Electronic, Resonance-Raman, and Infrared Spectroscopic Studies of the Thiometalate Complexes [NEt$_4$]$_2$[(PhS)$_2$FeS$_2$MS$_2$], M = Mo or W

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Infrared and resonance-Raman spectra of the thiometalate complexes [NEt$_4$]$_2$[(PhS)$_2$FeS$_2$MS$_2$], M = Mo or W, have been studied and bands assigned to the ν(Fe–S), ν(M–S$_t$), and ν(M–S$_{br}$) fundamentals. Electronic absorption spectra and Raman-band excitation profiles indicate that the absorption bands in the visible region of the spectra arise from S→M charge-transfer transitions, red shifted from those of the parent [MS$_4$]$^{2-}$ ions, and that the valence electrons on the iron(II) part of the complexes are extensively delocalized. This is in contrast to the situation for mixed-metal complexes in which the second metal ion has a closed (d^{10}) valence shell.

During the last decade, considerable interest has developed in complexes in which the tetrathiomolybdate(VI) ion, [MoS$_4$]$^{2-}$, is ligated to another transition metal. Some such species are model compounds of the MoFe cofactor of nitrogenase. The literature pertaining to these complexes and their [WS$_4$]$^{2-}$ analogues has been summarized in two reviews.[1,2]

Recent work in this laboratory has been concerned with an in-depth study of the lowest energy electric-dipole-allowed charge-transfer transitions in [MoS$_4$]$^{2-}$ [3] and [WS$_4$]$^{2-}$ [4] by low-temperature absorption and resonance-Raman (r.R.) spectroscopy. The results of these studies enabled, *inter alia*, the calculation in each case of vibrational constants for the ground electronic state and of the magnitudes of the extension of the metal–sulphur bond lengths attendant upon electronic excitation.

In this paper we report the electronic, r.R., and i.r. spectra of the complexes [(PhS)$_2$FeS$_2$MoS$_2$]$^{2-}$ (black, appearing dark purple to red when ground to a powder) and [(PhS)$_2$FeS$_2$-
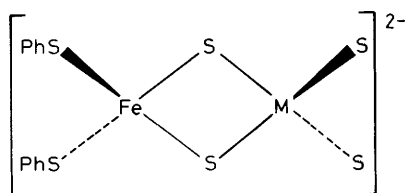
M = Mo or W

WS$_2$]$^{2-}$ (brown). Although the formal oxidation states of Fe and M in these complexes are +2 and +6 respectively, ^{57}Fe Mössbauer studies[1] have shown that the apparent oxidation state of Fe is intermediate between +2 and +3. There is, therefore, some valence delocalization in the electronic ground state and the Mössbauer isomer-shift values indicate that delocalization is the greater for the molybdenum complex. The ν$_1$ (a_1) and ν$_3$ (t_2) stretching vibrations of the parent [MS$_4$]$^{2-}$ anion would give rise to a total of four components in the spectra of the complexes, in which the MS$_4$ units adopt a C_{2v} microsymmetry. Similarly, splittings of the electronic absorption bands occur and, by plotting the excitation profiles of resonance-enhanced bands throughout the visible region, tentative electronic assignments can be made.

Experimental

Samples of [NEt$_4$]$_2$[(PhS)$_2$FeS$_2$MoS$_2$] and [NEt$_4$]$_2$[(PhS)$_2$-FeS$_2$WS$_2$] were provided by Dr. C. D. Garner, University of Manchester. Due to their air- and moisture-sensitivity, these compounds were handled either under argon or in a dry-box under an atmosphere of nitrogen. Resonance-Raman spectra were obtained from KBr discs for the survey spectra and calibration, and K[NO$_3$] discs for excitation-profile measurements, all discs being held at *ca.* 80 K using a liquid-nitrogen-cooled cell. To minimize thermal decomposition the laser power was maintained at <120 mW.

Raman spectra were recorded on Spex 1401 and 14018 (Ramalog 6) spectrometers in conjunction with Coherent Radiation model CR3 and CR15UV argon-ion and CR500 K and CR3000 K krypton-ion lasers. Detection of the scattered radiation was by standard photon-counting techniques, using RCA C31034 photomultipliers. Wavenumber measurements were calibrated with the emission spectrum of neon, and band intensities were determined as the products of peak heights and full-widths at half-maxima and corrected for the spectral response of the instrument. Resonance-Raman excitation profiles were constructed using the band of K[NO$_3$] at 1 050 cm^{-1} as internal intensity standard. The r.R. spectra of the title complexes are an order of magnitude less intense than those of the parent [MS$_4$]$^{2-}$ ions at resonance.

