Electronic Spectra, Resonance–Raman Spectra, and Excitation Profiles of the Mixed-valence Compound Reihlen's Green $[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}Br_2(C_2H_5NH_2)_4]Br_4\cdot4H_2O$

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The mixed-valence compound Reihlen's green, $[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}Br_2(C_2H_5NH_2)_4]Br_4\cdot4H_2O$, displays a resonance-Raman (r.r.) spectrum when irradiated within the contour of the mixed-valence charge-transfer transition in the visible. It is characterised by a progression in ν_1, the Br–Pt^{IV}–Br symmetric breathing fundamental, which reaches $7\nu_1$. Additional progressions $n\nu_1 + \nu_2$ [where ν_2 is the δ(Br–Pt^{IV}–N) bending fundamental] to $n = 4$ and $n\nu_1 + \nu_3$ (where ν_3 is probably a lattice mode) to $n = 3$ are also observed. The observation of such progressions permits the spectroscopic constants ω_1, x_{11}, x_{12}, and x_{13} to be determined as 179.6, −0.37, 0.3, and 0.3 cm^{-1} respectively. The diffuse-reflectance spectrum of the compound indicates that there are two overlapped mixed-valence charge-transfer transitions in the visible (main band at 18 250 cm^{-1}, shoulder at *ca.* 16 000 cm^{-1}) both of which (on the basis of previous single-crystal work) are polarised parallel to the chain axis. The excitation profile of ν_1 (Stokes), $2\nu_1$ (Stokes), and ν_1 (anti-Stokes) have maxima at 16 100, 16 300, and 15 800 cm^{-1} respectively. The observation that axial vibrational modes are resonance-enhanced on irradiation of a compound with an exciting line whose frequency falls within the band contour of an axially polarised electronic transition is considered to be an important result which may open the way to making more precise assignments of the electronic spectra of many compounds.

RESONANCE-RAMAN (r.r.) studies [1,2] have recently been directed towards mixed-valence compounds of class II (using the scheme proposed by Robin and Day),[3] and in particular to the use of exciting lines whose frequencies fall within the contours of the broad and sometimes strong intervalence charge-transfer (c.t.) bands which are characteristic of these compounds. R.r. spectra have been observed for mixed-valence compounds of antimony [4,5] and of platinum and palladium,[6] and in all cases a wide variety of higher-order features have been observed. The degree of intensity enhancement of any fundamental is not, however, very large. On the other hand, the mixed-valence platinum compound Wolffram's red, $[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}(C_2H_5NH_2)_4Cl_2]Cl_4\cdot4H_2O$, displays [7] a striking r.r. spectrum characterised by a very intense progression in ν_1, the Cl–Pt^{IV}–Cl symmetric stretching fundamental, reaching $9\nu_1$.

Reihlen's green [8] is the bromo-analogue of Wolffram's red and, like other class II mixed-valence compounds, it exists only in the solid state. A crystal-structure determination of the salt has established [9] that it consists, like Wolffram's red, of octahedral platinum(IV) and square-planar platinum(II) complex ions alternately in chains of the sort shown in Figure 1. Minor differences between this structure and that of the (orange) anhydrous form, however, occur. In Reihlen's green, the ethylamine ligands attached to the platinum(IV) and platinum(II) ions are eclipsed when viewed down the chain axis, whereas in the anhydrous form they are staggered in this respect. Further, in Riehlen's green the platinum(II) ion is centrally placed between the platinum(IV) ions, but in the anhydrous form this is not the case, the two Pt^{II}–Pt^{IV} chain distances being 5.61

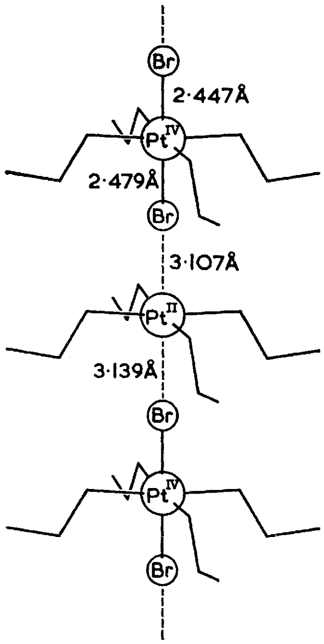

FIGURE 1 Structure of Reihlen's green, $[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}Br_2(C_2H_5NH_2)_4]Br_4\cdot4H_2O$

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[1] J. Behringer, *Specialist Periodical Report*, 'Molecular Spectroscopy,' eds.R. F. Barrow, D. A. Long, and D. J. Millen, The Chemical Society, London, vol. 4, 1975, p. 100.

