Resonance-Raman Spectroscopy of Tris(1,2-dithiolene) Complexes of Vanadium, Molybdenum, and Tungsten

By **Robin J. H. Clark** * and **Philip C. Turtle**, Christopher Ingold Laboratories, 20 Gordon Street, London WC1H 0AJ

The resonance-Raman spectra of the complexes $[V(S_2C_2Ph_2)_3]$, $[V(S_2C_2Ph_2)_3]^-$, and $[M(mnt)_3]^{2-}$ (M = V, Mo, or W) have been recorded with a variety of exciting lines in the visible region. The results of this investigation are combined with an existing molecular-orbital scheme to produce a set of assignments for the electronic transitions of the complexes in the visible region.

THIS is the second of two papers involving the application of resonance-Raman (r.R.) spectroscopy to typical 1,2-dithiolene complexes of the transition metals. In the first paper we reported [1] our results on three bis(maleonitriledithiolato)-complexes, *viz.* $[M(mnt)_2]^{2-}$ (M = Ni, Pd, or Pt). In this paper we are concerned with the tris complexes $[M(mnt)_3]^{2-}$ (M = V, Mo, or W) and the tris(1,2-diphenylethylene-1,2-dithiolato)-complexes $[V(S_2C_2Ph_2)_3]$ and $[V(S_2C_2Ph_2)_3]^-$. Much of the research on tris(1,2-dithiolene) complexes has been directed towards determining the reason why some complexes have trigonal-prismatic geometry, some octahedral, and some an intermediate geometry. Since there is no structural contraint on any of the metal–ligand systems, the occurrence of different geometries must be connected with the electronic structures of the complexes. Resonance-Raman spectroscopy is an important technique which has recently been shown to yield much unique information on the nature of the excited states of molecules,[2] and the present paper has the object of learning more about these states in the complexes specified. The understanding of these energy-level orderings is important, not only from the general standpoint of inorganic chemistry [3] but also owing to the importance of transition metal-to-sulphur co-ordination in biological systems such as non-haeme iron proteins, a subject to which r.R. spectroscopy has already made significant contributions.[4]

EXPERIMENTAL

Literature methods were used to prepare the complexes $[AsPh_4]_2[V(mnt)_3]$,[5] $[NBu_4]_2[M(mnt)_3]$ (M = Mo or W),[6] $[V(S_2C_2Ph_2)_3]$,[7] and $[NEt_4][V(S_2C_2Ph_2)_3]$.[7]

Raman spectra were recorded using a Spex 1401 double monochromator and a photon-counting detection system employing an RCA C31034 photomultiplier tube. Exciting radiation was provided by Coherent Radiation model 52 Kr^+ and CR12 Ar^+ ion lasers, and a model 490 tunable dye laser employing rhodamine 6G or sodium fluorescein in ethane-1,2-diol. Solutions were 10^{-3}—10^{-4} mol dm^{-3} with respect to each complex. Absorption spectra were recorded on a Cary 14 spectrophotometer. Low-temperature spectra were obtained by use of a standard Applied Physics Dewar.

Background to Previous Molecular-orbital Calculations.— Molecular-orbital (m.o.) calculations have been performed on two systems having trigonal-prismatic geometry: Schrauzer and Mayweg [8] investigated the $[Mo(S_2C_2H_2)_3]$ system and Stiefel *et al.*[9] the $[Re(S_2C_2Ph_2)_3]$ system. Only in the latter case was any attempt made to explain why the complex had trigonal-prismatic geometry. It was suggested that either interligand sulphur–sulphur interactions, or overlap between the ligand π_h and π_v orbitals and the metal d_{z^2} and $d_{x^2-y^2}$, d_{xy} orbitals, respectively, might stabilise the trigonal-prismatic structure. Support for the latter suggestion has recently come from *X*-ray structure determinations [10-12] on the iso-electronic series $[Mo(S_2C_6H_4)_3]$, $[Nb(S_2C_6H_4)_3]^-$, and $[Zr(S_2C_6H_4)_3]^{2-}$. This work highlighted the importance of both the energies of the *d* orbitals and their degree of overlap with the ligand π orbitals in stabilising the different structures.

Of the two proposed m.o. schemes, that of Schrauzer and Mayweg is generally regarded as incorrect because of its

---

[1] R. J. H. Clark and P. C. Turtle, *J.C.S. Dalton*, 1977, 2142.

[2] R. J. H. Clark, M. L. Franks, and P. C. Turtle, *J. Amer. Chem. Soc.*, 1977, **99**, 2473; J. R. Campbell and R. J. H. Clark, *Mol. Phys.*, submitted for publication.

[3] R. J. H. Clark, Plenary Lecture, The Chemical Society, Reading, September 1975.

[4] T. G. Spiro and T. M. Loehr, in 'Advances in Infrared and Raman Spectroscopy', vol. 1, eds. R. J. H. Clark and R. E. Hester, Heyden, London, 1975, p. 98.

[5] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, 1964, **86**, 2799.

[6] E. I. Stiefel, L. E. Bennett, Z. Dori, T. H. Crawford, C. Simo, and H. B. Gray, *Inorg. Chem.*, 1970, **9**, 281.

[7] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1965, **4**, 55.

[8] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 1966, **88**, 3235.

[9] E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, 1966, **88**, 2956.

[10] M. Cowie and M. J. Bennett, *Inorg. Chem.*, 1976, **15**, 1584.

[11] M. Cowie and M. J. Bennett, *Inorg. Chem.*, 1976, **15**, 1589.

