Electronic, Infrared, and Resonance-Raman Spectra of Linear-chain Mixed-valence Complexes of Platinum with 1,2-Diaminopropane

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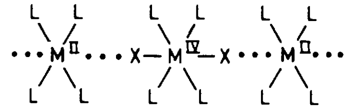
The electronic, infrared, and resonance-Raman spectra of the linear-chain complexes $[Pt(pn)_2][Pt(pn)_2X_2]Y_4$ (X = Cl, Br, or I; Y = ClO_4 and X = Br; Y = BF_4, where pn = 1,2-diaminopropane) are reported. The electronic spectrum of each complex is characterised by an intense, broad, intervalence band ($Pt^{IV} \longleftarrow Pt^{II}$) in the visible region, the wavenumber maximum of which depends on particle size. Irradiation within the intervalence band contour leads to strong intensification of the Raman band attributed to the totally symmetric stretching mode ν_1, $\nu_{sym}(X-Pt^{IV}-X)$ and its overtones. The excitation profiles (e.p.) of ν_1 and its overtones are also sensitive to particle size, and maximise on the low-energy side of the intervalence band maximum in each case. The e.p. maxima and the intervalence band maxima both increase in wavenumber as the particle size is reduced. The wavenumbers of ν_1 and its overtones are independent of particle size, but do depend slightly on the exciting line used to gather data. This dispersion of the ν_1 mode is related to the extent of valence delocalisation along the $\cdots -X-Pt^{IV}-X \cdots Pt^{II} \cdots$ chains.

Linear-chain mixed-valence complexes of platinum and palladium are of considerable interest, owing to their peculiar optical and electrical properties.[1-5] One such family of complexes, that which involves halogen bridges between platinum(II) and platinum(IV) (see below), displays remarkably intense and anisotropic electronic and resonance-Raman spectra, the latter being dominated by long progressions in the symmetric chain-stretching mode, ν_1, $\nu_{sym}(X^-Pt^{IV}-X)$. We have already studied complexes in which both M^{II} and M^{IV} are each either Pt [6-8] or Pd,[9] and recently ones for which M^{II} = Pd while M^{IV} = Pt [10] (X = Cl, Br, or I). These studies have related to linear-chain species of all possible charge types (+2, +1, 0, −1, or −2 per PtL_4 unit), and studies where L = unidentate amine (aliphatic or aromatic),[11-13] L–L = bidentate amine,[14,15] and L–L–L = terdentate amine.[16] For the charged species, a variety of different counter ions have been used *viz.* K^+, Cs^+, $[NH_4]^+$ as cations [13] and Cl^-, Br^-, I^-, $[HSO_4]^-$, $[ClO_4]^-$, $[BF_4]^-$, as well as polymeric copper–halide chains such as $[CuX_4]^{3-}$ and $[Cu_3Br_5]^{2-}$, as anions.[17]



This paper is concerned with a detailed spectroscopic study of the +2 charge-type 1,2-diaminopropane (pn) complexes $[Pt^{II}(pn)_2][Pt^{IV}(pn)_2X_2]Y_4$ (X = Cl, Br, or I, and Y = ClO_4; X = Br, Y = BF_4). *X*-Ray crystallographic studies of the perchlorate salts have demonstrated that the complexes contain linear chains of stacked $[Pt^{II}(pn)_2]^{2+}$ (square planar) and $[Pt^{IV}(pn)_2X_2]^{2+}$ (*trans*-tetragonal bipyramidal) entities.[18-20] The key bond lengths for these complexes are given in Table 1.

Electronic spectral work on some of these complexes has demonstrated the remarkable anisotropy of their specular reflectance as well as unusual size effects on the transmission spectra of their suspensions in carbon tetrachloride.[21-24] Earlier vibrational work has been restricted to room temperature Raman studies only.[21-24] Yet it is now well known that much improved signal-to-noise ratios are obtained from the resonance-Raman spectra of samples held at *ca.* 80 K or lower. The present study thus consists of (*a*) a detailed resonance-Raman (r.R.) study (at *ca.* 80 K) of all the complexes mentioned above; (*b*) the derivation of various spectroscopic constants for the complexes; (*c*) i.r. studies of the complexes; (*d*) excitation profile (e.p.) studies of the resonance-enhanced bands and their overtones, all derived from *ca.* 80 K measurements; (*e*) detailed studies of size effects on the intervalence band maxima, e.p. maxima, and ν_1 band wavenumbers; and (*f*) studies of the ν_1 band dispersion with change of exciting line.

