$ (to $n = 4$), $n\nu_1 + 2\nu_3$ (to $n = 6$), $n\nu_1 + 3\nu_3$ (to $n = 4$), $n\nu_3 + \nu_1$ (to $n = 3$), $n\nu_3 + \nu_2$ ($n = 2$ or 3), $n\nu_6 + \nu_5$ (to $n = 3$), and $n\nu_6 + (\nu_2 + \nu_5)$ (to $n = 3$) (Table 6).

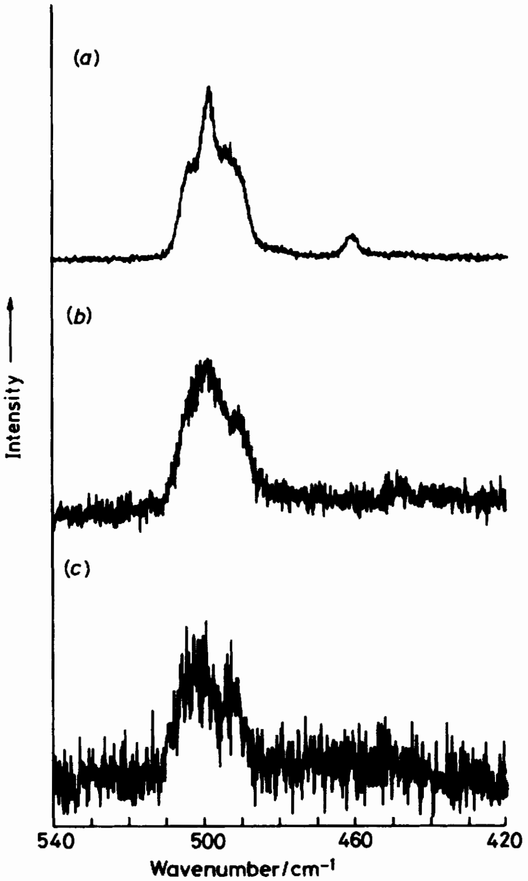


Figure 6. Off-resonance Raman spectra of $[NPr^n_4]_2[M'(WS_4)_2]$ [M' = Ni (*a*), Pd (*b*), or Pt (*c*)] at λ_0 = 568.2 nm

Table 4. Bands observed in the resonance-Raman spectra of $[NPr^n_4]_2[M'(WS_4)_2]$ (M' = Ni, Pt, or Pt)^a

$\tilde{\nu}$/cm^{-1}				
M' = Ni	M' = Pd	M' = Pt	Assignment	
254				$\delta(WS_4)$
267	275	242		
330	315.5	301	ν_4	$\nu(M'{-}S)$
301.5 (p)^b	317 (p)^c	342 (p)^d	ν_1 (a_{1g})	
458.5 (p)^e	447.7 (p)^f	451.5 (p)^g	ν_2 (a_{1g})	$\nu(W{-}S_b)$
462	464	468.5 (sh)		
492.5	493	493	ν_5	$\nu(W{-}S_t)$
496	498	499	ν_6	
499.7 (p)^h	501 (p)^i	503 (p)^j	ν_3 (a_{1g})	

^{a} sh = Shoulder, p = polarized. ^{b} ρ = 0.61 or 0.35 with 406.7 or 356.4 nm excitation respectively. ^{c} ρ = 0.43 with 356.4 nm excitation. ^{d} ρ = 0.37 or 0.58 with 413.1 or 337.5 nm excitation respectively. ^{e} ρ = 0.62 with 406.7 nm excitation. ^{f} ρ = 0.43 or 0.40 with 413.1 or 406.7 nm excitation respectively. ^{g} ρ = 0.33 with 413.1 nm excitation. ^{h} ρ = 0.32 with 365.4 nm excitation. ^{i} ρ = 0.35 or 0.46 with 413.1 or 406.7 nm excitation respectively. ^{j} ρ = 0.38 with 413.1 nm excitation.

