Electronic-absorption, Raman, and Resonance-Raman Spectroscopy of Square-planar Bis(tetraethylammonium) Bis(maleonitriledithiolato)-nickelate(II), -palladate(II), and -platinate(II)

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Resonance-Raman spectra of square-planar $[NEt_4]_2[M\{S_2C_2(CN)_2\}_2]$ complexes [M = Ni, Pd, or Pt; $S_2C_2(CN)_2$ = maleonitriledithiolate] have been recorded with a variety of exciting lines. The results of this study together with the results obtained by low-temperature (80 K) absorption spectroscopy are combined to produce a set of assignments of the electronic transitions of these complexes in the visible region.

TRANSITION-METAL complexes of maleonitriledithiolate (mnt), $[C_2S_2(CN)_2]^{2-}$, were first prepared by Gray and his co-workers during the period of general interest in compounds containing 1,2-dithiolene ligands. Both bis-[1,2] and tris-(maleonitriledithiolato)-complexes[3,4] have been synthesised and, in general, they are characterised by their relatively high stability, intense colours, and ability to take part in a series of one-electron reductions or oxidations.[2] These three properties, particularly the last one, prompted intensive investigations into the electronic structures of the complexes. Besides molecular-orbital (m.o.) calculations,[5,6] numerous

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[1] H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, 1962, **84**, 3596.

[2] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1963, **2**, 1227.

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

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

[5] S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.*, 1964, **86**, 4594.

[6] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 1965, **87**, 3585.

experimental techniques have been employed in the study of the complexes, including i.r.,[7,8] e.s.r.,[2,3] and photoelectron spectroscopy[9,10] (see below).

In this paper, the first of two on typical mnt complexes, we report the results of a resonance-Raman (r.R.) spectroscopic investigation of the complexes $[M(mnt)_2]^{2-}$ (M = Ni, Pd, or Pt). The frequencies of the Raman-active fundamentals of these anions have been measured for the first time. While these quantities may give us information on the properties of the electronic ground state of each complex, we are primarily concerned in this paper with the variation of Raman band intensities with exciting frequency since this variation is determined by the vibrational interactions in or between *excited* electronic states. Additionally, low-temperature (80 K) absorption spectra have been recorded which contain more detail than the room-temperature solution absorption spectra previously available.

EXPERIMENTAL

The sodium salt of the ligand[11] and the three complexes[1] were prepared by literature methods.

Raman spectra were recorded using a Spex 1401 double monochromator with a standard photon-counting system. Exciting lines were provided by Coherent Radiation model 52 krypton- and CR12 argon-ion lasers, and a model 490 dye laser employing rhodamine 6G (pumped by 5 W of the all-wave power of the CR12 laser). Frequencies were measured with respect to emission lines from a neon lamp, the lines being superimposed directly on the spectra. Both solid and solution Raman spectra were obtained using rotating sample holders. Intensity measurements for solutions were made relative to the bands of acetonitrile at 378, 918, or 2 252 cm^{-1} (the solvent band nearest in frequency to the band of the complex was used in each case), except for the lower-frequency bands of the palladium and platinum complexes for which the band of nitromethane at 657 cm^{-1} was used. The concentrations of the solutions were *ca.* 10^{-3} mol dm^{-3} with respect to the complex. In nitromethane solution the platinum complex was slightly photosensitive and the final intensity results are a composite of measurements on different solutions.

Electronic-absorption spectra were recorded either on a Pye Unicam SP 1800 (room-temperature solution spectra) or on a Cary 14 spectrophotometer (80-K absorption spectra). The transmission spectra of the complexes were recorded as KBr discs held in a standard Dewar.

RESULTS

Raman Spectra.—The bis(maleonitriledithiolato)-complexes of nickel, palladium, and platinum are all planar ions with the following structure. They each therefore have D_{2h} symmetry and a group theoretical analysis shows that the vibrational representation of such an ion is $\Gamma_{\text{vib.}} = 8a_g + 7b_{1g} + 3b_{2g} + 3b_{3g} + 4a_u + 4b_{1u} + 8b_{2u} + 8b_{3u}$; the g modes are Raman-active only, and the u modes (with the exception of the a_u modes which are inactive) are i.r.-active only.

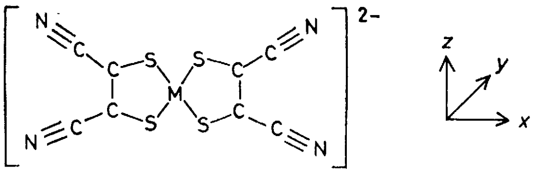

Table 1

Raman bands (cm^{-1}) of $[M(mnt)_2]^{2-}$ ions[a]