[2] R. J. H. Clark, in 'Advances in Infrared and Raman Spectroscopy,' eds. R. J. H. Clark and R. E. Hester, Heyden, London, vol. 1, 1975, p. 143.

[3] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[4] R. J. H. Clark and W. R. Trumble, *J.C.S. Chem. Comm.*, 1975, 318.

[5] R. J. H. Clark and W. R. Trumble, *J.C.S. Dalton*, 1976, 1145.

[6] R. J. H. Clark and W. R. Trumble, *Inorg. Chem.*, 1976, **15**, 1030.

[7] R. J. H. Clark, M. L. Franks, and W. R. Trumble, *Chem. Phys. Letters*, 1976, **41**, 287.

[8] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1956, **29**, 894.

[9] B. M. Craven and D. Hall, *Acta Cryst.*, 1966, **21**, 177; K. L. Brown and D. Hall, *Acta Cryst.*, 1976, **B32**, 279.

and 6.53 Å. Extensive disorder occurs in both structures, these being strictly periodic only along the chain direction with a variable tendency towards order in the other directions. The weak interactions between adjacent chains enable them to slip past each other easily and thus lead to the occurrence of stacking mistakes. The Pt^{IV}–Cl, Pt^{IV}–Br, and Pt–N bond lengths in these compounds are close to the covalent bond lengths found for isolated platinum complexes.

Polarised single-crystal electronic spectra of Reihlen's green indicate the existence of a broad band whose maximum is estimated to be at 17 000 ± 1 000 cm^{-1} from the published figure.* This transition is polarised parallel to the chain axis [8] and it thus seems probable that it is due to a mixed-valence transition along the infinite chains. No further investigation of this compound has been carried out although more recent electronic-spectral data are available for Wolffram's red.[7,10,11]

TABLE 1

Wavenumbers (cm^{-1}) of i.r. and Raman bands in the spectra * of Reihlen's green and its constituent complexes together with proposed assignments

$[Pt(C_2H_5NH_2)_4]Cl_2$		$[PtBr_2(C_2H_5NH_2)_4]Br_2$		Reihlen's green		
I.r.	Raman	I.r.	Raman	I.r.	Raman	Assignments
548m		546m		547m, br		ν(Pt–N)
	541w		543vw			
	525w		514vw			
503m		498w				
		284m				δ(N–Pt–N) (in-plane)
248w	266m					
			233m			
		212m	212vw	212m		ν(Pt–Br)
			200vs		179vs	
			98s		92m	δ(Br–Pt–N)
					39s	Lattice mode

* Neglecting internal fundamentals of the ethylamine ligand. Qualitative intensities: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; br = broad.

The present study was thus undertaken to remeasure the electronic spectrum of Reihlen's green in the visible region and to establish whether a r.r. spectrum could be obtained by tuning the exciting frequency within the contour of the mixed-valence band, and, if so, of defining the excitation profiles of any resonantly-enhanced bands and their overtones.

EXPERIMENTAL

Reihlen's green was prepared according to the method of Reihlen and Flohr [12] {Found: C, 15.2; H, 4.5; Br, 37.3; N, 8.65. Calc. for $[Pt(C_2H_5NH_2)_4][PtBr_2(C_2H_5NH_2)_4]Br_4 \cdot 4H_2O$: C, 14.75; H, 4.95; Br, 36.8; N, 8.60%}.

The Raman spectra were recorded by use of a Spex 1401 double spectrometer in conjunction with Coherent Radiation model CR12 Ar^+ (457.9, 465.8, 472.7, 476.5, 488.0, 496.5, 501.7, and 514.5 nm) and model 52 Kr^+ (530.9, 568.2, 647.1, 676.4, and 752.5 nm) ion lasers, and a model 490 tunable dye laser employing rhodamine 6G. The powers of all the lines were in the range 100 mW—1 W. Detection was by means of a cooled, Grade I, RCA C31034 phototube, with linear response. The system is described in detail elsewhere.[13] Spectra were calibrated by reference to the emission lines of neon which were superimposed directly onto the recording. Band areas were determined by the trace and cut-and-weigh procedure and then corrected for the spectral response of the instrument. Relative intensities were measured with respect to the band at 981 cm^{-1} of potassium sulphate as internal standard. Samples were rotated at *ca.* 1 400 rev. min^{-1} in order to minimise thermal decomposition of the sample at the beam focus.[14,15]

Diffuse-reflectance spectra were recorded using a Cary 14 spectrometer, employing a liquid-nitrogen attachment, thus enabling spectra to be obtained at *ca.* 100 K. Infrared spectra were recorded as Nujol mulls down to 200 cm^{-1} on a Perkin-Elmer 225 spectrometer, and in the range 60—300 cm^{-1} on an R.I.I.C. interferometer.