Electronic absorption spectra from KBr discs at *ca.* 14 K were recorded on a Cary 14 spectrometer using an Air Products Displex cryostat in association with a type TM120 Leybold-Heraeus turbopump. Infrared spectra from CsI discs at room temperature were recorded on a Perkin-Elmer 225 grating spectrophotometer.

Results and Discussion

Resonance-Raman spectra of [NEt$_4$]$_2$[(PhS)$_2$FeS$_2$MoS$_2$] and [NEt$_4$]$_2$[(PhS)$_2$FeS$_2$WS$_2$] were recorded using laser excitation in the range 454.5—676.4 nm, representative spectra being shown in Figures 1 and 2. Band-wavenumber measurements and their assignments, including i.r. data, are listed in Table 1. The bases for the proposed assignments are as follows.

(1) For the [NBu$_4$]$^+$ salts of [MS$_4$]$^{2-}$, the metal–sulphur stretching wavenumbers are ν$_1$ = 451 and ν$_3$ = 470 cm^{-1} for M = Mo [2,3] and ν$_1$ = 478 and ν$_3$ = 463 cm^{-1} for M = W.[4] The title complexes exhibit groups of bands in the regions 476—505 and 422—447 cm^{-1}. These are assigned to the terminal and bridging modes ν(M–S$_t$) and ν(M–S$_{br}$) respectively since, from the crystal structure of [(PhS)$_2$FeS$_2$MoS$_2$]$^{2-}$, it is established that r(Mo–S$_t$) = 2.153 Å and r(Mo–S$_{br}$) = 2.246 Å.[5] The space group is $P2_1/c$ (C_{2h}^5) with four molecules per unit cell, each on sites of C_i symmetry. Thus, each of the four ν(M–S) modes is split into four components in the solid

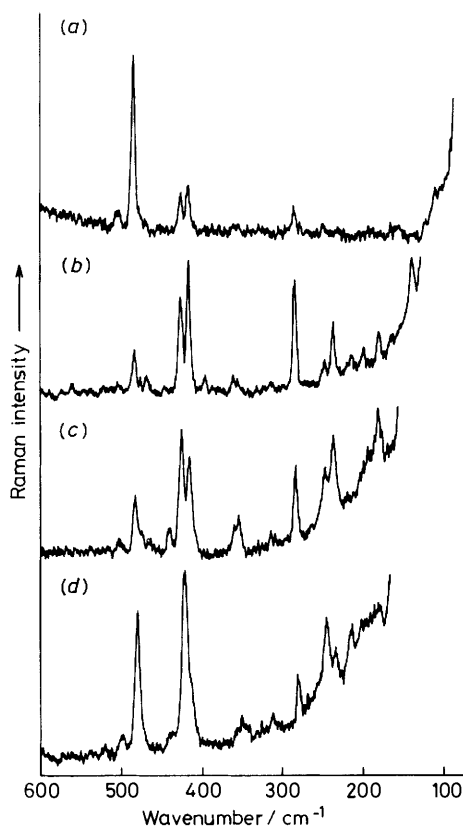**Figure 1.** Resonance-Raman spectra of [NEt₄]₂[(PhS)₂FeS₂MoS₂] at 80 K recorded with excitation at 647.1 (a), 568.2 (b), 514.5 (c), and 488.0 nm (d)
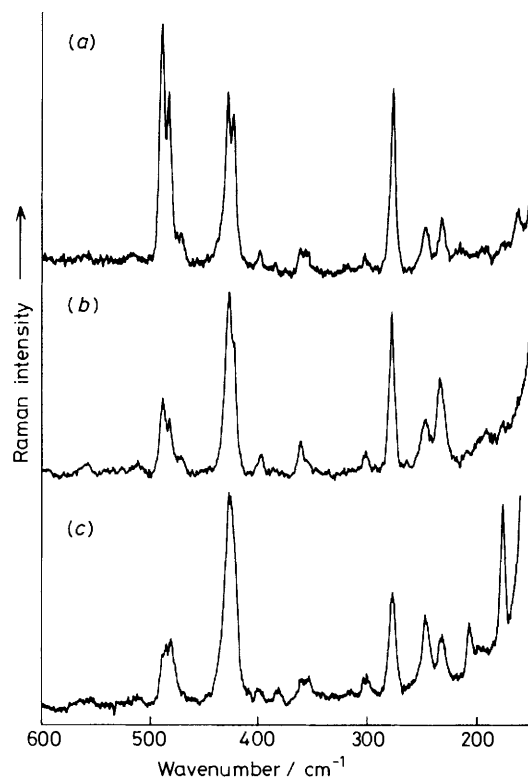
Figure 2. Resonance-Raman spectra of [NEt₄]₂[(PhS)₂FeS₂WS₂] at 80 K recorded with excitation at 568.2 (a), 530.9 (b), and 496.5 nm (c)