[12] M. Cowie and M. J. Bennett, *Inorg. Chem.*, 1976, **15**, 1595.

inability to explain the results derived from e.s.r. spectroscopy [13,14] and, in one case, those derived from electronic-absorption spectroscopy.[15] In contrast, the scheme proposed by Stiefel *et al.*[9] has met with some success in explaining general electronic-spectral trends and is consistent with the e.s.r. measurements.[13,14] The latter scheme will therefore be adopted here. The electronic configurations of the five complexes which are the subject of this paper, based on the scheme of Stiefel *et al.*, are shown in Figure 1.

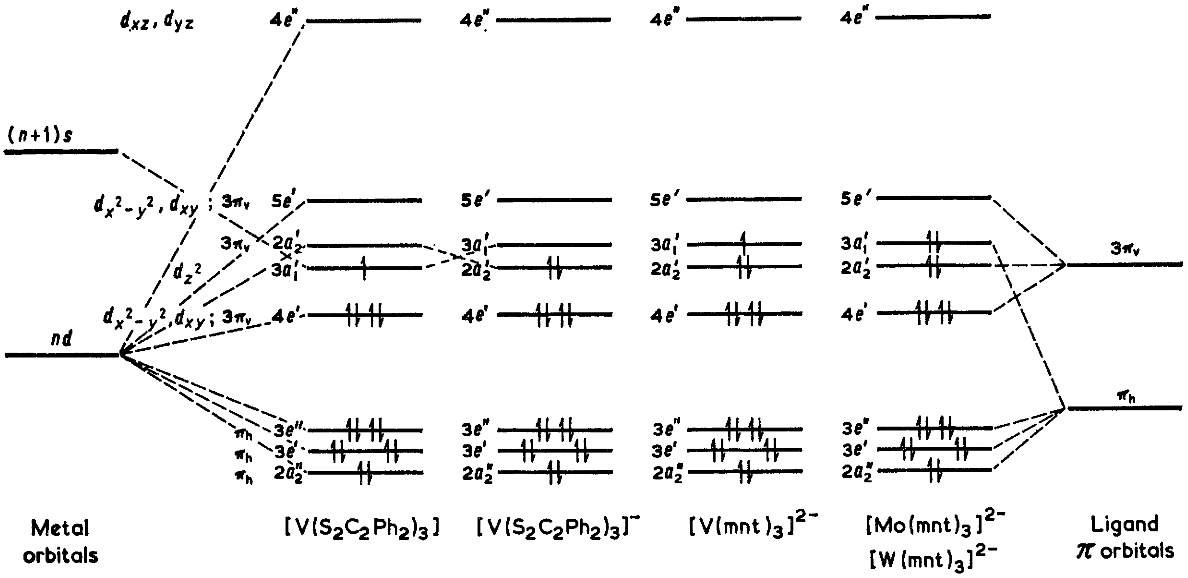
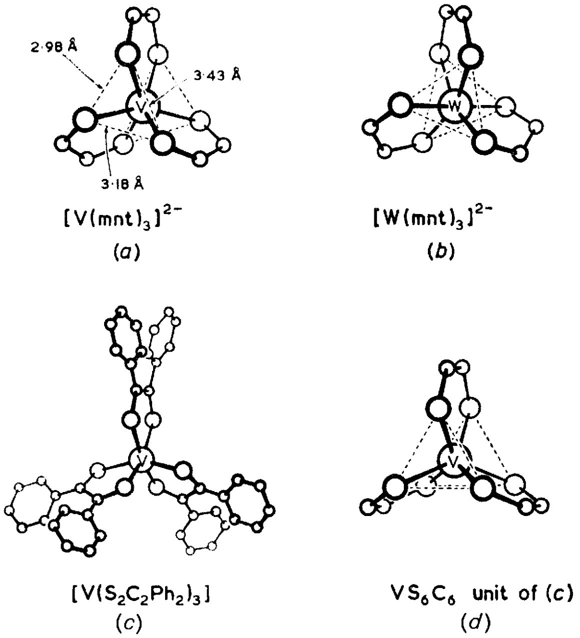


FIGURE 1 Electronic configurations of the complexes $[V(S_2C_2Ph_2)_3]$, $[V(S_2C_2Ph_2)_3]^-$, and $[M(mnt)_3]^{2-}$ (M = V, Mo, or W) based on the m.o. scheme of Stiefel *et al.*[9]

The three dianionic complexes all have structures in between trigonal prismatic and octahedral, and possess approximately D_3 symmetry. The crystal structures show that the vanadium complex [16] [Figure 2(*a*)] is slightly more distorted than the molybdenum and tungsten complexes [17] [Figure 2(*b*)], but this has been ascribed [17] to the effect of the smaller counter ion in the case of the vanadium complex. The neutral $[V(S_2C_2Ph_2)_3]$ complex has trigonal-prismatic geometry [13] [Figure 2(*c*) and (*d*)] but is slightly distorted by a trigonal twist of 8.5°. The structure of the $[V(S_2C_2Ph_2)_3]^-$ ion is unknown, but it has been argued [18] that the complex has trigonal-prismatic geometry because its electronic-absorption spectrum is similar to that of the isoelectronic molecule $[Cr(S_2C_2Ph_2)_3]$, which is itself isomorphous [19] with trigonal-prismatic $[V(S_2C_2Ph_2)_3]$.

Before turning to our experimental results on these systems it is necessary to give some details of the m.o. scheme [9] (Figure 1). The $4e''$ orbital is described as strongly antibonding and localised primarily on the metal (d_{xz}, d_{yz}) set. The $3a_1'$ orbital is antibonding and largely metal d_{z^2} in character; the corresponding bonding orbital ($2a_1'$) is largely the π_h ligand orbital based on the sulphur atoms. The $2a_2'$ orbital is non-bonding (π_v) and localised on the ligand. The $5e'$ and $4e'$ orbitals both contain considerable metal *d*- and ligand π-orbital character and are highly delocalised over the metal–ligand system. Both the $3a_1'$ and $5e'$ orbitals are regarded as antibonding with respect to the trigonal prism while the bonding equivalents ($2a_1'$ and $4e'$) stabilise the prism. Thus it should be possible to explain the structures of the various complexes by considering the degree of occupancy of these orbitals. Other effects which have been shown [10-12] to be important, however, are the size of the central atom and the tendency of the ligand towards either the dithioketonic [S=C(R)–C(R)=S] or dithiolate [$^-$S–C(R)=C(R)–S$^-$] limiting structures.