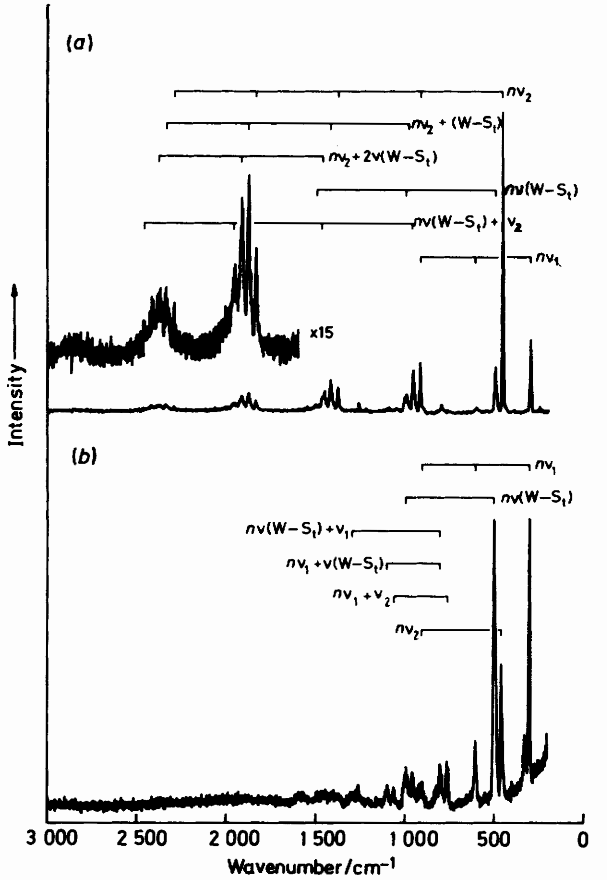


Figure 7. Resonance-Raman spectra of $[NPr^n_4]_2[Ni(WS_4)_2]$ at λ_0 = (*a*) 413.1 and (*b*) 356.4 nm

Table 5. Details of the r.R. spectra of $[NPr^n_4]_2[Ni(WS_4)_2]$; λ_o in nm

λ_0 = 406.7		λ_0 = 413.1		λ_0 = 406.7		λ_0 = 356.4		λ_0 = 356.4 or 413.1	
n	$n\nu_1$	n	$n\nu_2$	n	$n\nu_3$	n	$n\nu_6$	n	$n\nu_4$
1	301.5	1	458.5	1	499.7	1	496	1	330
2	604	2	919	2	996	2	991	2	653
3	908	3	1 377.5	3	1 494				
		4	1 838						
		5	2 298						

λ_0 = 356.4		λ_0 = 406.7		λ_0 = 356.4		λ_0 = 406.7					
n	$n\nu_1 + \nu_2$	n	$n\nu_1 + \nu_3$	n	$n\nu_1 + \nu_6$	n	$n\nu_3 + \nu_1$	n	$n\nu_3 + 2\nu_1$	n	$n\nu_3 + \nu_1 + \nu_2$
1	762.5	1	801			1	801	1	1 108	1	1 259
2	1 066	2	1 108	2	1 101	2	1 299	2	1 605		
n	$n\nu_1 + \nu_2 + \nu_3$	n	$n\nu_1 + \nu_2 + \nu_6$	n	$n\nu_1 + 2\nu_3$	n	$n\nu_3 + \nu_2$	n	$n\nu_3 + 2\nu_2$	n	$n\nu_3 + 3\nu_2$
1	1 259					1	960	1	1 423		
2	1 568	2	1 558	2	1 605	2	1 458	2	1 917		
						3	1 956	3	2 417	3	2 877

λ_0 = 406.7						λ_0 = 356.4					
n	$n\nu_2 + \nu_3$	n	$n\nu_2 + 2\nu_3$	n	$n\nu_2 + 3\nu_3$	n	$n\nu_6 + \nu_1$	n	$n\nu_6 + \nu_2$	n	$n\nu_4 + \nu_2$
1	960	1	1 458	1	1 956	1				1	822
2	1 423	2	1 917	2	2 417	2	1 292	2	1 449		
3	1 881	3	2 378	3	2 877			3	1 942		
4	2 338	4	2 833								
5	2 800										

λ_0 = 356.4 or 413.1				λ_0 = 413.1	
n	$n\nu_2 + \nu_1$	n	$n\nu_2 + \nu_1 + \nu_3$	n	$n\nu_2 + \nu_6$
1	762.5	1	1 259	2	1 419
2	1 214			3	1 875

$[NPr^n_4]_2[Pt(WS_4)_2]$. At resonance with the electronic absorption band at 413 nm the Raman bands attributed to $\nu(W-S_b)$ and $\nu(W-S_t)$ are both enhanced, the former being slightly the more intense; in addition, the band attributed to $\nu(Pt-S)$ is somewhat enhanced. There is also some enhancement of all these bands but especially that attributed to $\nu(Pt-S)$ using the 337.5 nm line, the wavelength of which lies under the contour of the electronic absorption band at 316 nm.