RESULTS AND DISCUSSION

Vibrational Band Assignments.—The i.r. and Raman spectra of the compounds $[Pt^{II}(C_2H_5NH_2)_4]Cl_2 \cdot 2H_2O$ and *trans*-$[Pt^{IV}Br_2(C_2H_5NH_2)_4]Br_2 \cdot 2H_2O$ were recorded and the band maxima are listed in Table 1 (ignoring the internal vibrations of ethylamine). Also in Table 1 are the i.r. spectral data for Reihlen's green itself. It may be noted that it was unnecessary to prepare the compound $[Pt^{II}(C_2H_5NH_2)_4]Br_2 \cdot 2H_2O$ as the platinum(II) component of Reihlen's green is $[Pt(C_2H_5NH_2)_4]^{2+}$ which is present in the chloride originally made. The band assignments were obtained by reference to those of analogous compounds.[16,17] As was the case for Wolffram's red, and as is generally the case for mixed-valence compounds of Class II, the i.r. spectrum of Reihlen's

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* The captions to Figures 1 and 3 of ref. 8 should be transposed.

[10] L. V. Interrante, K. W. Browall, and F. P. Bundy, *Inorg. Chem.*, 1974, **13**, 1158.

[11] P. Day, in 'Low-dimensional Co-operative Phenomena,' ed. H. J. Keller, Plenum, New York, 1975, p. 191.

[12] H. Reihlen and E. Flohr, *Ber.*, 1934, **67**, 2010.

[13] R. J. H. Clark and M. L. Franks, *J. Amer. Chem. Soc.*, 1975, **97**, 2691.

[14] W. Kiefer and H. J. Bernstein, *Appl. Spectroscopy*, 1971, **25**, 501.

[15] R. J. H. Clark, *Spex Speaker*, 1973, **18**, 1.

[16] D. W. James and M. J. Nolan, *J. Raman Spectroscopy*, 1973, **1**, 271.

[17] D. M. Adams, 'Metal–ligand and Related Vibrations,' Edward Arnold, London, 1967, ch. 2.

green is virtually the superposition of the spectra of the constituent species.

The symmetry of the *trans*-$[Pt^{IV}Br_2(C_2H_5NH_2)_4]^{2+}$ ion, neglecting hydrogen atoms, in the lattice of Reihlen's green [9] is C_{4v}. The symmetric and antisymmetric Br–Pt^{IV}–Br stretching fundamentals of such an ion, according to the selection rules appropriate to C_{4v} symmetry, would each be predicted to be both i.r. and Raman active, the symmetric being much the more intense in the Raman spectrum, the antisymmetric much the more intense in the i.r. spectrum. Were it not for the fact that the ethylamine ligand groups destroy the mirror planes perpendicular to the chain direction, the platinum(IV) constituent would in fact have D_{4h} symmetry, and under these selection rules the symmetric stretch would be Raman active only, and the antisymmetric stretch i.r.-active only. In practice this is the actual situation, the band at 179 cm^{-1} appearing only in the Raman spectrum, and the band at 212 cm^{-1} only in the i.r. spectrum. Results from other *trans*-$[Pt^{IV}L_4X_2]$ complexes with D_{4h} symmetry show that the i.r.-active X–Pt^{IV}–X stretch is usually of higher frequency than the Raman-active one. This is consistent with the assignments shown in Table 1. Comparison with the analogous Cl–Pt^{IV}–Cl stretching vibrations in Wolffram's red shows a typical reduction in frequency (by a factor of *ca.* 0.6) on changing the axial ligands from chlorine to bromine.

TABLE 2

Wavenumbers and half-bandwidths (cm^{-1}) of the $\nu_1(Pt^{IV}–Br)$, $\nu_1(a_{1g})$, fundamental and its overtones and members of the two other progressions observed in the resonance-Raman spectrum of Reihlen's green (514.5-nm excitation)

Band	Maximum	$\Delta\nu_{\frac{1}{2}}$	Band [a]	Maximum	$\Delta\nu_{\frac{1}{2}}$	Band [b]	Maximum	$\Delta\nu_{\frac{1}{2}}$
ν_1	178.9	14	ν_2	92.2	10	ν_3	39.3	9
$2\nu_1$	356.8	27	$\nu_1 + \nu_2$	270.7	14	$\nu_1 + \nu_3$	218	15
$3\nu_1$	534.3	39	$2\nu_1 + \nu_2$	448.8	19	$2\nu_1 + \nu_3$	396	20
$4\nu_1$	710.9	48	$3\nu_1 + \nu_2$	625.6	24	$3\nu_1 + \nu_3$	573	26
$5\nu_1$	887	62	$4\nu_1 + \nu_2$	802	30			
$6\nu_1$	1 062	75						
$7\nu_1$	1 236	95						

The band at 92.2 cm^{-1} is assigned to the δ(Br–Pt–N) bending fundamental. [b] The assignment of the band at 39.3 cm^{-1} is uncertain, but a lattice mode seems probable.