M			Assignment[b]	
Ni	Pd	Pt		
132.1				
161.9	160.0			
177.0		173.6		p
(177)				
192.3		194.5		
	221.7	221.5		
	268.5	273.4		
	273.6	283.1		
		290.2		
283.3	292.2	311.1	ν(M–S)	dp
(284)	(291)	(310)		
335.1	349.5	377.6	ν(M–S)	p
(334)	(349)	(378)		
	357.8	392.1		
415.8	415.2	421.8		dp
(417)	(416)	(421)		
498.4	494.6	495.5		p
507.4	510.1	511.1		dp
528.0	530.4	533.4		
		567.3		
605		613		
674		671		
	699		2ν(M–S)	
866			ν(C–S)	
1 001	1 005	1 007	ν(C–C) + ν(C–S)	p
(1 004)		(1 005)		
1 046	1 045	1 043		p
(1 041)	(1 042)	(1 042)		p
1 063	1 062	1 057		p
(1 057)	(1 058)	(1 054)		
1 109	1 109			
1 116		1 137		
1 147	1 144	1 148		dp
(1 143)				
1 302				
1 480	1 482	1 479	ν(C=C)	p
(1 484)	(1 483)	(1 481)		
		1 683		
		1 704		
1 750				
1 772				
1 816	1 830	1 856	ν(C=C) + ν(M–S)	
1 977	1 975	1 972	ν(C=C) + 498, *etc.*	
2 183			ν(C≡N)	
2 193	2 195	2 194		
(2 197)	(2 199)	(2 199)		p
2 211	2 208	2 222		
2 942			2ν(C=C)	
3 670			ν(C=C) + ν(C≡N)	

[a] Figures in parentheses refer to the band in MeCN or $MeNO_2$ solution. [b] p and dp refer to polarised and depolarised bands respectively. Because of the variation of ρ with exciting frequency, actual values are not given for bands labelled p.

The i.r. spectra of these complexes have been reported[7,8] and a normal-co-ordinate analysis of the b_{2u} and b_{3u} fundamentals has been performed.[8] The frequencies of all the bands observed in the Raman spectra of the complexes are given in Table 1 together with the assignments, where

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[7] D. M. Adams and J. B. Cornell, *J. Chem. Soc.* (*A*), 1968, 1299.

[8] C. W. Schläpfer and K. Nakamoto, *Inorg. Chem.*, 1975, **14**, 1338.

[9] S. O. Grim, L. J. Matienzo, and W. E. Swartz, *J. Amer. Chem. Soc.*, 1972, **94**, 5116.

[10] S. O. Grim, L. J. Matienzo, and W. E. Swartz, *Inorg. Chem.*, 1974, **13**, 447.

[11] A. Davison and R. H. Holm, *Inorg. Synth.*, 1967, **10**, 8.

possible, as polarised (a_g) or depolarised (b_{ng}). In general the r.R. spectra contained fewer bands due to fundamentals than the off-resonance Raman spectra {*e.g.* $[Ni(mnt)_2]^{2-}$ in *Figure 1*}, *owing to* selective enhancement of certain bands under resonance conditions. For this reason the data for the palladium and platinum complexes are not as complete as for the nickel complex, since the off-resonance spectra of the first two were obscured by fluorescence. As one might expect from the structure shown above, the normal-co-ordinate analysis showed that there was considerable mixing of the symmetry co-ordinates. Nevertheless, it is convenient to assign bands according to the symmetry co-ordinate which makes the predominant contribution to the normal co-ordinate. Such assignments are given for some of the bands in Table 1, based partly on those of Schläpfer and Nakamoto.[8] In the series Ni, Pd, Pt the frequencies of bands arising principally from corresponding ligand vibrations differ very little from one another and hence we may readily identify metal-sensitive bands. For instance, the a_g ν(M–S) vibration increases in frequency as we pass down the group Ni (335) < Pd (349) < Pt (378 cm^{-1}), reflecting the increase in metal-*d*–ligand-π orbital overlap. Also the bands at 283 and 415 cm^{-1} in the Raman spectrum of the nickel complex shift to 292 and 415 cm^{-1} for the palladium complex and to 310 and 421 cm^{-1} for the platinum complex.

TABLE 2

Electronic-absorption spectra in acetonitrile solution

Ion	$\tilde{\nu}$ / cm^{-1}	ε / dm^3 mol^{-1} cm^{-1}	Assignment *a*	Assignment *b*
$[Ni(mnt)_2]^{2-}$	17 500	570	$^1B_{3g}\leftarrow{}^1A_g(xy\leftarrow xz)$	$^1B_{3u},{}^1B_{2u}\leftarrow{}^1A_g$(M←S)
(Red)	19 250	1 250	$^1A_u\leftarrow{}^1A_g$(L←M)	$^1B_{1g}\leftarrow{}^1A_g$(M←S)
	21 000	3 800	$^1B_{2u}\leftarrow{}^1A_g$(L←M)	n.a.
	26 400	6 600	$^1B_{3u},{}^1B_{2u}\leftarrow{}^1A_g$(M←L)	n.a.
$[Pd(mnt)_2]^{2-}$	15 700	64	$^1B_{1g}\leftarrow{}^1A_g(xy\leftarrow x^2-y^2)$	$^1B_{1g}\leftarrow{}^1A_g(xy\leftarrow x^2-y^2)$
(Green)	22 700	5 700	$^1B_{3u},{}^1B_{2u}\leftarrow{}^1A_g$(M←L)	$^1B_{1g}\leftarrow{}^1A_g$(M←S)
	25 800	2 840	$^1A_u\leftarrow{}^1A_g$(L←M)	n.a.
$[Pt(mnt)_2]^{2-}$	15 650	56	$^3B_{3g}\leftarrow{}^1A_g(xy\leftarrow xz)$	n.a.
(Red)	18 500	1 220	$^1A_u,{}^1B_{1g}\leftarrow{}^1A_g$(L←M,$xy\leftarrow x^2-y^2$)	n.a.
	21 100	3 470	$^1B_{2u}\leftarrow{}^1A_g$(L←M)	n.a.
	32 300	13 400	$^1B_{3u},{}^1B_{2u}\leftarrow{}^1A_g$(M←L)	n.a.