At resonance with the electronic absorption band at 413 nm, overtone progressions are observed in ν_1 (to $2\nu_1$), ν_2 (to $2\nu_2$), ν_3 (to $3\nu_3$), $n\nu_2 + \nu_1$ (to $3\nu_2$), and $n\nu_3 + n'\nu_5$ (to $n = 1, n' = 3$), together with many combination bands involving at least three different fundamentals (Table 7).

Harmonic band wavenumbers and anharmonicity constants for all three tungsten complexes are included in Table 3.

Discussion

1. *Tetrathiomolybdates.*—The observation of progressions $n\nu_2 + \nu_a$, where $\nu_2 = \nu(Mo-S_b)$, and the enhancement of bands attributed to $Mo-S_t$ and M′-S modes for the palladium and platinum complexes is compatible with a delocalised bonding scheme. However, the preferential enhancement of ν_2 $[\nu(Mo-S_b)]$ over ν_3 $[\nu(Mo-S_t)]$ and the fact that ν_2 is the progression-forming mode suggest that the resonant electronic transition is localised on the $MoS_2M'S_2Mo$ part of the ion. In the complex, $[NBu^n_4]_2[MoS_4]$, a significant increase in the bond length of 0.035 Å is observed on excitation to the lowest $^1T_2$ state.[15,21] This may be contrasted with the situation for the ion $[(PhS)_2FeS_2MoS_2]^{2-}$,[22] for which the geometric changes attendant upon electronic excitation are very small and spread out over the whole of the $S_2FeS_2MoS_2$ framework; thus overtones, even at resonance, are of very low intensity.[23]

When $[MoS_4]^{2-}$ is bound to copper or silver, *e.g.* as in $LM'S_2MoS_2M'L$ (M′ = Cu or Ag, L = PPh_3), or in $[Ag(MoS_4)]^-$, long overtone progressions in $\nu(MoS)$ are observed in the Raman spectrum at resonance with the lowest $Mo \longleftarrow S$ charge-transfer band, whereas no bands associated with other parts of the molecule were detected;[24,25] this indicates a high degree of localisation of the resonant electronic transition on the MoS_4 core; the degree of localisation is more pronounced for silver than for copper.[25]

The excitation profiles of the resonance-enhanced bands all display structure, part of which is undoubtedly vibrational in nature, but part results from overlapping electronic bands [in the C_{2v} local symmetry of the Mo (or W) atoms, the $^1T_2$ upper state in T_d nomenclature would split into three components (A_1, B_1, and B_2)]. The ρ values of bands attributed to the various skeletal modes all approach $\frac{1}{3}$ at resonance, an observation which agrees with the requirement that the resonant state is non-degenerate. Moreover, interference is possible between the contributions to the Raman intensity from the different vibronic levels of each excited state. All profiles peak under the absorption maximum, which occurs near 520 nm for all three complexes. Attempts to reproduce the excitation profiles by Franck–Condon calculations based upon a single resonant transition were unsuccessful, consistent with the idea that more than one electronic transition contributes to the resonant absorption band.

Table 6. Details of the r.R. spectra of $[\mathrm{NPr^n}_4]_2[\mathrm{Pd(WS_4)_2}]$;* λ_o in nm

$\lambda_o = 356.4$		$\lambda_o = 413.1$		$\lambda_o = 356.4$		$\lambda_o = 413.1$				$\lambda_o = 356.4$	
n	$n\nu_1$	n	$n\nu_2$	n	$n\nu_3$	n	$n\nu_4$	n	$n\nu_5$	n	$n\nu_6$
1	317	1	447.7	1	501	1	315.5	1	493	1	498
2	634	2	896	2	1 001	2	628	2		2	996
3	(948)			3	1 501			3	1 484	3	1 492
4	1 265							4	1 977		
5	1 578										
6	1 897										
7	2 211										