The band at 179 cm^{-1} is hence assigned to an axial Pt^{IV}–Br stretching mode, *viz.* the symmetric Br–Pt^{IV}–Br breathing fundamental. This same fundamental occurs at 200 cm^{-1} in the free *trans*-$[PtBr_2(C_2H_5NH_2)_4]^{2+}$ ion. As is the case for Wolffram's red as compared with its free Pt–N complex ion, the lower value for this fundamental in Reihlen's green than for the free ion is consistent with the presence of halogen bridges in the structure; the isolated complex ion only contains terminal Pt–Br bonds which invariably give rise to higher stretching frequencies than is the case for bridged species.[17,18]

Resonance-Raman Spectra.—From the previous discussion the Raman spectrum of Reihlen's green might be expected to be the superposition of the Raman spectra of both the platinum(II) and platinum(IV) constituent species. However, with all the exciting lines used in the visible region of the spectrum, the Raman spectrum was dominated by an extremely intense band at 179 cm^{-1} and its associated overtone progression. Reihlen's green is, in fact, an exceptionally good scatterer, even better than Wolffram's red. The intense r.r. spectrum completely overwhelmed the rest of the spectrum, and no bands arising from the ethylamine ligand could be observed. Not even the antisymmetric Br–Pt^{IV}–Br stretching vibration (observed at 212 cm^{-1} in the i.r. spectrum) could be observed. Two other bands were observed, however, at 92 and 39 cm^{-1}, the best spectra being obtained when Reihlen's green was diluted several times with $K_2[SO_4]$ (the resulting mixture is almost white). It was therefore possible to scan much closer to the exciting line with this mixture than with the undiluted compound. These two bands were assigned to the δ(Br–Pt^{IV}–N) symmetric bending vibration (92 cm^{-1}) and to a lattice mode (39 cm^{-1}) and designated subsequently as ν_2 and ν_3 respectively.

Apart from the main progression in 179 cm^{-1}, two other progressions in this fundamental were also observed, namely $n\nu_1 + \nu_2$ and $n\nu_1 + \nu_3$ where ν_1 is the band at 179 cm^{-1} (Br–Pt^{IV}–Br symmetric breathing fundamental); these reached as far as $n = 4$ for the former and $n = 3$ for the latter with most of the exciting lines used. The wavenumbers and half-bandwidths of the members of all the three progressions are listed in Table 2. Overtones as far as $7\nu_1$ could be observed with most exciting lines and the spectrum obtained with 514.5-nm excitation is displayed in Figure 2.

The observed overtone progressions were sufficiently strong to allow the determination of the harmonic frequency (ω_1) and the anharmonicity constant (x_{11}). The observed wavenumber $\nu(n)$ of any overtone of an anharmonic oscillator is given [19] by the expression (1).

$$\nu(n) = n\omega_1 + (n^2 + n)x_{11} + \text{higher-order terms} \quad (1)$$

A plot of $\nu(n)/n$ against n should thus be a straight line of gradient x_{11} and intercept $\omega_1 + x_{11}$ (neglecting the higher terms). The plot for the $n\nu_1$ progression gave values of 179.6 ± 0.6 and −0.37 ± 0.04 cm^{-1} for ω_1 and

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[18] R. J. H. Clark, in 'Halogen Chemistry,' ed. V. Gutmann, Academic Press, London, 1967, vol. 3, p. 85.