$[V(mnt)_3]^{2-}$ (*a*)
$[W(mnt)_3]^{2-}$ (*b*)
$[V(S_2C_2Ph_2)_3]$ (*c*)
VS_6C_6 unit of (*c*) (*d*)

FIGURE 2 Structures of 1,2-dithiolene complexes

---

[13] R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 1967, **6**, 1844.

[14] W.-L. Kwik and E. I. Stiefel, *Inorg. Chem.*, 1973, **12**, 2337.

[15] J. L. Martin and J. Takats, *Inorg. Chem.*, 1975, **14**, 73.

[16] E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, 1967, **89**, 3353.

[17] G. F. Brown and E. I. Stiefel, *Inorg. Chem.*, 1973, **12**, 2140.

[18] R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, 1966, **88**, 2874.

[19] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1966, **5**, 411.

The $[V(S_2C_2Ph_2)_3]$ complex, with a configuration of $\ldots(4e')^4(3a_1')$ (note that the $2a_2'$ and $3a_1'$ levels have been reversed in the case of this complex in accordance with the suggestion of Eisenberg and Gray[13]), is trigonal prismatic but with a slight distortion. This distortion has been ascribed[10–12] to the relatively small size of the vanadium atom which causes the prism to twist in order to maximise the π–d overlap. The $[V(mnt)_3]^{2-}$ ion has a highly distorted structure[16] inbetween a trigonal prism and octahedron, but has the same electronic configuration, $\ldots(4e')^4(2a_2')^2(3a_1')^1$, as the $[Re(S_2C_2Ph_2)_3]$ complex, which *is* trigonal prismatic. The reason for this large distortion in the case of the vanadium complex is believed to be that the ligand is tending towards the dithiolate limit. This results in larger dimensions for the C–S bonds of the ligand and hence reduced overlap of the ligand π and metal d orbitals.[12] The two complexes $[Mo(mnt)_3]^{2-}$ and $[W(mnt)_3]^{2-}$, with configurations $\ldots(4e')^4(2a_2')^2(3a_1')^2$, have essentially identical structures midway between that of a trigonal prism and an octahedron.[17] In these two cases metal–ligand overlap is more favourable because of the larger metal atoms, but the antibonding $3a_1'$ orbital is doubly occupied. The configuration of the $[V(S_2C_2Ph_2)_3]^-$ ion could be either $\ldots(4e')^4(2a_2')^2$ or $\ldots(4e')^4(3a_1')^2$; in either case some distortion from trigonal-prismatic geometry would be expected, either because of expansion of the trigonal prism in the first case, or double occupancy of the (antibonding) $3a_1'$ orbital in the second case. The frequency of the i.r.-active ν(C=C) (dithiolene) fundamental is higher[8] in the monoanion than in the neutral complex which indicates increased dithiolate character and probable occupancy of the $2a_2'$ orbital. This point will be discussed later in connection with the r.R. evidence.

TABLE 1

Wavenumbers (cm^{-1}) of the Raman bands of $[M(mnt)_3]^{2-}$ ions[a]

V	Mo	W	Assignment[b]	
	152.5			
168.0				
184.4				
193.4	191.3	197.5		
234.9				
240.6				
262.6				
264.5		264.3		
271.4	278.5			dp
	(280)			
		291.6		
	324.8	330.9		p
	(323)			
314.1	353.6	366.5	ν(M–S)	p
(312)[c]	(353)			
350.4				dp?
(351)				
368.8	371.6			dp
	409.7			
	489.8			
	504.4			
522	527	526		
	676			
628	708	733	2ν(M–S)	
666				
942				
1 001	991			
	1 032			
1 053	1 044		ν(C–C) +ν(C–S)	
	1 103			
1 122				
1 149	1 142	1 147		
1 256				
1 465			ν(C=C)	
1 469	1 492	1 497		p
	(1 497)	(1 490)		
		2 181		
2 203	2 201	2 202		
	(2 197)	(2 195)	ν(C≡N)	p
2 214				

[a] $[AsPh_4]^+$, $[NBu_4]^+$, and $[NBu_4]^+$ salts for M = V, Mo, and W respectively. [b] p and dp refer to polarised and depolarised bands respectively. [c] Figures in parentheses refer to the band wavenumbers in solution.

RESULTS

Raman Spectra.—The frequencies of the bands observed in the Raman spectra of the complexes are listed in Tables 1 and 2. No ' normal ' Raman spectrum could be obtained from any of the complexes because of the strong absorption bands in the visible region. For this reason, the listing of frequencies is not complete owing to the selective enhancement of certain bands and the consequent obscuration of non-enhanced bands. In the case of the $[V(S_2C_2Ph_2)_3]$ complex, for instance, Raman bands arising from the phenyl groups are very weak. This is because these groups lie out of the plane of the dithiolene ligands[13] and are therefore not conjugated with them.