$\lambda_o = 356.4$					
n	$n\nu_1 + \nu_2$	n	$n\nu_1 + \nu_3$	n	$n\nu_1 + 2\nu_3$
1	765	1	819	1	1 316
2	1 081	2	1 135	2	1 636
3	(1 392)	3	(1 448)	3	1 948
4	1 714	4	1 764	4	2 266
		5	2 082	5	2 577
		6	2 398	6	2 902
		7	2 714		
n	$n\nu_1 + 3\nu_3$	n	$n\nu_1 + 2\nu_2$	n	$n\nu_1 + 2\nu_6 + \nu_2$
1	1 815	1	1 257		
2	2 132			2	2 445
3	2 449			n	$n\nu_1 + 3\nu_3$
4	2 767			3	2 449
n	$n\nu_3 + \nu_1$	n	$n\nu_3 + \nu_2$	n	$n\nu_3 + 2\nu_1$
1	819	1		1	1 135
2	1 316	2	(1 448)	2	1 636
3	1 815	3	1 948	3	(2 132)
n	$n\nu_2 + \nu_1$	n	$n\nu_2 + \nu_3$	n	$n\nu_6 + \nu_2 + 2\nu_1$
1	765	1	(948)	1	(2 132)
2	1 257	2	1 396	2	2 445

$\lambda_o = 413.1$					
n	$n\nu_2 + \nu_4$	n	$n\nu_2 + \nu_5$	n	$n\nu_2 + \nu_6$
1	758	1	941	1	948
2	1 207			2	1 392
n	$n\nu_2 + \nu_5 + \nu_6$	n	$n\nu_2 + \nu_4 + \nu_5$	n	$n\nu_2 + \nu_5 + 2\nu_6$
1	(1 439)	1	1 257	1	1 937
2	1 888	2	1 702		
n	$n\nu_2 + \nu_4 + 2\nu_5$	n	$n\nu_4 + \nu_2$	n	$n\nu_4 + \nu_5$
1	2 204	1	758	1	809
				2	1 129
n	$n\nu_5 + \nu_2$	n	$n\nu_5 + 2\nu_6$	3	(1 439)
4	2 452	2	1 985	4	1 753
				5	2 077
n	$n\nu_5 + \nu_2 + \nu_6$				
3	2 430				
n	$n\nu_5 + \nu_4$	n	$n\nu_5 + \nu_6 + 2\nu_2$	n	$n\nu_5 + 2\nu_2 + \nu_4$
1	809	1	1 888	1	1 702
		2	2 381	2	2 204
n	$n\nu_6 + \nu_4$	n	$n\nu_6 + \nu_2$	n	$n\nu_6 + \nu_5$
1	815	1	948	1	993
2		2	1 444	2	1 489
3	1 808			3	1 987
n	$n\nu_6 + \nu_5 + \nu_2$	n	$n\nu_6 + 2\nu_5$	n	$n\nu_6 + 2\nu_2$
1	1 439	2	2 902		
2	1 937				
3	2 442	n	$n\nu_6 + \nu_4 + \nu_5$		
		2	1 805		
				4	2 902

* Values in parentheses denote a band to which more than one combination tone or overtone may contribute.

Table 7. Details of r.R. spectra of $[\mathrm{NPr^n}_4]_2[\mathrm{Pt(WS_4)_2}]$

$\lambda_0 = 406.7$ nm													
n	$n\nu_1$	n	$n\nu_2$	n	$n\nu_3$	n	n'	$n\nu_3 + n'\nu_5 + \nu_1$	n	n'	$n\nu_3 + n'\nu_5$		
1	342	1	451.5	1	503	1	0	844	0	2	993		
2	682	2	900	2	1 004	1	1	1 339	1	2	1 493		
				3	1 505	2	1	1 842	2	2	1 992		
						2	2	2 338	1	3	1 986		
n	$n\nu_2 + \nu_1$	n	$n\nu_2 + \nu_4$	n	$n\nu_2 + \nu_3$	n	n'	$n\nu_3 + n'\nu_5 + \nu_2$	n	n'	$n\nu_3 + n'\nu_5 + \nu_4$		
1	794	1	754	1	953	0	1	942.5	1	0	805		
2	1 245					1	0	952	1	1	1 300		
3	1 698					1	1	1 444	0	3	1 781		
n	$n\nu_2 + \nu_5$	n	$n\nu_2 + 2\nu_5$	n	$n\nu_3 + 2\nu_1$	2	0	1 454	1	3	2 285		
1	942.5			1	1 186	1	2	1 941	2	2	2 291		
2	1 394	2	1 892	2	1 690	1	3	2 435					
						1	4	2 929	n	n'	$n\nu_3 + n'\nu_5 + 3\nu_2$		
n	$n\nu_1 + \nu_2$	n	$n\nu_1 + \nu_3$			3	2	2 944	0	3	2 833		
1	794	1	844						1	2	2 840		
2	1 135	2	1 186										