Table 1. Details of the i.r. and resonance-Raman spectra of [NEt₄]₂[(PhS)₂FeS₂MS₂], M = Mo or W

Assignment *	Mo complex, $\tilde{\nu}$/cm⁻¹		W complex, $\tilde{\nu}$/cm⁻¹	
	r.R.	i.r.	r.R.	i.r.
		230w	230	231w
	240	240⎱db, m	244	244w
		246⎰		
ν(Fe⁻S)	251		281	280m
	288	287w		355m
		358ms		360 (sh)
	422	422w	426	426ms
ν(M⁻S$_{br}$)	431	434m	431	431ms
		447ms		441ms
		477m		476 (sh)
ν(M⁻S$_t$)	488	489s	486	485s
		505s	492	492s

* S$_{br}$ = Bridging sulphur atom, S$_t$ = terminal sulphur atom.

state, of which two are i.r. active (a_u) and two are Raman active (a_g). Observation of less than the predicted number of bands may be due to near coincidences, suggesting that any factor-group splitting is small.

(2) Bands attributable to iron–sulphur stretching vibrations have been shown to occur in the region 230—360 cm⁻¹ for a variety of μ₃-bridged iron–sulphur compounds.[6-8] Although the complexes investigated in the present study are of the μ₂-
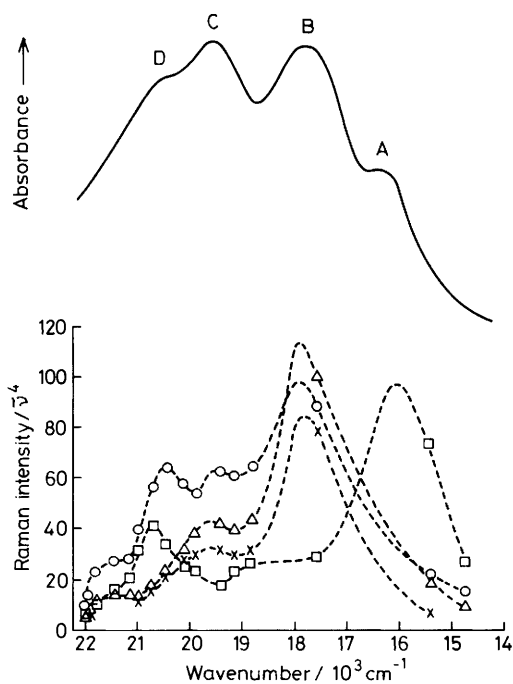

Figure 3. Electronic absorption spectrum (KBr disc) of [NEt₄]₂-[(PhS)₂FeS₂MoS₂] at 14 K and the excitation profiles (K[NO₃] disc) of the 288 [×, ν(Fe⁻S)], 422 (△), 431 [O, ν(Mo⁻S$_{br}$)], and 488 cm⁻¹ [□, ν(Mo⁻S$_t$)] bands at 80 K