[a] Given in ref. 5. [b] Given in ref. 6. n.a. = Not assigned.

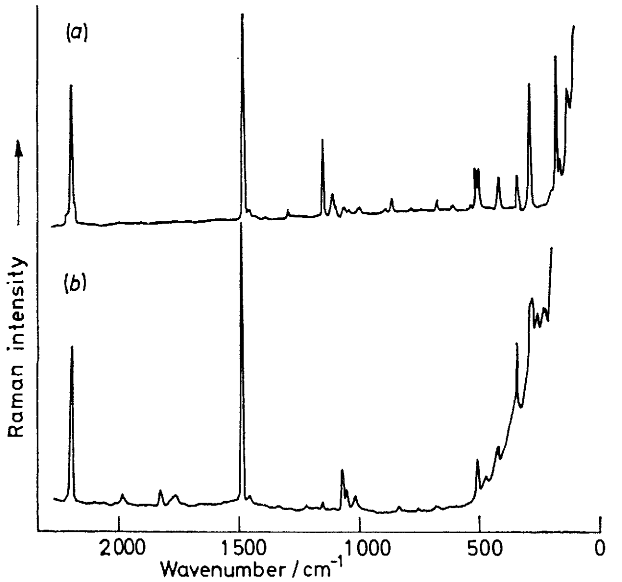

FIGURE 1 Raman spectra of the complex $[NEt_4]_2[Ni(mnt)_2]$ recorded with (*a*) 635- and (*b*) 457.9-nm excitation. Spectral slit widths *ca.* 3 cm^{-1}

Absorption Spectra.—The details of the solution electronic-absorption spectra of the nickel, palladium, and platinum complexes in the visible and near-u.v. regions have been reported previously [1,5] and are given in Table 2 together with the proposed assignments.

In order to see whether better resolution of the absorption bands could be attained in the solid state, we recorded the absorption spectra of KBr discs of the complexes at room and liquid-nitrogen temperatures. The spectra recorded at *ca.* 80 K (Figures 2—4) showed considerable structure in the absorption bands; frequencies and probable assignments are given in Table 3. We shall discuss these results and their relation to the r.R. spectra later.

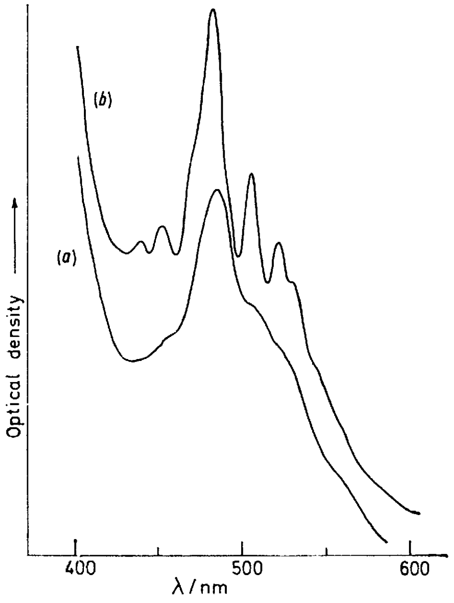

FIGURE 2 Absorption spectra of the complex $[NEt_4]_2[Ni(mnt)_2]$ in a KBr disc at (*a*) room (293 K) and (*b*) liquid-nitrogen temperatures (80 K)

The assignments of Gray and his co-workers [5] were based on the results of an m.o. calculation on the $[Ni(mnt)_2]^{2-}$ system, while those of Schrauzer and Mayweg [6] were made using the energy-level diagram obtained from calculations on the neutral $[Ni(S_2C_2H_2)_2]$ complex. Gray's calculations led to a ground-state configuration of . . . $(4b_{2g})^2(4a_g)^2$ while those of Schrauzer gave . . . $(2b_{3g})^2(4a_g)^2(3b_{2g})^2$. One purpose of the present investigation is to attempt, *via* r.R. and low-temperature absorption-spectral studies, to distinguish between alternative electronic band assignments consequent on these different proposed ground-state configurations.