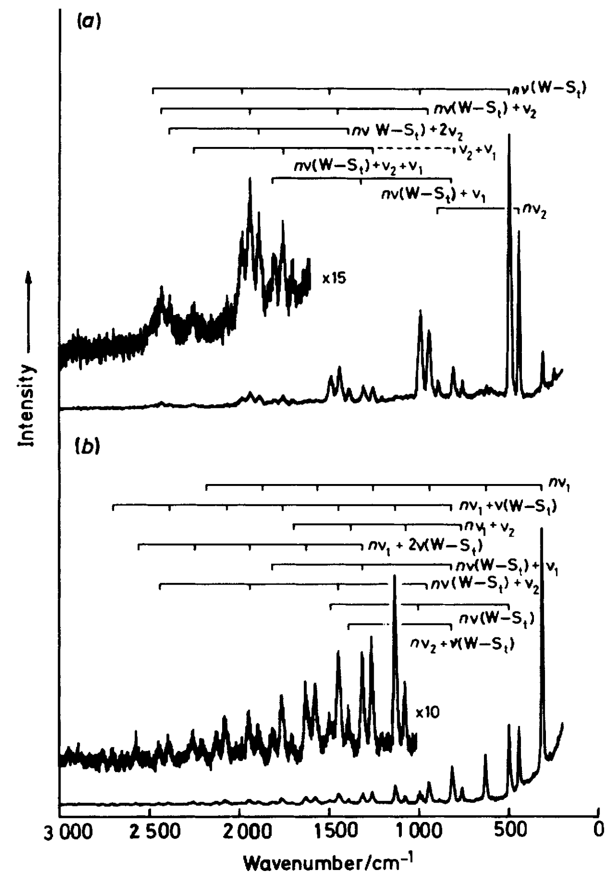


Figure 8. Resonance-Raman spectra of $[NPr^n_4]_2[Pd(WS_4)_2]$ at λ_0 = (*a*) 406.7 and (*b*) 356.4 nm

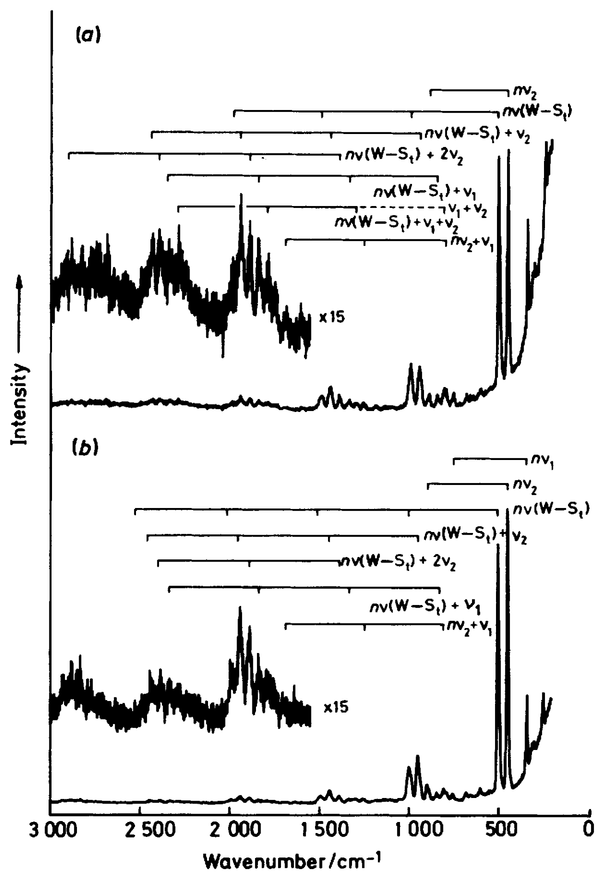


Figure 9. Resonance-Raman spectra of $[NPr^n_4]_2[Pt(WS_4)_2]$ at λ_0 = (*a*) 413.1 and (*b*) 406.7 nm