[19] G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, Princeton, 1966, p. 205.

x_{11} respectively (by least-squares analysis). As is the case from previous studies on systems displaying the r.r. effect, for example $[AuBr_4]^-$,[20] $[CrO_4]^{2-}$,[21] TiI_4,[22] and the compound $[Ru_2Cl(O_2CMe)_4]$,[23] the anharmonicity constant x_{11} is very small. The further progressions allow additional determinations of ω_1 and x_{11}; thus from the $n\nu_1 + \nu_2$ progression ω_1 and x_{11} are calculated to be 179.3 ± 0.6 and −0.37 ± 0.05 cm^{-1} respectively, and from the $n\nu_1 + \nu_3$ progression they are calculated to be 179.3 ± 0.6 and −0.34 ± 0.05 cm^{-1} respectively. The differences between the ω_1 value obtained from the $n\nu_1$ progression on the one hand and from the $n\nu_1 + \nu_2$ or $n\nu_1 + \nu_3$ progression on the other hand (*ca.* 0.3 cm^{-1}) are equal to the cross terms x_{12} and x_{13} respectively.[24-26] It should be noted that higher terms in the expression for $\nu(n)$ contribute to a change of intercept and therefore these will, if significant, restrict the accuracy of evaluation of ω_1.

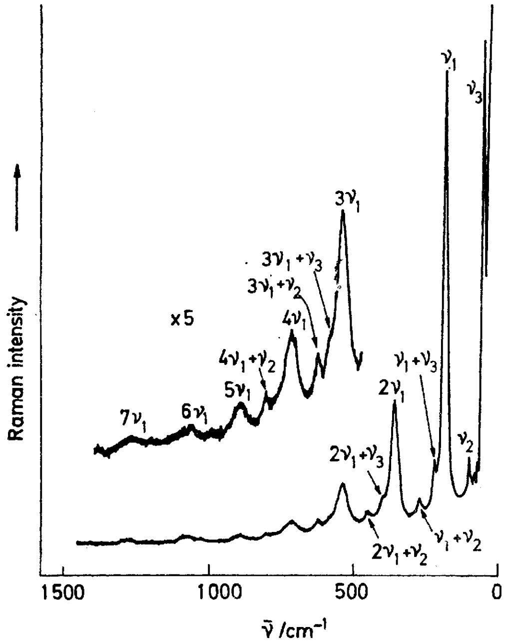

FIGURE 2 Resonance-Raman spectrum of Reihlen's green obtained with 514.5-nm excitation. Slit widths 150, 250, and 150 μm (3 cm^{-1})

Electronic Spectra and Excitation Profiles.—The diffuse-reflectance spectra of Reihlen's green and its constituents are shown in Figure 3. It can be seen that this compound shows a broad, strong, asymmetric absorption band in the visible region of the spectrum which is not displayed by either component complex ion. The band maximum is at 548 nm (18 250 cm^{-1}) and at lower frequency (*ca.* 16 000 cm^{-1}) a shoulder can be seen which is not resolved from the main band at temperatures of *ca.* 100 K. The spectrum differs somewhat from the polarised single-crystal spectrum reported by Yamada and Tsuchida,[8] although these workers make it clear that both the band and the shoulder are polarised parallel to the chain axis.

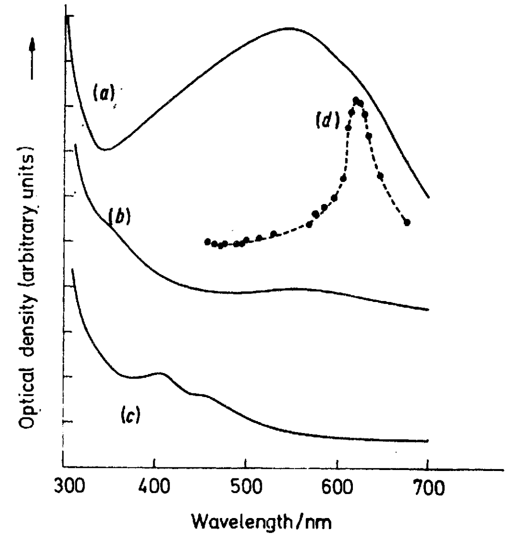

FIGURE 3 Diffuse-reflectance spectra of Reihlen's green (*a*) and its constituent complexes $[Pt^{II}(C_2H_5NH_2)_4]Cl_2\cdot 2H_2O$ (*b*) and $[Pt^{IV}Br_2(C_2H_5NH_2)_4]Br_2\cdot 2H_2O$ (*c*) at *ca.* 100 K, together with the excitation profile for the Stokes Raman band at 179 cm^{-1} (*d*)