TABLE 2

Wavenumbers (cm^{-1}) of the Raman bands of the complexes $[V(S_2C_2Ph_2)_3]$ and $[V(S_2C_2Ph_2)_3]^-$[a]

$[V(S_2C_2Ph_2)_3]$	$[V(S_2C_2Ph_2)_3]^-$	Assignment[b]	
168.5	172.6		
217.8	218.2		
267.3 (267)[c]			
	289.0 (289)		
340.5			
343.4 (343)	351.6 (350)	ν(V–S)	p
379.5			p
407.2	415.0 (416)		dp
477			
	527		
607			
	645	ν(V–S) + 289.0	
684 (686)	705	2ν(V–S)	p
720 (721)		ν(V–S) + 379.5	
746 (750)		ν(V–S) + 407.2	
	763		
	874		
903			
	1 003		
1 024 (1 033)		3ν(V–S)	
	1 135		
1 153			
1 182			
1 368			
1 399 (1 409)		ν(C=C) (dithiolene)	
	1 431		
1 447			
	1 459	ν(C=C) (dithiolene)	
1 492	1 499	ν(C=C) (phenyl)	
1 593	1 592		

[a] $[NEt_4]^+$ salt. [b] p and dp refer to polarised and depolarised bands respectively. [c] Figures in parentheses refer to the band wavenumbers in solution.

In the metal–sulphur stretching region, 250—400 cm^{-1}, the complexes have, characteristically, three or four medium to strong bands. One of these bands is usually stronger than the others and is also polarised. This band is therefore believed to arise from the totally symmetric metal–sulphur stretching vibration. Of the other two or three bands in this region one was always found to be depolarised. Most of the remaining bands have depolarisation ratios of 0.5—0.6

and their assignments are therefore not definite. With the exception of the $[V(S_2C_2Ph_2)_3]^-$ ion, the totally symmetric ν(M–S) band has a ρ value in the range 0.14—0.17. This is close to the value of 0.125 expected[20] when the resonant electronic state is doubly degenerate (and the ground state is non-degenerate). The totally symmetric ν(V–S) band of the $[V(S_2C_2Ph_2)_3]^-$ ion has a ρ value of *ca.* 0.5 but, since this band is overlapped by another, possibly depolarised, band, the actual ρ value could be less than this.

A group theoretical analysis of a $[M(S_2C_2R_2)_3]$ complex gives the following results:

D_{3h} (trigonal prism)

$$\Gamma_{\text{vib.}} = 6a_1' + 2a_2' + 3a_1'' + 6a_2'' + 9e' + 8e''$$
$$\Gamma_{\text{i.r.}} = 9e' + 6a_2''$$
$$\Gamma_{\text{Raman}} = 6a_1' + 9e' + 8e'' \ (+2a_2')$$

Considering only stretching vibrations of the MS_6 unit, the representation is $a_1' + a_2'' + e' + e''$, of which the a_1', e', and e'' modes are all Raman active.

D_3 (distorted prism)

$$\Gamma_{\text{vib.}} = 9a_1 + 8a_2 + 17e$$
$$\Gamma_{\text{i.r.}} = 8a_2 + 17e$$
$$\Gamma_{\text{Raman}} = 9a_1 + 17e \ (+8a_2)$$

The representation of the stretching vibrations of the MS_6 unit is $a_1 + a_2 + 2e$.

In both cases it can be seen that there is only one totally symmetric metal–sulphur stretching mode to be expected. It is rather difficult, therefore, to explain the appearance of *two* polarised bands in the metal–sulphur stretching region of the Raman spectrum of the $[V(S_2C_2Ph_2)_3]$ complex.

TABLE 3

Details of the absorption spectra (cm^{-1}) of KBr discs of tris(1,2-dithiolene) complexes at room and liquid-nitrogen temperatures

Complex	R.t.[a]	L.t.[b]
$[V(mnt)_3]^{2-}$	9 850	10 240
	14 655	14 505
		14 795
		15 060
	16 675	16 975
	19 185	19 495
	22 945	23 555
$[Mo(mnt)_3]^{2-}$	15 125	14 925
	19 285	19 230
	20 975	20 860
		24 045
	28 570	27 685
$[W(mnt)_3]^{2-}$	17 350	17 450
		18 845
		19 130
	20 170	20 495
	22 460	22 060
$[V(S_2C_2Ph_2)_3]$		12 320
	13 025	13 180
	17 745	17 900
	22 695	23 140
$[V(S_2C_2Ph_2)_3]^-$	13 800	14 040
	16 460	16 875
	18 700	18 835
		22 380

[a] R.t. = Room temperature, *ca.* 293 K. L.t. = Liquid-nitrogen temperature, *ca.* 80 K.

Both have ρ values close to 0.125, *viz.* 0.17 (343 cm^{-1}) and 0.14 (380 cm^{-1}). The weaker band of the two (380 cm^{-1}) is definitely also connected with the VS_6 unit in view of (*a*) its resonance enhancement with the same transitions as the band at 343 cm^{-1}, and (*b*) the appearance of a combination band involving the fundamental at 343 cm^{-1}.

Absorption Spectra.—The solution absorption spectra of all the complexes have been reported previously.[2,10,13] Low-temperature absorption spectra of the complexes (as KBr discs) were recorded but, unlike the cases of the bis(mnt) complexes,[1] vibrational structure was not generally observed. Nevertheless the low-temperature spectra did reveal several bands which had not previously been reported (Table 3).

DISCUSSION

$[V(S_2C_2Ph_2)_3]$.—For resonance with the transitions of this complex at both 17 940 and 13 310 cm^{-1} the Raman spectrum is dominated by bands arising from ν(V–S) fundamentals. The first and second overtones of the stronger a_1' fundamental are also present, together with combination bands involving the fundamentals at 380 and 407 cm^{-1} (Figure 3). The excitation profiles of the three ν(V–S) Raman bands at 343(a_1'), 375(a_1'), and 406(e' or e'') cm^{-1} (Figure 4) indicate that the bands are enhanced for resonance with the transitions both at 17 940 and 13 310 cm^{-1}, but in the case of the former transition it is the band at 343 cm^{-1} which shows much the greatest effect. The slightly red-shifted excitation profiles are probably a result of constructive interference between the contributions to the scattering tensor from the two transitions at 17 940 and 13 310 cm^{-1}.