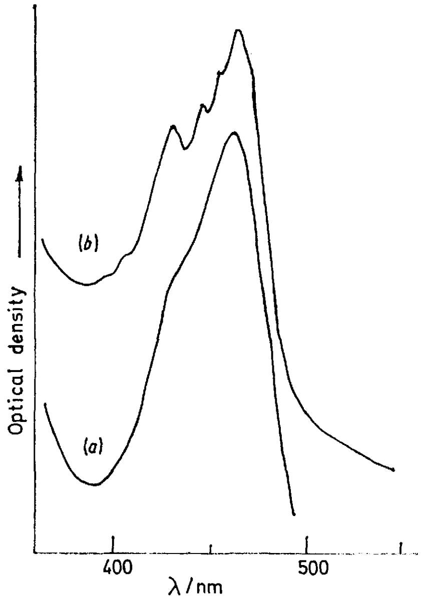

FIGURE 3 Absorption spectra of the complex $[NEt_4]_2[Pd(mnt)_2]$ in a KBr disc at (*a*) room and (*b*) liquid-nitrogen temperatures

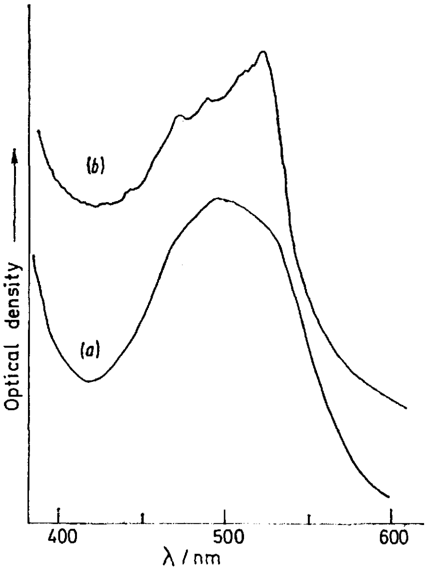

FIGURE 4 Absorption spectra of the complex $[NEt_4]_2[Pt(mnt)_2]$ in a KBr disc at (*a*) room and (*b*) liquid-nitrogen temperatures

DISCUSSION

It is obvious from Table 2 that there are considerable differences between the two sets of electronic-spectral assignments, especially as to the question of whether a band is dipole-allowed or -forbidden. Schrauzer and Mayweg [6] criticised the work of Gray and his co-workers [5] basically on the grounds that the treatment implies some charge separation between the metal and the ligands. They also pointed out that the monoanions would have the odd electron in a $4a_g$ orbital which would be inconsistent with the results of an e.s.r. study.[2,3] Some years later, however, Grim *et al.*[10] used *X*-ray photoelectron spectroscopy to determine the 3*d* nickel binding energy in $[Ni(mnt)_2]^{2-}$, and deduced that the charge on the nickel atom was +0.26 in exact agreement with the results of Gray's calculations. Although the exact agreement is undoubtedly fortuitous, these results of Grim *et al.* strongly support Gray's assignment. Schrauzer and Mayweg's application of the $[Ni(S_2C_2H_2)_2]$ results to the $[Ni(mnt)_2]^{2-}$ system could itself be criticised on two grounds: (*i*) as they themselves stated, their energy-level diagram is not strictly applicable to the dianions since it does not take into account changes in the nature of the ligand which are known to occur on reduction; and (*ii*) the probable conjugation of the CN groups with the ligand π system is not allowed for, whereas it is in the treatment of Gray and his co-workers.

$[Ni(mnt)_2]^{2-}$.—The transition in this complex which is most easily assigned is that giving rise to the band at 21 000 cm^{-1} in acetonitrile solution. The observation of combination bands and one overtone for resonance with this transition, together with the strong enhancement

TABLE 3

Bands observed in the 80-K transmission spectra

Complex	λ/nm	$\tilde{\nu}$/cm^{-1}	Assignment
$[Ni(mnt)_2]^{2-}$	557.1	17 950	$^1B_{3g}\leftarrow{}^1A_g$
	544.0	18 382	$^1A_u\leftarrow{}^1A_g$, vibronic origin
	530.8	18 839	$+\nu$(Ni–S) (292, 335, 415)
	521.2	19 175	$+2\nu$(Ni–S)
	505.3	19 790	$+\nu$(C=C)
	482.5	20 725	ν_{00}, $^1B_{2u}\leftarrow{}^1A_g$
	470.6	21 249	$\nu_{00}+\nu$(Ni–S), 2ν(Ni–S)
	451.1	22 168	$\nu_{00}+\nu$(C=C)
	437.2	22 872	$\nu_{00}+\nu$(C≡N)
	425.0	23 529	$\nu_{00}+2\nu$(C=C)
$[Pd(mnt)_2]^{2-}$	470.3	21 263	$^1B_{2u}$, $^1B_{3u}\leftarrow{}^1A_g$ $+n\nu$(Pd–S)
	463.4	21 579	
	454.9	21 982	
	445.3	22 456	
	431.3	23 185	ν_{00}, $^1B_{2u}\leftarrow{}^1A_g$
	425.0	23 529	$\nu_{00}+\nu$(Pd–S)
	419.0	23 866	$\nu_{00}+2\nu$(Pd–S)
	406.1	24 624	$\nu_{00}+\nu$(C=C)
	395.5	25 284	$\nu_{00}+\nu$(C≡N)
	384.2	26 028	$\nu_{00}+2\nu$(C=C)
$[Pt(mnt)_2]^{2-}$	522.1	19 153	$^1B_{2u}$, $^1B_{3u}\leftarrow{}^1A_g$ $+n\nu$(Pt–S)
	509.4	19 630	
	488.2	20 483	
	472.1	21 181	ν_{00}, $^1B_{2u}\leftarrow{}^1A_g$
	457.6	21 853	$\nu_{00}+\nu$(Pt–S), 2ν(Pt–S)
	442.0	22 624	$\nu_{00}+\nu$(C=C)
	429.0	23 310	$\nu_{00}+\nu$(C≡N)