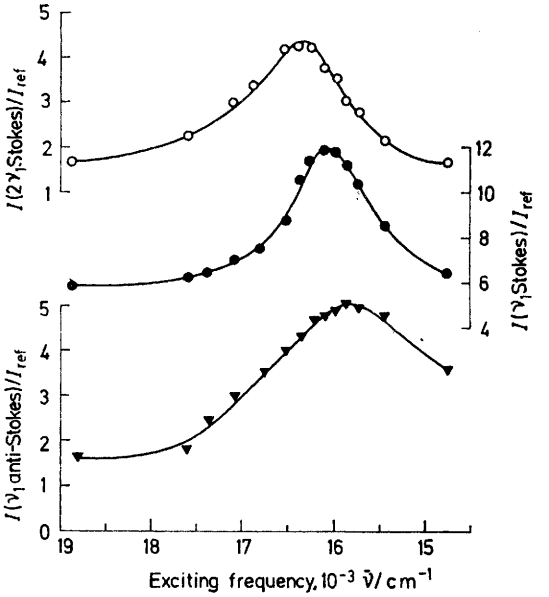

FIGURE 4 Detailed excitation profiles for the band at 179 cm^{-1} [Stokes (●) and anti-Stokes (▼)] and its first overtone [Stokes only (○)] obtained from the resonance-Raman spectrum of Reihlen's green

Although the r.r. spectra obtained with each exciting line are generally similar to one another, it is of con-

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[20] Y. M. Bosworth and R. J. H. Clark, *Chem. Phys. Letters*, 1974, **28**, 611.

[21] W. Kiefer and H. J. Bernstein, *Mol. Phys.*, 1972, **23**, 835.

[22] R. J. H. Clark and P. D. Mitchell, *J. Raman Spectroscopy*, 1974, **2**, 399.

[23] R. J. H. Clark and M. L. Franks, *J.C.S. Dalton*, 1976, 1825.

[24] R. J. H. Clark and M. L. Franks, *Chem. Phys. Letters*, 1975, **34**, 69.

[25] Y. M. Bosworth and R. J. H. Clark, *J.C.S. Dalton*, 1975, 381.

[26] R. J. H. Clark and M. L. Franks, *J. Amer. Chem. Soc.*, 1976, **98**, 2763.

siderable interest, in the light of the electronic spectrum obtained, to plot the excitation profiles for the band at 179 cm^{-1} (Stokes and anti-Stokes) and its first overtone (Stokes only). The intensities of these bands relative to the $\nu_1(a_1)$ band of the sulphate ion (981 cm^{-1}) as internal standard are shown in Table 3 for different exciting lines. There is very little change in these values for exciting lines in the range 457.9—514.5 nm (Figure 3). Each plot (Figure 4) reveals a maximum at a slightly different frequency. That for $I(\nu_1$ Stokes$)/I(981$ cm$^{-1})$ is at *ca.* 16 100 cm^{-1}, that for $I(2\nu_1$ Stokes$)/I(981$ cm$^{-1})$ is at *ca.* 16 300 cm^{-1}, and that for $I(\nu_1$ anti-Stokes$)/I(981$ cm$^{-1})$ is at *ca.* 15 800 cm^{-1}.

TABLE 3

Intensities * of the ν_1(Pt–Br) band (Stokes and anti-Stokes) and of its first overtone (Stokes only) relative to the band at 981 cm^{-1} of the sulphate ion as internal standard

Exciting wavelength/nm	$\frac{I(\nu_1 \text{ Stokes})}{I_{SO_4^{2-}}}$	$\frac{I(2\nu_1) \text{ Stokes}}{I_{SO_4^{2-}}}$	$\frac{I(\nu_1 \text{ anti-Stokes})}{I_{SO_4^{2-}}}$
457.9	5.5	1.2	1.5_5
465.8	5.3_5	1.2	1.5
472.7	5.3	1.2_5	1.4_5
476.5	5.4	1.3	1.5
488.0	5.5	1.3_5	1.5
496.5	5.5_5	1.4	1.6
501.7	5.6	1.4_5	1.6
514.5	5.7	1.4_5	1.6_5
530.9	5.9_5	1.6_5	1.6_5
568.2	6.3	2.1	1.8
575.0	6.9	2.6	2.4_5
585.0	7.0	3.3	3.0
595.0	7.4_5	3.7	3.5_5
605.0	8.3	4.1_5	4.0
610.0	10.6	4.2	4.3_5
615.0	11.3	4.1_5	4.7
620.0	11.8_5	3.6_5	4.7_5
625.0	11.7	3.5	4.8
630.0	11.2	3.0	5.0
635.0	10.3	2.7_5	4.9_5
647.1	8.5	2.1_5	4.8
676.4	6.4	1.6_5	3.6
752.5	5.2	1.4	2.4

* Corrected for the spectral response of the instrument.