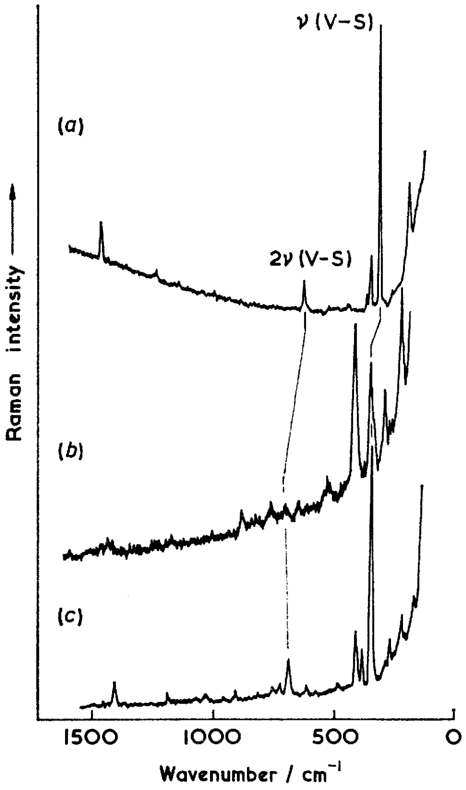


FIGURE 3 Resonance-Raman spectra of (*a*) the $[V(mnt)_3]^{2-}$ ion (647.1-n.m. excitation), (*b*) the $[V(S_2C_2Ph_2)_3]^-$ ion (568.2-nm excitation), and (*c*) the complex $[V(S_2C_2Ph_2)_3]$ (568.2-nm excitation). Slit width *ca.* 2 cm^{-1}

---

[20] O. S. Mortensen, *Chem. Phys. Letters*, 1969, **3**, 4.

The lowest-energy transition in this complex (at 9 850 cm^{-1}) occurs at a wavenumber which is similar to that of the lowest-energy transition in the $[V(mnt)_3]^{2-}$ ion, this transition being absent from the spectrum of the $[V(S_2C_2Ph_2)_3]^-$ ion. Since the $3a_1'$ orbital is empty in the monoanion (see below) it is probable that the lowest-energy band of the neutral complex arises from a transfer of an electron from the $3a_1'$ orbital. By analogy with the assignments of the electronic transitions of the $[Re(S_2C_2Ph_2)_3]$ complex[3] (which has a very similar absorption spectrum), the band at 9 850 cm^{-1} is assigned to the $2a_2' \leftarrow 3a_1'$ transition.

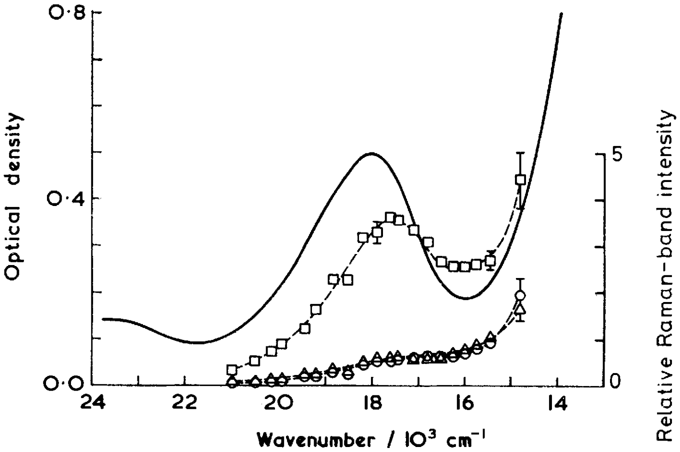


FIGURE 4 Excitation profiles of the bands at 343 (□), 375 (○), and 406 cm^{-1} (△) of the complex $[V(S_2C_2Ph_2)_3]$, relative to the band of benzene at 606 cm^{-1}. The electronic spectrum of the complex in benzene solution is indicated by the full line

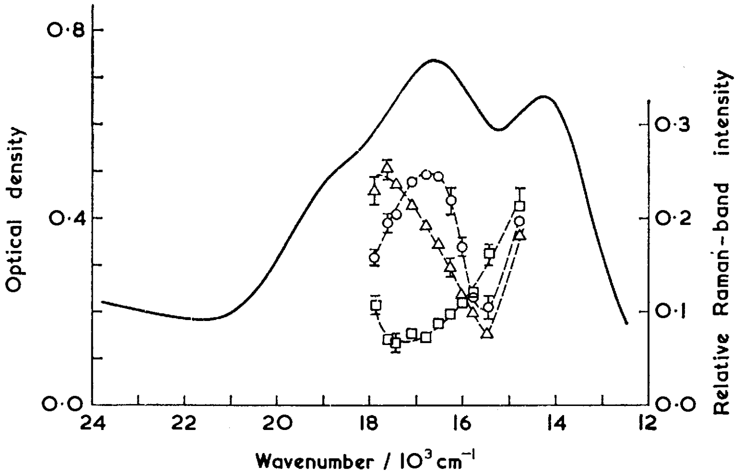


FIGURE 5 Excitation profiles of the bands at 289 (□), 350 (○), and 416 cm^{-1} (△) of the complex $[NEt_4][V(S_2C_2Ph_2)_3]$, relative to the band of acetone at 790 cm^{-1}. The electronic spectrum of the ion in acetone solution is indicated by the full line