Table 2. Electronic absorption bands in the visible spectra of $[(PhS)_2FeS_2MoS_2]^{2-}$ and $[(PhS)_2FeS_2WS_2]^{2-}$

| | $[(PhS)_2FeS_2MoS_2]^{2-}$ | | $[(PhS)_2FeS_2WS_2]^{2-}$ | | Raman band enhancement | |
Band	λ/nm	$\tilde{v}/10^3$ cm^{-1}	λ/nm	$\tilde{v}/10^3$ cm^{-1}	Mo	W
A	610	16.3	560	17.9	$v(Mo-S_t)$	$v(W-S_t)$ $v(W-S_{br})$ $v(Fe-S)$
B	560	17.9	473	21.1	$v(Mo-S_{br})$ $v(Fe-S)$	$v(W-S_t)$ $v(W-S_{br})$
C	510	19.7	430	23.2	$v(Mo-S_{br})$ $v(Fe-S)$	—
D	485	20.6	—	—	$v(Mo-S_t)$ $v(Mo-S_{br})$	—

bridged type, their $v(Fe-S)$ wavenumbers are expected to occur in the same spectral region because their Fe-S bond lengths are close to those of the μ_3-bridged species.[1,8] Moreover, $v(Fe-S)$ is expected to lie below $v(MoS)$ on account of the formal oxidation-state difference ($+2$ and $+6$) of the two metal ions.[9] Two groups of $v(Fe-S)$ bands are observed, in the 230—280 and 350—360 cm^{-1} regions; these are tentatively assigned to $v(Fe-SPh)$ and $v(Fe-SM)$, respectively, on the grounds that $r(Fe-SPh) = 2.312$ Å and $r(Fe-SMo) = 2.250$ Å in $[(PhS)_2FeS_2MoS_2]^{2-}$.

Resonance-Raman excitation profiles of the most intense bands of $[(PhS)_2FeS_2MoS_2]^{2-}$ and $[(PhS)_2FeS_2WS_2]^{2-}$ are shown in Figures 3 and 4 together with their electronic absorption spectra, for which the band maxima are listed in Table 2. The Raman-intensity behaviour throughout the visible absorption spectrum may be summarized as follows.

Band A, Mo : Enhancement of $v(Mo-S_t)$ alone
     W : Enhancement of $v(W-S_t)$, $v(W-S_{br})$, and $v(Fe-S)$
Band B, Mo : Enhancement of $v(Mo-S_{br})$ and $v(Fe-S)$
     W : Enhancement of $v(W-S_t)$ and $v(W-S_{br})$; $v(W-S_{br})$ and $v(Fe-S)$ display intensity maxima between bands A and B, at ca. 19 000 cm^{-1}
Band C, Mo : Enhancement of $v(Mo-S_{br})$ and $v(Fe-S)$
Band D, Mo : Enhancement of $v(Mo-S_{br})$ and $v(Mo-S_t)$. The excitation profile of the latter is shifted ca. 300 cm^{-1} to the blue

These observations, together with our knowledge of the electronic properties of the parent anions,[3,4] lead us to postulate the following electronic band assignments, which are at variance with those suggested by other authors.[1]

Band A.—Predominantly $S_t \rightarrow M$ charge transfer, i.e. the analogue of the band of $[MoS_4]^{2-}$ at 470 nm and of $[WS_4]^{2-}$ at 400 nm ($^1T_2 \leftarrow ^1A_1$, $e \leftarrow t_1$). However, there is evidence that the valence electrons are more delocalized in this excited state for the tungsten complex than for the molybdenum one. This conclusion follows from the observation that, in the molybdenum case, only $v(Mo-S_t)$ is enhanced at resonance but in the tungsten case not only $v(W-S_t)$ is enhanced but also $v(W-S_{br})$ and $v(Fe-S)$. The greater delocalization of the valence electrons in the $^1T_2$ state of the tungsten as compared with the molybdenum complex may be a consequence of the greater spatial extension of the $5d$ than $4d$ orbitals. Note that for the ground states of these complexes, Mössbauer results imply that it is the tungsten complex which has the more localized valences.[1]