The maximum enhancement to the intensity of a totally symmetric fundamental under r.r. conditions seems to occur in practice for an exciting frequency between that of $\nu_{\text{max.}}$ and $\nu_{\text{max.}} \pm \nu_1'$, where $\nu_{\text{max.}}$ is the frequency of the maximum of the resonant electronic band and ν_1' is the frequency of this fundamental as it occurs in the resonant electronic state (plus sign for the Stokes band, minus sign for the anti-Stokes band). In addition, the maximum enhancement of the first overtone (Stokes) of this fundamental seems in practice to occur at $\nu_{\text{max.}} + 2\nu_1'$. Such is indeed the situation for Wolffram's red.[7]

The behaviour of Reihlen's green seems to be similar in all respects to that of Wolffram's red. Inspection of the values for the maxima of the excitation profiles shows that those for $I(2\nu_1$ Stokes) and $I(\nu_1$ Stokes) differ by 200 cm^{-1} and that those for $I(\nu_1$ Stokes) and $I(\nu_1$ anti-Stokes) differ by 300 cm^{-1}. Considering the likely error in these values (*ca.* ± 75 cm^{-1}), these are close to being equivalent to one and two quanta respectively of ν_1 (ground-state value 179 cm^{-1}). Taking this, and the parallel behaviour of Wolffram's red, into consideration it seems likely that resonance is with a $\mathrm{Pt^{IV}} \longleftarrow \mathrm{Pt^{II}}$ $d_{z^2} \longleftarrow d_{z^2}$ axial transition whose maximum is deduced from the above values to be at 15 950 cm^{-1}. These results also closely parallel those obtained for the $\nu_1(a_1)$ band of the $[\mathrm{FeBr_4}]^-$ ion under resonance conditions.[27]

The band at 15 950 cm^{-1}, identified above from excitation profiles, clearly corresponds to the shoulder at *ca.* 16 000 cm^{-1}, 2 300 cm^{-1} to the low-frequency side of the main mixed-valence band observed at 18 250 cm^{-1} by diffuse-reflectance spectroscopy (Figure 3). Precisely the analogous observation has been made for Wolffram's red;[7] the excitation profile for the ν_1(Cl–Pt$^{\mathrm{IV}}$–Cl) band has a maximum at 17 450 cm^{-1}, 3 550 cm^{-1} lower than the maximum (at 21 000 cm^{-1}) of the more intense mixed-valence transition in this compound. Table 4 summarises comparative data on the two salts under discussion.

A qualitative diagram (assuming a dimeric model for the compound) of the relative *d*-orbital energies in the square-planar and octahedral constituent ions of Wolffram's red and Reihlen's green is given in Figure 5. The relative *d*-orbital energies in the former case have been dictated by the results given by the X_α-scattered wave method[28] and by the recent polarised single-crystal spectra[29] of $[\mathrm{PdCl_4}]^{2-}$ and $[\mathrm{PdBr_4}]^{2-}$. For the octahedral constituent ion, the *d*-orbital energies given are those expected for an axially distorted species in which the *z*-axis ligands have lower ligand-field strengths than the ligands along the other axes. The mixed-

TABLE 4

Comparative data on Wolffram's red and Reihlen's green

	Mixed-valence band maxima (cm^{-1})		Wavenumber difference,	ω_1(X–Pt$^{\mathrm{IV}}$–X)	x_{11}	r(Pt–Pt) [b]
Compound	Main band (A)	Shoulder [a] (B)	(A) − (B)/cm^{-1}	cm^{-1}	cm^{-1}	Å
Wolffram's red	21 000	17 450	3 550	319.5	−2.00	5.39
Reihlen's green	18 250	15 950	2 300	179.6	−0.37	5.86

[a] Located accurately from the Stokes and anti-Stokes excitation profiles of the ν_1(X–Pt$^{\mathrm{IV}}$–X) band. [b] See Figure 1.

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[27] R. J. H. Clark and P. C. Turtle, *J.C.S. Faraday II*, 1976, 1885.

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valence transition indicated in Figure 5, $d_{z^2}(\mathrm{Pt^{IV}}) \longleftarrow d_{z^2}(\mathrm{Pt^{II}})$, would be axially polarised, as found experimentally, and would be at lower energy for Reihlen's green than for Wolffram's red (as also found experimentally) owing to the lower ligand-field strength of bromine than of chlorine which would specifically affect the energy of the d_{z^2} orbital on $\mathrm{Pt^{IV}}$. Moreover, the $d_{z^2}(\mathrm{Pt^{IV}}) \longleftarrow d_{z^2}(\mathrm{Pt^{II}})$ transition will have both spin-allowed and spin-forbidden components, the latter being not only the less intense but the one which occurs, owing to the effects of exchange forces, at the lower energy.