The r.R. spectra show that the transitions giving rise to the absorption bands at 13 310 and 17 940 cm^{-1} affect, principally, the geometry of the VS_6 unit, which implies that the transferred electron enters the $3a_1'$ metal-localised antibonding orbital. The transition at 13 310 cm^{-1} is therefore assigned as $3a_1' \leftarrow 4e'$ and that at 17 940 cm^{-1} is assigned as $3a_1' \leftarrow 3e'$ (by analogy with the assignments for the rhenium complex). The ρ values of the a_1' ν(V–S) bands for resonance with the transition at 17 940 cm^{-1} are *ca.* 0.125, so that the transition must be predominantly $3a_1' \leftarrow 3e'$ ($^2E' \leftarrow {}^2A_1'$), *i.e.* any contribution from the $3a_1' \leftarrow 2a_2''$ ($^2A_2'' \leftarrow {}^2A_1'$) transition (as suggested[9] in the rhenium case) must be small. The low-temperature absorption spectrum revealed a shoulder on the low-frequency side of the band at 13 310 cm^{-1} which is possibly due to the $5e' \leftarrow 3a_1'$ transition.

$[V(S_2C_2Ph_2)_3]^-$.—The absorption spectrum of this ion in the visible region is dominated by three relatively strong transitions at 14 490, 16 750, and 18 380 cm^{-1}. Resonance with all three transitions produced fairly similar Raman spectra dominated by bands arising from the ν(V–S) fundamentals (Figure 3). Raman spectroscopy provides two additional reasons for concluding that this complex has the electronic configuration $\ldots (4e')^4(2a_2')^2$. The first is that the wavenumber of the a_1' ν(V–S) fundamental increases from 341 to 352 cm^{-1} on going from the neutral to the monoanionic complex. Since the $3a_1'$ orbital is antibonding between the metal and sulphur atoms one would expect a decrease in ν(V–S) from 341 cm^{-1} if this orbital were to become doubly occupied, and an increase if it were to become unoccupied. Secondly, the transition at 16 750 cm^{-1} in the monoanion produces the same sort of r.R. effects as does that at 17 940 cm^{-1} in the neutral complex, *i.e.* preferential enhancement of the a_1' ν(V–S) bands. Since the resonance effect is localised principally on the VS_6 unit, the transferred electron would again have to enter the $3a_1'$ orbital. This would be impossible if the ground-state configuration were $\ldots (4e')^4(3a_1')^2$. The other two transitions at 14 490 and 18 380 cm^{-1} produce somewhat different resonance effects (Figure 5). All three ν(V–S) bands are enhanced for resonance with the transition at 14 490 cm^{-1}, but only the bands at 289 and 415 cm^{-1} appear to be enhanced by resonance with the transition at 18 380 cm^{-1}.

Schrauzer and Mayweg[8] suggested that the band at 14 490 cm^{-1} of the $[V(S_2C_2Ph_2)_3]^-$ ion arose from the same transition as that responsible for the band at 15 150 cm^{-1}

of the $[W(S_2C_2Ph_2)_3]$ complex ($5e'\leftarrow 2a_2'$). Qualitative observations on the r.R. spectra of the latter complex indicate that bands arising from both ligand and metal–sulphur vibrations are enhanced for resonance with the transition at 15 150 cm^{-1}. This behaviour is not the same as that observed for the vanadium monoanion. It is worth noting that the r.R. behaviour of the tungsten complex is consistent with the assignment of Stiefel *et al.*[3] of $5e'\leftarrow 2a_2'$, *i.e.* to a metal–ligand delocalised (antibonding) orbital from a non-bonding orbital. A more reasonable assignment for the transition of 14 490 cm^{-1} in the vanadium monoanion is $3a_1'\leftarrow 4e'$ since all the three ν(V–S) bands are enhanced by resonance with this transition, as for the neutral complex. The transition at 16 750 cm^{-1} is assigned as $3a_1'\leftarrow 3e'$. The third transition at 18 380 cm^{-1} is rather more difficult to assign. Strong fluorescence prevented any intensity measurements from being made above *ca.* 18 000 cm^{-1}, thus precluding the possibility of completing the profiles of the three ν(V–S) bands. Two possible assignments are $3a_1'\leftarrow 2a_2''$ and $4e''\leftarrow 2a_2'$. Since this transition is absent in the neutral complex it is probably due to an electron being transferred from the $2a_2'$ orbital which is doubly occupied in the monoanion. Although the $4e''\leftarrow 2a_2'$ transition is electric-dipole forbidden in D_{3h} symmetry, it could become vibronically allowed by coupling with an e'' vibration (such as may give rise to the bands at 289 and 416 cm^{-1}) or become dipole allowed if the symmetry were reduced to D_3 by a trigonal distortion.

$[V(mnt)_3]^{2-}$.—The r.R. spectrum of this complex, for excitation between *ca.* 13 000 and 20 000 cm^{-1}, is dominated by the band arising from the a_1 ν(V–S) fundamental, and resembles that of the neutral vanadium complex (Figure 3). The wavenumber of this mode is much lower for the dianion (314 cm^{-1}) than for the neutral complex (341 cm^{-1}). The reduction in wavenumber is probably due to the reduced d–π overlap [10–12] referred to earlier.

Some assignments have been proposed for the $[V(mnt)_3]^{2-}$ ion by Kwik and Stiefel[14] and Atherton and Winscom.[21] In ref. 14 the bands at 10 300 and 23 400 cm^{-1} were assigned to the $5e'\leftarrow 3a_1'$ and $4e''\leftarrow 3a_1'$ transitions respectively, whereas in ref. 21 the bands at 10 300, 15 600, and 23 400 cm^{-1} were assigned to the $3a_1'\leftarrow(2a_2',4e')$, $4e''\leftarrow 3a_1'$, and $(5e'',2a_1'')\leftarrow 3a_1'$ transitions respectively.