2. *Tetrathiotungstates*.—The enhancement of bands attributable to $W–S_b$, $W–S_t$, and $M'–S$ stretching modes and the observation of bands attributable to overtone progressions in all three modes as well as to numerous combination bands indicates a high degree of valence-electron delocalisation in these complexes. At resonance with the electronic absorption band around 410 nm both $\nu(W–S_b)$ and $\nu(W–S_t)$ are enhanced but it is $\nu(W–S_b)$ which is preferentially enhanced.

For $[Ni(WS_4)_2]^{2-}$ and $[Pd(WS_4)_2]^{2-}$, at resonance with the electronic absorption band around 360 nm, both $\nu(M'–S)$ and $\nu(W–S_t)$ are enhanced and, in the case of $[Pd(WS_4)_2]^{2-}$, also $\nu(W–S_b)$. This suggests the presence of two electronic transitions in this region, one localised on the $S_2M'S_2$ part and one on the WS_4 part of the ion.

The excitation profiles of the Raman bands of the tetrathiotungstates do not show structure corresponding to that seen for those of the tetrathiomolybdates.

Conclusions

All six complexes show significant valence-electron delocalisation in the resonant excited states,[26] more for the tetrathiotungstates than for the tetrathiomolybdates, as indicated by the nature of the r.R. spectra. Greater delocalisation of the (MS_4) sulphur π electrons for the tetrathiotungstates would also be suggested by the smaller separation between $\nu(W–S_b)$ and $\nu(W–S_t)$ than between $\nu(Mo–S_b)$ and $\nu(Mo–S_t)$, *i.e.* the terminal and bridging bonds are more alike in the tungsten case.

For $[Pd(MoS_4)_2]^{2-}$ and $[Pt(MoS_4)_2]^{2-}$ the resonant excited state involves bond length changes (intuitively increases, as for the parent ion $[MoS_4]^{2-}$) mainly of the bridging bonds, and hence at least one of the electronic transitions contributing to the absorption band involves $S_b \longrightarrow M$ charge transfer. A degree of delocalisation in the excited state is indicated by the enhancement of bands attributable to both $\nu(Mo–S_t)$ as well as $\nu(M'–S)$.

The weakness of the overtones in the r.R. spectrum of $[Ni(MoS_4)_2]^{2-}$ indicates that excitation to the resonant electronic state involves smaller changes in the $Mo–S_b$ bond lengths than for $[Pd(MoS_4)_2]^{2-}$ and $[Pt(MoS_4)_2]^{2-}$. Moreover, the lack of enhancement of bands attributable to Ni–S modes and the absence of strong combination bands at resonance also argue for less delocalisation in $[Ni(MoS_4)_2]^{2-}$ than for the analogous palladium and platinum complex ions.

Similarly, for the tetrathiotungstates, the electronic absorption band around 410 nm involves $S_b \longrightarrow W$ charge transfer, as indicated by the preferential enhancement of $\nu(W–S_b)$. By contrast, the resonant excited state associated with the first electronic absorption band in the u.v. involves preferential enhancement of $\nu(M'–S)$, which suggests that this band is attributable to $S \longrightarrow M'$ or $M' \longrightarrow S$ charge transfer. The enhancement of $\nu(W–S_t)$ in the r.R. spectra of the palladium and nickel species must arise from resonance with a $S_t \longrightarrow M$ electronic transition. The different behaviour of $[Ni(MoS_4)_2]^{2-}$ could be accounted for if the resonant transition involved excitation from a h.o.m.o. of mixed character to a l.u.m.o. of predominantly molybdenum character[20] resulting in little change in the electron distribution in the central portion of the molecule, whereas for the palladium and platinum analogues the l.u.m.o. is of mainly palladium (or platinum) character.