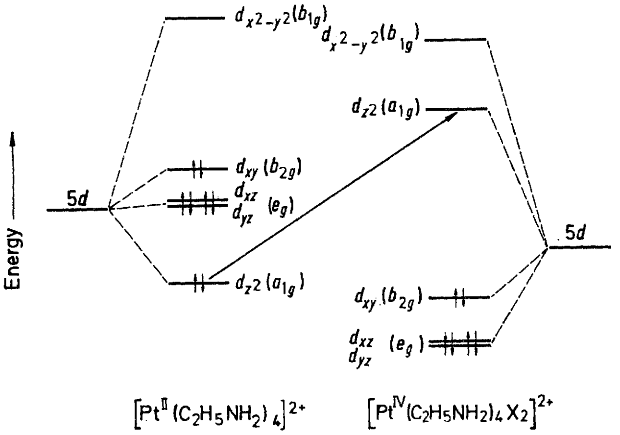

FIGURE 5 Qualitative picture of the relative d-orbital energies in the constituent ions $[\mathrm{Pt^{II}(C_2H_5NH_2)_4}]^{2+}$ and $[\mathrm{Pt^{IV}(C_2H_5NH_2)_4X_2}]^{2+}$ in Wolffram's red and Reihlen's green (X = Cl or Br, *i.e.* a ligand of lower ligand-field strength than ethylamine). The lowest axially polarised intervalence charge-transfer transition is indicated (dimeric mode assumed; more detailed treatments currently under consideration take account not only of the chain nature of the complex but also the effects of the p orbitals on the intervening halogen atoms)

Although it seems tempting, therefore, to associate the two parallel electronic transitions with the spin-allowed and spin-forbidden components of the $d_{z^2}(\mathrm{Pt^{IV}}) \longleftarrow d_{z^2}(\mathrm{Pt^{II}})$ transition (especially as the energy difference between spin-allowed and corresponding spin-forbidden transitions of $\mathrm{K_2[PdBr_4]}$ is *ca.* 3 000 cm^{-1}),[29] there seems to be no obvious reason for the excitation profile of the X–$\mathrm{Pt^{IV}}$–X symmetric stretching mode selectively to parallel the spin-forbidden mode in each compound. It may be, alternatively, that the observed band excitation profiles are a consequence of destructive interference between different terms in the expression for the scattering tensor,[30-33] *cf.* the recent work of Stein *et al.*[33] Further theoretical work on the electronic-spectral properties of chain polymers will be required in order to comprehend the full significance of this result.

R.r. enhancement in the case of resonance with mixed-valence transition is thought to arise[5,6] mainly by way of a single-state mechanism, whereby the vibrational modes whose potential surfaces are displaced in the electronic transition show the most pronounced r.r. effects.[30-32] Assuming this mechanism to be correct, then the r.r. effects observed for Reihlen's green are entirely consistent with resonance with a mixed-valence $d_{z^2} \longleftarrow d_{z^2}$ transition. By far the greatest change in electron density during this transition occurs along the chain axis and correspondingly the r.r. spectrum is completely dominated by bands arising from the axial Br–$\mathrm{Pt^{IV}}$–Br stretching mode.

Conclusion.—The mixed-valence compound Reihlen's green has been found to display an extremely intense r.r. spectrum on excitation within the contour of the mixed-valence bands in the visible region. This has permitted the determination of the spectroscopic constants ω_1 and x_{11} for the axial Br–$\mathrm{Pt^{IV}}$–Br (totally symmetric breathing) fundamental of the compound. The excitation profiles of the fundamental at 179 cm^{-1} and its first overtone have maxima at 16 100 and 16 300 cm^{-1} respectively for Stokes bands while that of the anti-Stokes fundamental at 179 cm^{-1} has a maximum at 15 800 cm^{-1}. Comparison with r.r. results from previously studied systems has enabled the resonant electronic transition at 15 950 cm^{-1} to be identified with a $d_{z^2} \longleftarrow d_{z^2}$ transition. This band has been observed by diffuse-reflectance spectroscopy as a shoulder on the low-frequency side of the band at 18 250 cm^{-1} which is primarily responsible for the colour of the complex. The use of r.r. spectroscopy as an aid in assigning electronic spectra is thus well demonstrated, as is also the excellent spectral resolution of excitation profiles (see Figure 3). The fact that it is an axial vibration which is resonance-enhanced when the compound is irradiated with an exciting line whose frequency falls within the contour of an axially polarised electronic transition seems highly significant and could point the way to a means of making more precise assignments of the electronic spectra of many compounds.

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