of bands arising from totally symmetric modes (Figure 5), is entirely consistent with the assignment[5] of the band at 21 000 cm^{-1} as being the electric-dipole-allowed $^1B_{2u}\leftarrow{}^1A_g$ transition. The structure associated with this band, present in the 80-K absorption spectrum, can be assigned to vibronic transitions involving the ν(Ni–S) (335), ν(C=C) (1 480), and ν(C≡N) (2 193 cm^{-1}) fundamentals (Table 3). These assignments are confirmed by the fact that the Raman bands arising from these three fundamentals show the greatest resonance enhancement, in accord with the vibronic theory of Raman intensities.[12] Since the bands between 1 000 and 1 150 cm^{-1} are relatively weak in the Raman spectrum, and have excitation profiles which increase monotonically towards the blue (Figure 6), it is probable that they gain their Raman intensity from the transition responsible for the absorption band at 26 400 cm^{-1}.

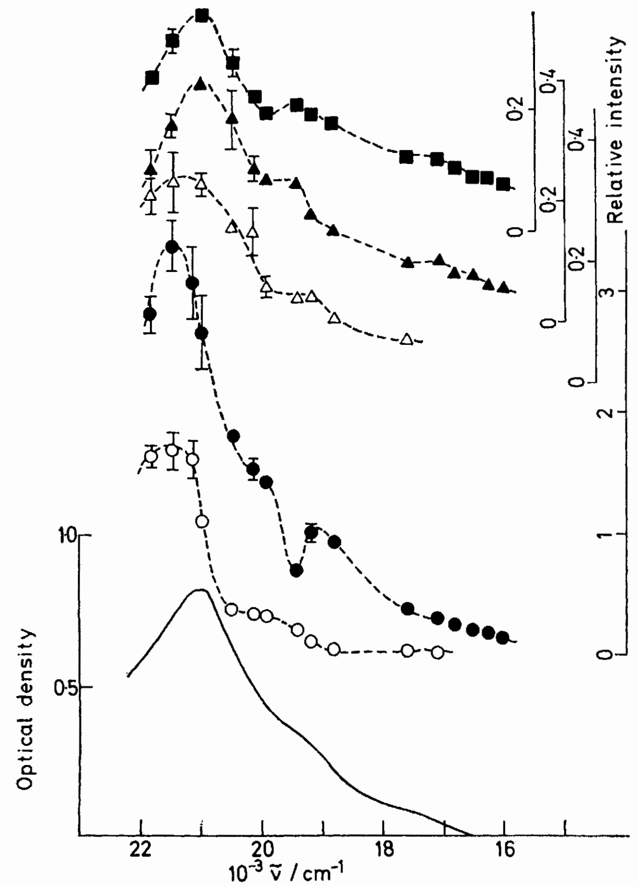

FIGURE 5 Excitation profiles of the bands of the [Ni(mnt)$_2$]$^{2-}$ ion at 335 (○), 1 484 (●), 417 (△), 284 (▲), and 2 197 (■) cm^{-1} in acetonitrile solution

The assignment of the band at 19 250 cm^{-1} as dipole-forbidden by both Gray and Schrauzer is consistent with the behaviour of the Raman band intensities for excitation in this region. No overtones or combination bands were observed for resonance with this transition band and the non-totally symmetric ν(Ni–S) Raman band at 283 cm^{-1} is stronger than the totally symmetric band at 335 cm^{-1}. The solid-state absorption spectrum shows some structure in this region but is less well resolved than in the case of the band at 21 000 cm^{-1}. With the assumption that the band at 19 250 cm^{-1} does arise from a forbidden transition, possible assignments can be made based on a vibronic origin at 18 382 cm^{-1} (Table 3). The weak absorption band occurring at 17 500 cm^{-1} in solution is barely visible in the solid-state spectrum and shows no structure at low temperature. The intensities of the Raman bands at 335, 1 480, and 2 197 cm^{-1} show very little enhancement for resonance with this transition band and it seems, therefore, highly probable that the transition is dipole-forbidden.

The intensity of the Raman band at 2 197 cm^{-1} assigned to a_g ν(C≡N) shows enhancement on resonance with all three electronic transitions in the visible region and this implies that the delocalisation of the molecular orbitals must extend to the CN groups, hence making clear the necessity of including these groups in calculations of the ligand energy levels.