Bands B and C.—Predominantly $S_{br} \rightarrow M$ charge transfer, but also involving the iron orbitals. Again, greater electron delocalization in the excited state occurs for the tungsten than
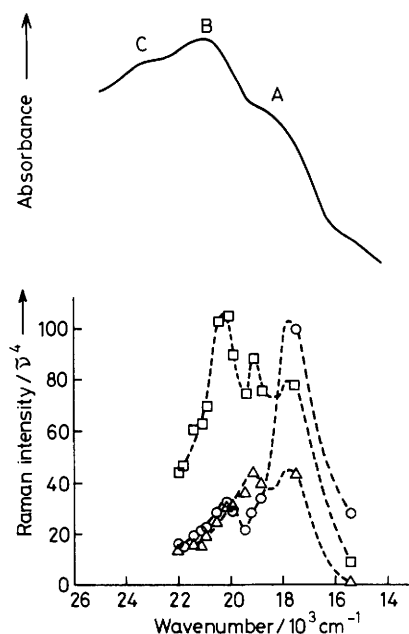
Figure 4. Electronic absorption spectrum (KBr disc) of $[NEt_4]_2$-$[(PhS)_2FeS_2WS_2]$ at 14 K and the excitation profiles ($K[NO_3]$ disc) of the 280 [$\triangle$, $v(Fe-S)$], 426/431 [$\square$, $v(W-S_{br})$], and 485/492 cm^{-1} [O, $v(W-S_t)$] bands at 80 K

for the molybdenum complex, as evidenced by the enhancement of $v(W-S_t)$ in the r.R. spectrum of the former, but not of $v(Mo-S_t)$ in that of the latter.

Band D.—An electronic transition localized on the $[MoS_4]^{2-}$ chromophore. This band may correspond to the second-lowest-energy electric-dipole-allowed ($^1T_2 \leftarrow ^1A_1$) transition of the parent anion, which occurs at 317 nm (31 500 cm^{-1}), previously thought to be due to $t_2{}^1t_1{}^5 \leftarrow t_1{}^6$ electron transfer[10] but now assigned to $e^1t_2{}^5 \leftarrow t_2{}^6$.[11]

In the absence of detailed molecular-orbital calculations on these systems, the assignments proposed here may only be regarded as tentative. However, some preliminary EH-SCCC-MO calculations[2] have demonstrated that the iron $3d$ orbitals lie at approximately the same energy as the t_1 non-bonding π orbitals of the free $[MS_4]^{2-}$ ions. The iron $3d$ orbitals are split in the tetrahedral ligand field to give a high-spin complex with four unpaired electrons, which is in agreement with magnetic measurements at 300 K ($\mu = 4.9$ μ_B).[5] The iron $3d$ orbitals are thought to be of comparable energies to those of the molybdenum $4d$ and tungsten $5d$ orbitals owing to cancellation of the opposing effects of oxidation

state ($M^{II} > M^{VI}$) and d shell ($5d > 4d > 3d$) on d-orbital energies. It was not possible to obtain Raman spectra at resonance with the Fe→Mo transitions at *ca.* 1 000 nm owing to the lack of suitable excitation lines. From the nature of the Raman bands enhanced at resonance it is suggested that, although band A is essentially S_t→M charge transfer in the case of the molybdenum complex, it also has considerable S_{br}→M and S→Fe character in the case of the tungsten complex. Moreover, bands B and C in all cases appear to have mixed S→M and S→Fe character, while band D (which could be studied only in the case of the molybdenum complex) has both S_t→Mo and S_{br}→Mo character. Transitions between the iron $3d$ orbitals and of the Fe→$[MS_4]^{2-}$ charge-transfer type may also occur; the latter could be responsible for absorption bands previously observed in the 1 000 nm region for the species in solution.[1]

Overtones of the fundamentals observed in the r.R. spectra were of such low intensity as to be barely discernible. This indicates that the geometric changes attendant upon electronic excitation are spread over the whole of the $S_2FeS_2MS_2$ framework and that only very small changes along particular bonds take place.[12] By contrast, the r.R. spectra of some compounds in which $[MoS_4]^{2-}$ is bound to Cu or Ag display long overtone progressions in v(Mo−S).[13] This information, together with the lack of observation of spectral features associated with the remainder of the molecule, indicates that the resonant electronic transition in the complexes of Cu or Ag is localized on the $[MoS_4]^{2-}$ moiety and that, on excitation, a substantial increase in the Mo−S bond distances takes place (*cf.* $\Delta r = 0.07$ Å for the parent anion [3]). In these complexes, the silver and copper ions possess filled d orbitals (effectively insulators) and interaction with the $[MoS_4]^{2-}$ orbitals is small; by contrast, for the complexes studied herein, the iron(II) ion possesses partly filled d orbitals which evidently permit extensive valence-electron delocalization over the whole complex anion, not only in the ground state but also in the first charge-transfer excited state.

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