By analogy with the assignment for the band at 9 850 cm^{-1} in the electronic spectrum of the neutral complex, we assign the band at 10 300 cm^{-1} as $5e'\leftarrow 3a_1'$, in agreement with ref. 14. The transitions giving rise to the next three absorption bands affect, principally, the VS_6 unit. These transitions might correlate exactly with the three transitions of the $[V(S_2C_2Ph_2)_3]^-$ ion in the visible region. The transition at 17 200 cm^{-1} is assigned as $3a_1'\leftarrow 3e'$ by analogy with assignments for the neutral and monoanionic complexes. The transition at 15 600 cm^{-1} could be $3a_1'\leftarrow 4e'$, or $4e''\leftarrow 3a_1'$ as suggested in ref. 21. If the former is correct then the intensity of this transition would have decreased continuously on passing from the neutral to dianionic complexes, a result which would be attributed to increased metal d-orbital character in the $4e'$ orbital. The transition at 18 900 cm^{-1} is probably identical with that at 18 380 cm^{-1} in the monoanion, and is assigned as $4e''\leftarrow 2a_2'$. It should be pointed out that the absorption coefficients of the bands at 18 900 and 15 600 cm^{-1} (Table 3) give a misleading impression of the band intensities. The degree of enhancement of the a_1 band at 312 cm^{-1} produced by resonance with the transition at 18 900 cm^{-1} (Figure 6) gives a better indication of the intensity of this absorption band. The assignment in ref. 14 of the transition at 23 400 cm^{-1} as $4e''\leftarrow 3a_1'$ is not consistent with the r.R. observations. Although solution intensity measurements could not be made on the ν(C=C) and ν(C≡N) bands in this region because of fluorescence, it was clear from the solid-state Raman spectra that these bands become stronger as the wavenumber of the exciting radiation is made to approach the band at 23 400 cm^{-1}. An assignment of $4e''\leftarrow 3a_1'$ is not consistent with this, since it involves a transition between orbitals of the type, metal-localised←metal-localised. An assignment of $5e''\leftarrow 3a_1'$ or $5e''\leftarrow 2a_2'$ seems reasonable in this case.

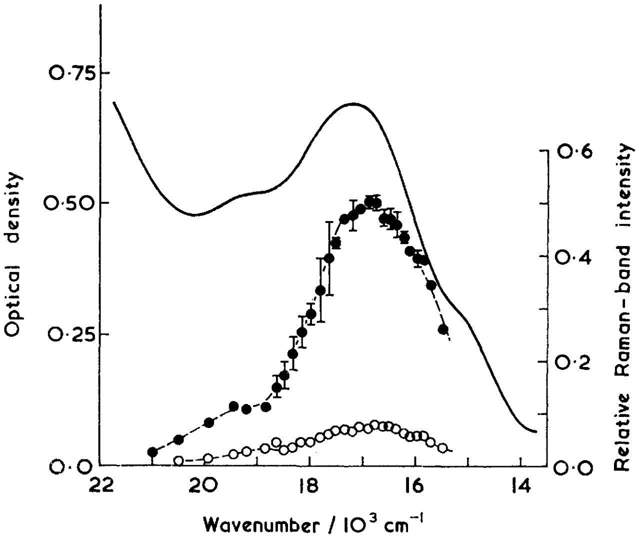


FIGURE 6 Excitation profiles of the bands at 312 (●) and 350 cm^{-1} (○) of the complex $[AsPh_4]_2[V(mnt)_3]$, relative to the band of nitromethane at 657 cm^{-1}. The electronic spectrum of the ion in nitromethane solution is indicated by the full line

$[M(mnt)_3]^{2-}$ (M = Mo *or* W).—Although these two diamagnetic complexes have identical structures within the estimated standard deviations and therefore would be expected to have the same configuration of . . . $(4e')^4(2a_2')^2(3a_1')^2$, their absorption spectra (which do not change on change of state) are known to be very different from one another. This is probably due to greater localisation of the valence electrons in the metal d orbitals in the case of dianions (rather than neutral complexes) and thus to electronic bands whose frequencies and intensities are very metal-sensitive. The wavenumber of the a_1 ν(W–S) fundamental is higher than that of the

---

[21] N. M. Atherton and C. J. Winscom, *Inorg. Chem.*, 1973, **12**, 383.

same vibration in the molybdenum complex, 367 *versus* 354 cm^{-1}. The reason for this is the same as that given for the change in ν(M–S) in the bis(mnt) complexes,[1] *viz.* greater *d*–π overlap in the complex containing the larger metal atom.

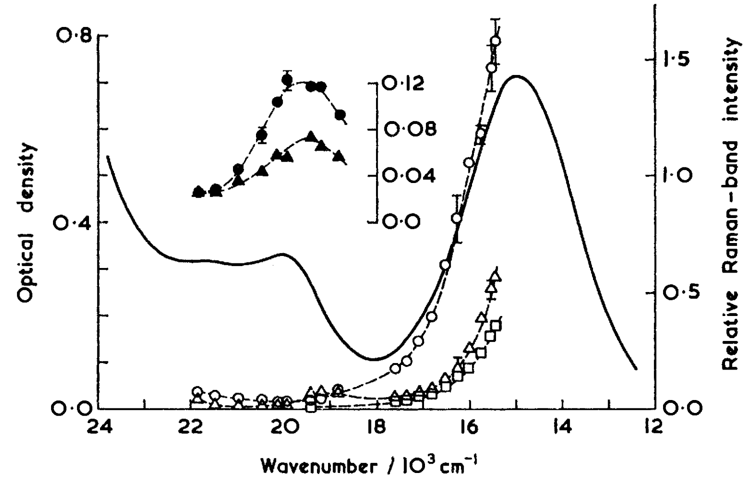


FIGURE 7 Excitation profiles of the at 279 (□), 325 (△), and 354 cm^{-1} (○) of the complex $[NBu_4]_2[Mo(mnt)_3]$, relative to the band of nitromethane at 657 cm^{-1}, and of the bands at 1 497 (●) and 2 197 cm^{-1} (▲), relative to the bands at 918 and 2 257 cm^{-1} of acetonitrile. The electronic absorption spectrum of the ion in nitromethane solution is indicated by the full line