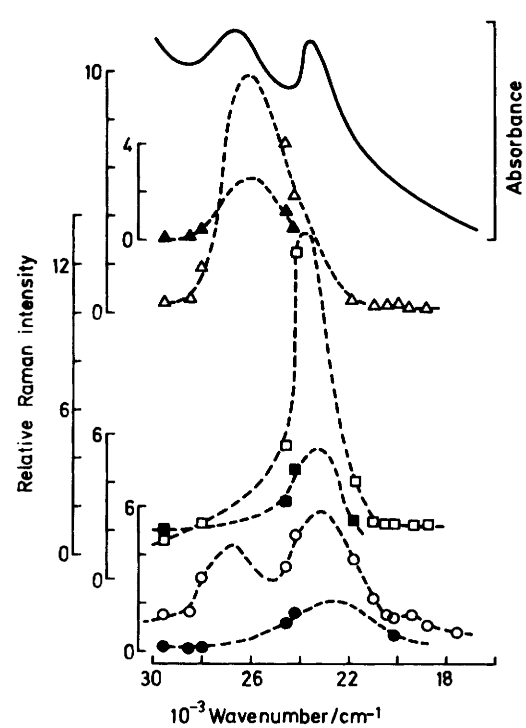


Figure 10. Excitation profiles of the ν_b (□), $2\nu_b$ (■), ν_t (○), $2\nu_t$ (●), ν(Ni–S) (△), and 2ν(Ni–S) (▲) bands of $[Ni(MoS_4)_2]^{2-}$ together with the electronic spectrum

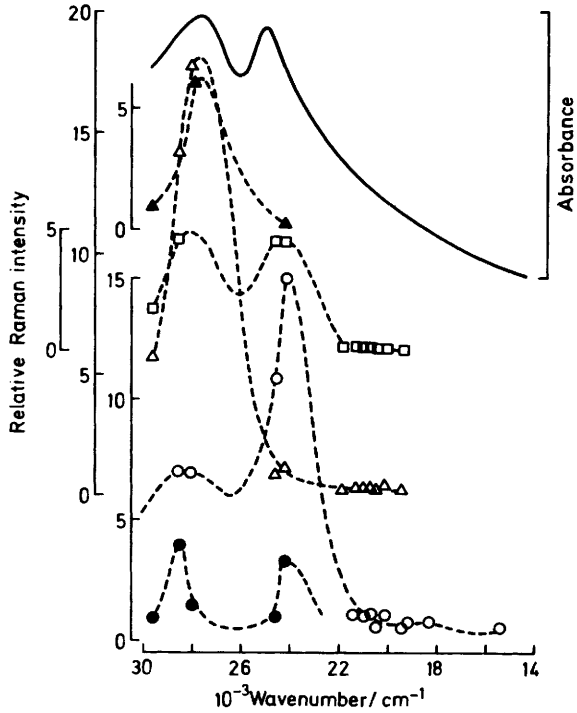


Figure 11. Excitation profiles of the ν_b (□), ν_t (○), $2\nu_t$ (●), ν(Pd–S) (△) and 2ν(Pd–S) (▲), bands of $[Pd(WS_4)_2]^{2-}$ together with the electronic spectrum

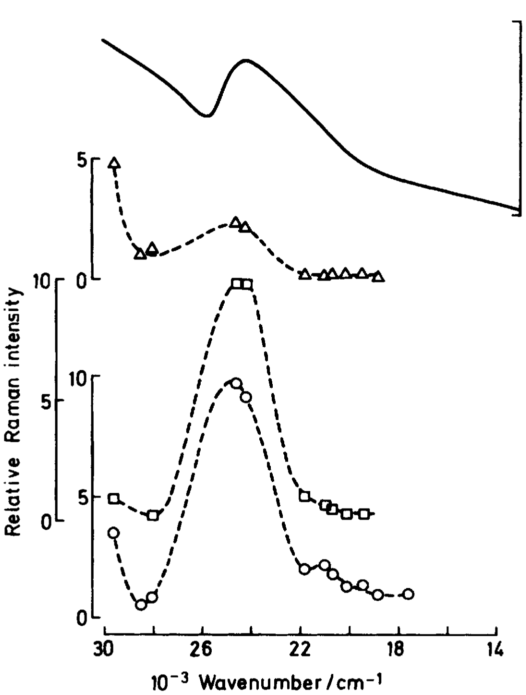


Figure 12. Excitation profiles of the ν_b (□), ν_t (○), and ν(Pt–S) (△) bands of $[Pt(WS_4)_2]^{2-}$ together with the electronic spectrum

However, on this basis, it would be anticipated that the band attributed to $\nu(Mo–S_t)$ would be more enhanced than that attributed to $\nu(Mo-S_b)$, whereas the reverse is found; moreover, this explanation does not account for the fact that $[Ni(WS_4)_2]^{2-}$ has similar resonance-Raman behaviour to $[Pd(WS_4)_2]^{2-}$.