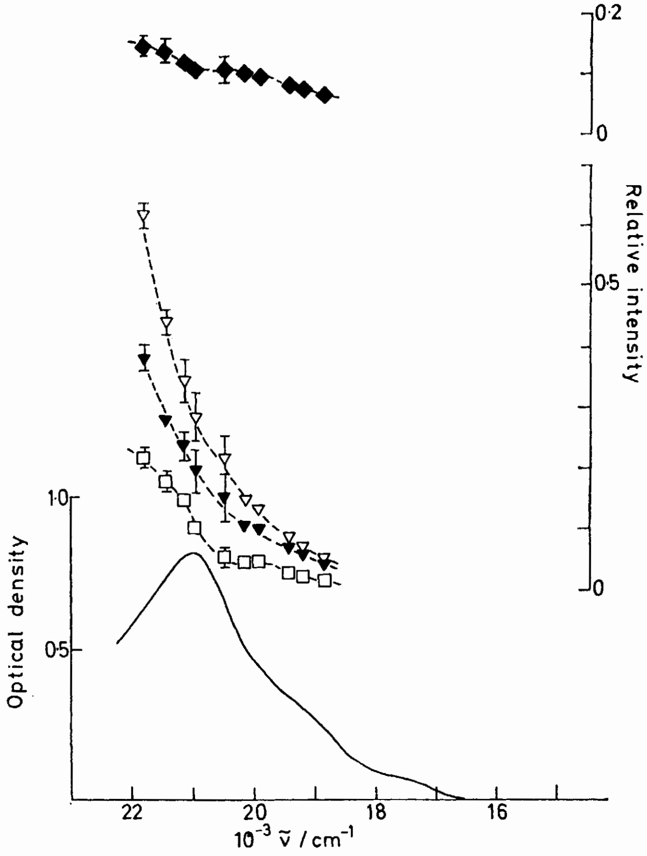

FIGURE 6 Excitation profiles of the bands of the [Ni(mnt)$_2$]$^{2-}$ ion at 1 004 (□), 1 041 (▼), 1 057 (▽), and 1 143 (♦) cm^{-1} in acetonitrile solution

Non-totally symmetric fundamentals such as those giving rise to the bands at 283, 416, and 1 147 cm^{-1} appear in the r.R. spectrum because they couple the $^1B_{2u}$

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[12] J. Tang and A. C. Albrecht, in ' Raman Spectroscopy,' vol. 2, ed. H. Szymanski, Plenum Press, New York, 1970.

state to a higher-energy state. If we make the reasonable assumption that ${}^1B_{1u}\leftarrow{}^1A_g$ transitions, *i.e.* those polarised perpendicular to the plane of the complex, occur only at relatively high energies, then a ${}^1B_{2u}$ or ${}^1B_{3u}$ state (at relatively low energy) will be vibronically coupled most strongly with other ${}^1B_{2u}$ or ${}^1B_{3u}$ states. The vibronic-coupling matrix element has the form $\langle e|\partial H/\partial Q|s\rangle$, where e and s are two excited electronic states and Q is a normal co-ordinate. Then if Γ_e and $\Gamma_s = B_{2u}$ or B_{3u}, $\Gamma(\partial H/\partial Q) = A_g$ or B_{1g}. Hence any non-totally symmetric bands which appear on resonance with a ${}^1B_{2u}$ or ${}^1B_{3u}$ state must arise from b_{1g} fundamentals, which is accordingly the assignment given to the bands at 283, 416, and 1 147 cm^{-1}.

$[Pd(mnt)_2]^{2-}$.—The absorption spectrum of this ion (Table 2, Figures 7 and 8) is very different from that of the nickel complex. The band at 22 700 cm^{-1} (solution value) was assigned by Schrauzer and Mayweg [6] as arising from a dipole-forbidden transition which, in view of its large absorption coefficient, seems an unlikely assignment. Our observation under resonance conditions of combination bands in the Raman spectrum involving ν(C=C) and ν(Pd–S) as well as a weak overtone of ν(Pd–S) is more consistent with an assignment in which this electronic transition is dipole-allowed. The strong enhancement of the bands at 350 [a_g ν(Pd–S)] and 1 482 cm^{-1} [a_g ν(C=C)] as compared with the bands at 291 and 416 cm^{-1} (b_{1g}) also supports this assignment. The vibrational structure on this absorption band (Figure 3, Table 3) observed in the low-temperature spectrum is not well resolved but is probably caused by vibronic transitions involving ν(Pd–S). The low-temperature absorption spectrum shows clearly, however, the presence of two transitions in the 430—470 nm region. The higher-energy transition (431.3 nm, 23 185 cm^{-1}) possesses some weak sidebands which can be assigned to vibronic transitions involving the ν(Pd–S), ν(C=C), and ν(C≡N) modes. In this respect the band resembles that arising from the allowed L←M transition in the nickel complex at 20 725 cm^{-1} and we therefore suggest that it is the ${}^1B_{2u}\leftarrow{}^1A_g$ (L←M) rather than the ${}^1A_u\leftarrow{}^1A_g$ transition.