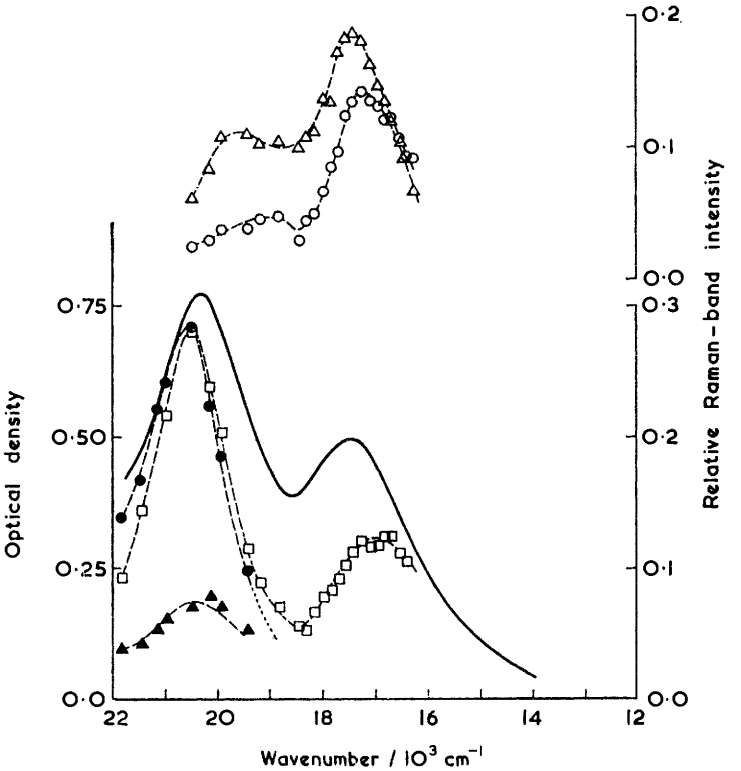


FIGURE 8 Excitation profiles of the bands at 244 (○), 332 (△), and 367 cm^{-1} (□) of the complex $[NBu_4]_2[W(mnt)_3]$, relative to the band of nitromethane at 657 cm^{-1}, and of the bands at 1 490 (●) and 2 190 cm^{-1} (▲) of the complex relative to the bands at 918 and 2 257 cm^{-1} of acetonitrile. The electronic absorption spectrum of the ion in nitromethane solution is indicated by the full line

The transition at 15 000 cm^{-1} in the molybdenum complex produces preferential enhancement of the ν(M–S) Raman bands as does that at 17 500 cm^{-1} in the tungsten complex. The difference between the two is that in the molybdenum complex the a_1 ν(Mo–S) band is much stronger than the other ν(Mo–S) bands, whereas in the tungsten complex all the ν(W–S) bands are of comparable intensity. Resonance with the transition of the molybdenum complex at 20 000 cm^{-1} does not produce any enhancement of the ν(Mo–S) bands but does produce enhancement of ν(C=C) and ν(C≡N) bands (Figure 7). In contrast, resonance with the transition of the tungsten complex at 20 000 cm^{-1} enhances bands arising from both tungsten–sulphur and ligand vibrations (Figure 8). The excitation profiles of the ν(W–S) bands at 244 and 332 cm^{-1} reveal another band at 19 250 ± 250 cm^{-1}, which undoubtedly corresponds to that observed at *ca.* 19 000 cm^{-1} in the low-temperature absorption spectrum (Table 3).

We can make the following suggestions as to the assignments for certain of the electronic bands of these complexes. Although the transitions responsible for the band at 15 000 cm^{-1} of $[Mo(mnt)_3]^{2-}$ and that at 17 500 cm^{-1} of $[W(mnt)_3]^{2-}$ do not produce identical r.R. spectral behaviour, we think it likely that the same transition is involved in each case. This would probably be $4e'' \leftarrow 3a_1'$ in view (r.R. evidence, see above) of the MS_6 localisation of the valence electrons; this assignment is consistent with the fact that ρ for the band arising from the a_1-type ν(M–S) mode in both cases is close to 0.125, indicating that the transition must be $^1E'' \leftarrow {}^1A_1'$ ($^1E \leftarrow {}^1A_1$ in D_3 symmetry). The transition of the tungsten complex at 20 000 cm^{-1} is probably $5e' \leftarrow 4e'$, since ligand as well as metal–sulphur vibrations are enhanced at resonance. The ρ value for the a_1-type ν(W–S) band is also close to 0.125, indicating that for this mode the largest contribution to the scattered intensity is from the $^1E \leftarrow {}^1A_1$ component of the $5e' \leftarrow 4e'$ transition. For the ν(C=C) and ν(C≡N) bands ρ = 0.64 and 0.44 respectively, which means that for these modes there is also some contribution to the scattering from the $^1A_2 \leftarrow {}^1A_1$ component of the $5e' \leftarrow 4e'$ transition. The assignment for the band of the molybdenum complex at 20 000 cm^{-1} is not clear since the r.R. effects are largely confined to ligand vibrations, with very little enhancement of those arising from metal–sulphur modes.

We thank the S.R.C. and the University of London Intercollegiate Research Service for support.

[8/200 *Received, 7th February,* 1978]