All six ions show appreciable excited-state electron delocalisation, although not to the same extent as for iron(II) complexes of this type {*cf.* $[(PhS)_2FeS_2MS_2]^{2-}$}. Higher delocalisation for the thiotungstates with respect to the thiomolybdates is compatible with the greater spatial extent of the 5*d* orbitals of tungsten than for the 4*d* orbitals of molybdenum.

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References

1 E. Diemann and A. Müller, *Coord. Chem. Rev.*, 1973, **10**, 79.
2 A. Müller, E. Diemann, R. Josles, and H. Bögge, *Angew. Chem.*, 1981, **20**, 934.
3 A. Müller, E. Diemann, and C. K. Jørgensen, *Struct. Bonding (Berlin)*, 1973, **14**, 23.
4 A. Müller, E. J. Baran, and R. O. Carter, *Struct. Bonding (Berlin)*, 1976, **26**, 81.
5 A. Müller and E. Diemann, *Chem. Commun.*, 1971, 65,
6 K. P. Callahan and P. A. Piliero, *Inorg. Chem.*, 1980, **19**, 2619.
7 A. Müller and W. E. Newton, in 'Nitrogen Fixation: Chemical, Biochemical, Genetics Interface,' Plenum Press, New York, 1981.
8 A. H. Gibson and W. E. Newton, in 'Current Perspectives in Nitrogen Fixation,' Australian Academy of Science, Canberra, 1981.
9 D. Coucouvanis, *Acc. Chem. Res.*, 1981, **14**, 201.
10 K. H. Schmidt and A. Müller, *Coord. Chem. Rev.*, 1974, **14**, 115.
11 A. H. Cormier, K. Nakamoto, A. H. Born, and A. Müller, *J. Mol. Struct.*, 1975, **25**, 43.
12 E. Königer-Ahlborn, A. Müller, A. D. Cormier, J. D. Brown, and K. Nakamoto, *Inorg. Chem.*, 1975, **14**, 2009.
13 K. P. Callahan and P. A. Piliero, *J. Chem. Soc., Chem. Commun.*, 1979, 13.

14 E. Königer-Ahlborn, A. Müller, A. D. Cormier, J. D. Brown, and K. Nakamoto, *Inorg. Chem.*, 1975, **14**, 2003.

15 R. J. H. Clark, T. J. Dines, and M. L. Wolf, *J. Chem. Soc., Faraday Trans. 2*, 1982, 679.

16 S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, 1964, **86**, 4594.

17 G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1965, **87**, 3585.

18 R. L. Schlupp and A. H. Maki, *Inorg. Chem.*, 1974, **13**, 44.

19 W. E. Geiger, C. S. Allen, T. E. Mines, and F. C. Senftleber, *Inorg. Chem.*, 1977, **16**, 2003.

20 G. A. Bowmaker, P. D. W. Boyd, G. K. Campbell, and M. Zvagulis, *J. Chem. Soc., Dalton Trans.*, 1986, 1065.

21 R. J. H. Clark, T. J. Dines, and J. M. Doherty, *Inorg. Chem.*, 1985, **24**, 2088.

22 R. J. H. Clark, T. J. Dines, and G. P. Proud, *J. Chem. Soc., Dalton Trans.*, 1983, 2299.

23 R. J. H. Clark and T. J. Dines, *Mol. Phys.*, 1981, **42**, 193.

24 A. Müller, A. H. Dommröse, W. Jägermann, E. Krickmayer, and S. Sarkar, *Angew. Chem.*, 1981, **20**, 1061.

25 A. Müller and W. Hellmann, *Spectrochim. Acta, Part A*, 1985, **41**, 359.

26 R. J. H. Clark, S. Joss, M. Zvagulis, C. D. Garner, and J. R. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1986, 1595.

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