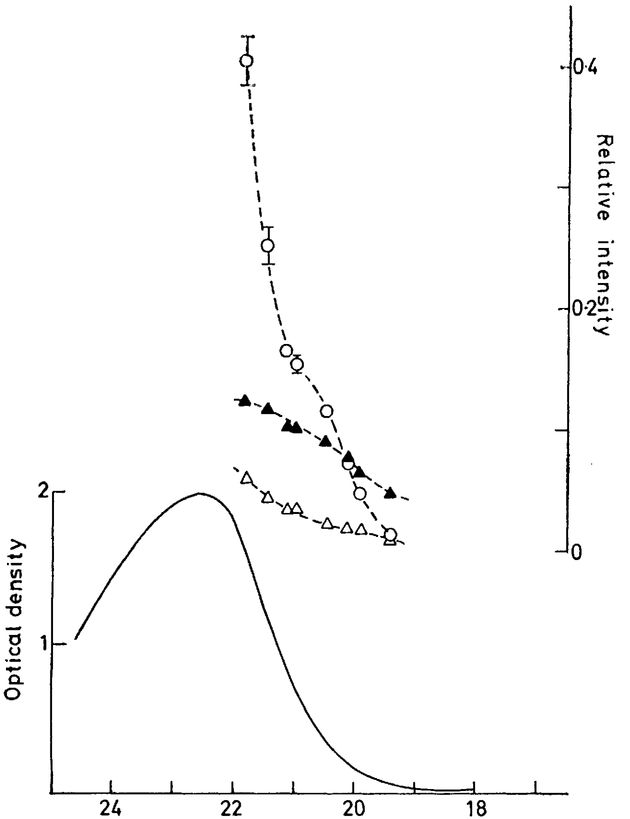

FIGURE 7 Excitation profiles of the bands of the $[Pd(mnt)_2]^{2-}$ ion at 291 (▲), 349 (○), and 416 (△) cm^{-1} in nitromethane solution

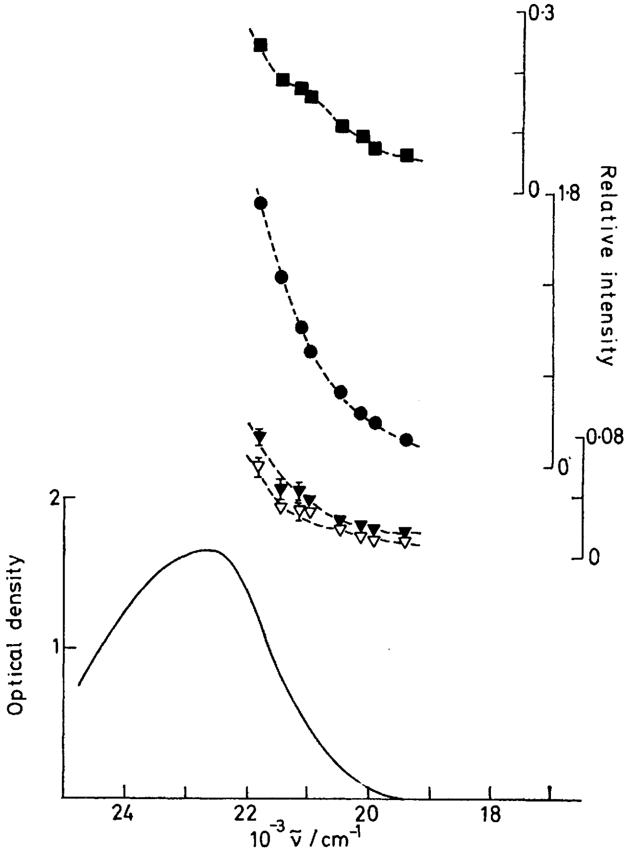

FIGURE 8 Excitation profiles of the bands of the $[Pd(mnt)_2]^{2-}$ ion at 1 058 (▽), 1 042 (▼), 1 482 (●), and 2 199 (■) cm^{-1} in acetonitrile solution

The depolarisation ratios of the bands at 350, 1 482, and 2 199 cm^{-1} are all close to $\frac{1}{3}$ when measured with the 457.9-nm exciting line (21 831 cm^{-1}), *i.e.* virtually at resonance. This can only occur when the Raman intensity is dominated by one diagonal element of the scattering tensor, *i.e.* α_{xx} or α_{yy} (assuming $\alpha_{zz} = 0$). Therefore either $\alpha_{xx} \gg \alpha_{yy}$ or *vice versa*. Gray's assignment of the band at 22 700 cm^{-1} as arising from the two transitions ${}^1B_{2u}$, ${}^1B_{3u}\leftarrow{}^1A_g$ can only be correct therefore if one of these transitions is very much stronger than the other.

$[Pt(mnt)_2]^{2-}$.—Although the platinum complex is the same colour as the nickel complex, the absorption bands are much broader for the former. Comparison of the absorption spectra obtained at room and liquid-nitrogen temperatures (Figure 4) shows that there are at least two transitions giving rise to the main absorption band. The low-temperature spectrum clearly resembles that of the palladium complex and the higher-energy band, with an origin at 21 181 cm^{-1} (Table 3), shows the same type of vibrational structure observed in the corresponding bands of the palladium complex with an origin at 23 185 cm^{-1}. This transition is accordingly assigned as $^1B_{2u}\leftarrow{}^1A_g$ (L←M). The lower-energy bands at 19 153, 19 630, and 20 483 cm^{-1} are assigned to the $^1B_{3u},{}^1B_{2u}\leftarrow{}^1A_g$ transitions. The resolution is not sufficiently good to allow definite assignments of vibrational structure to be made. A wavenumber of *ca.* 19 500 cm^{-1} for these transitions seems more reasonable than that of 32 300 cm^{-1} suggested by Gray and his co-workers.

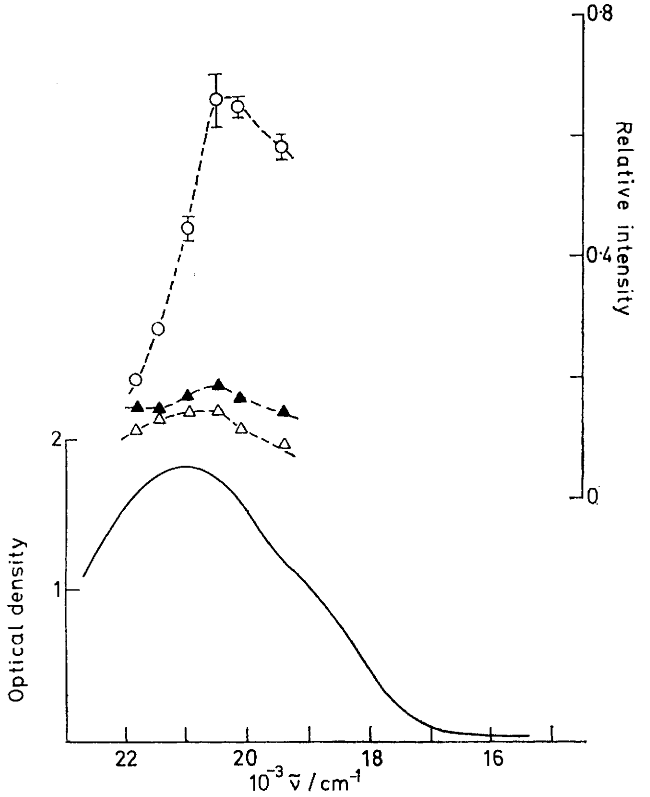

FIGURE 9 Excitation profiles of the bands of the $[Pt(mnt)_2]^{2-}$ ion at 378 (○), 311 (▲), and 421 (△) cm^{-1} in nitromethane solution

We were unable to take Raman-intensity measurements below *ca.* 19 000 cm^{-1} because of strong fluorescence which obscures the Raman spectrum. Nevertheless, the results that we obtained for excitation at >19 000 cm^{-1} confirm that there are two transitions in this region. While the excitation profiles of most of the Raman bands maximise at 20 600 ± 200 cm^{-1} (Figures 9 and 10), that of the ν(C=C) band maximises at 21 400 ± 100 cm^{-1}. This implies that the $^1B_{2u}\leftarrow{}^1A_g$ (L←M) transition causes a greater change in the C=C bond length than do the $^1B_{2u},{}^1B_{3u}\leftarrow{}^1A_g$ (M←L) transitions. It would be interesting to see if the same behaviour occurred in the palladium complex, but we are unable to extend our intensity measurements to >22 000 cm^{-1} at present.

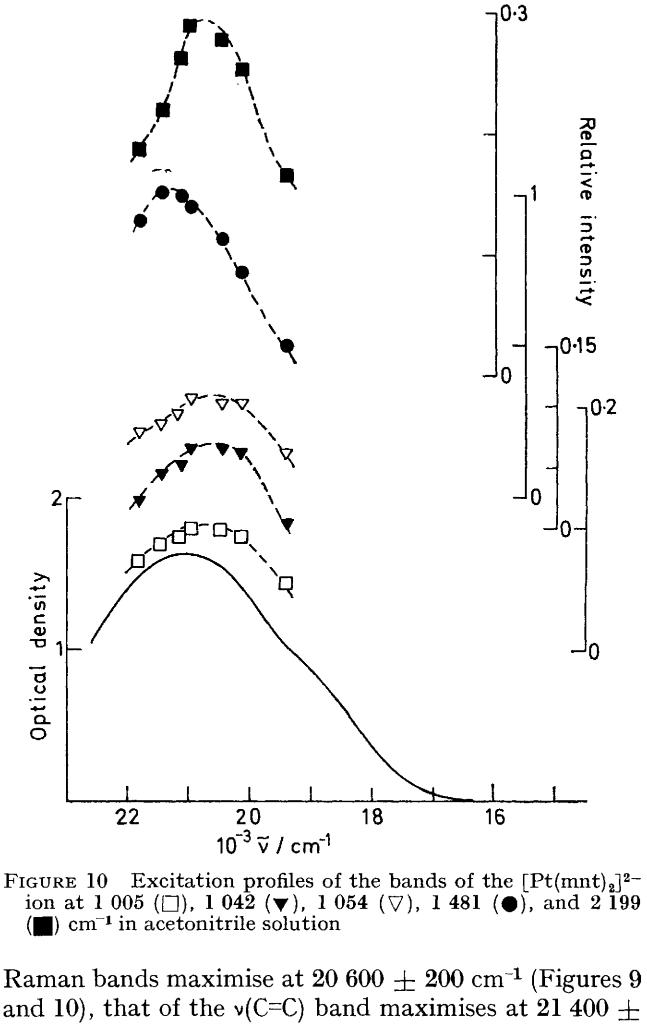

FIGURE 10 Excitation profiles of the bands of the $[Pt(mnt)_2]^{2-}$ ion at 1 005 (□), 1 042 (▼), 1 054 (▽), 1 481 (●), and 2 199 (■) cm^{-1} in acetonitrile solution

The weak absorption band which occurs at 18 500 cm^{-1} in acetonitrile solution is not visible in the solid-state spectrum possibly because of obscuration by the band at 19 153 cm^{-1}. Gray's suggestion of $^1A_u,{}^1B_{1g}\leftarrow{}^1A_g$ seems a reasonable assignment in this case.

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