Table 1. Structural data on 1,2-diaminopropane complexes

Complex	$r(Pt^{II}-Pt^{IV})$/Å	$r(Pt^{IV}-X)$/Å	$r(Pt^{II}-X)$/Å	ρ *
$[Pt(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$	5.512	2.29	3.22	0.71
		2.33	3.18	0.73
$[Pt(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$	5.64	—	—	—
$[Pt(pn)_2][Pt(pn)_2I_2][ClO_4]_4$	5.726	2.770	2.956	0.94

* $\rho = r(Pt^{IV}-X)/r(Pt^{II}-X)$. Data from refs. 18—20.

Experimental

Preparation of Complexes.—The complexes $[Pt(pn)_2][Pt(pn)_2X_2]Y_4$ (X = Cl, Br, or I; Y = ClO_4 and X = Br; Y = BF_4) were prepared [18] by cocrystallising equimolar amounts of $[Pt(pn)_2]^{2+}$ and $[Pt(pn)_2X_2]^{2+}$ in dilute perchloric or tetrafluoroboric acid. By slow cooling of concentrated solutions, long needles of the chloro (red), bromo (gold-green), and iodo (gold) complexes were obtained. The crystals were washed with cold water and ethanol, and then dried in air. All the complexes analysed satisfactorily for carbon, hydrogen, nitrogen, and halogen.

Complexes of different particle size, as suspensions in chloroform, were prepared as described previously.[23] For the Raman experiments, the suspensions were filtered through finely ground $K_2[SO_4]$ and shaken mechanically (without grinding) so as to give an even distribution. The suspensions were then dried in air and pressed into discs. The disc colours were identical with those of the original powders.

Instrumental Details.—Electronic spectra of the complexes were recorded at room temperature on a Cary 14 spectrometer

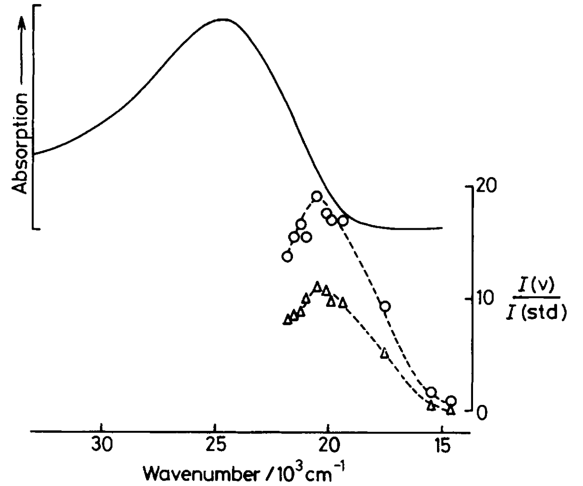


Figure 1. Electronic spectrum ($K[ClO_4]$ disc at 295 K) and excitation profiles (*ca.* 80 K) of the ν_1 (○) and $2\nu_1$ (△) bands of $[Pt(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$

as pressed discs in $K[ClO_4]$ or $Cs[BF_4]$ or as suspensions in chloroform.

Infrared spectra were recorded on Nujol mulls using a Perkin-Elmer 225 spectrometer (4 000—200 cm^{-1}) and a Nicolet 7199 interferometer (400—50 cm^{-1}) (courtesy of Dr. P. L. Goggin, University of Bristol).

Raman spectra were recorded using a Spex 1401 double monochromator with Bausch and Lomb gratings (1 200 line mm^{-1}) and a Spex 14018 (R6) double/triple monochromator with Jobin-Yvon holographic gratings (1 800 line mm^{-1}). Coherent Radiation models CR3 Ar^+ and Kr^+ and models CR12 Ar^+ lasers were used as the exciting sources. Detection was by photon-counting techniques employing cooled RCA C31034 photomultiplier tubes. Spectra at *ca.* 80 K were obtained using a Dewar assembly from pressed discs of the complexes dispersed in $K[ClO_4]$, $K_2[SO_4]$, or $Cs[BF_4]$, in conjunction with a cylindrical lens to line-focus the laser beam and thus to prevent decomposition and heating.

All excitation profile measurements were made at *ca.* 80 K, band intensities being measured with respect to that of the a_1 band of $[ClO_4]^-$ or $[SO_4]^{2-}$ and corrected for the spectral response of the instrument. Band wavenumbers were calibrated by reference to the emission spectrum of neon.

Results and Discussion

Electronic Spectra.—The crystals of the complexes are strongly dichroic and highly reflecting needles. The chloride is orange-red with the electric vector of the incident beam parallel to the needle axis of the crystals but colourless with it perpendicular thereto. The bromide and iodide complexes appear gold by reflection, and appear blue with the electric vector of the incident beam parallel to the needle axis and light yellow with it perpendicular thereto.

When the crystals are ground, they lose their metallic sheen and give highly coloured powders (chloride, yellow; iodide, blue). However, the bromide complexes change colour from blue to violet and eventually to red on further grinding, clearly a particle size effect, such as that responsible for the various possible colours of metallic gold.

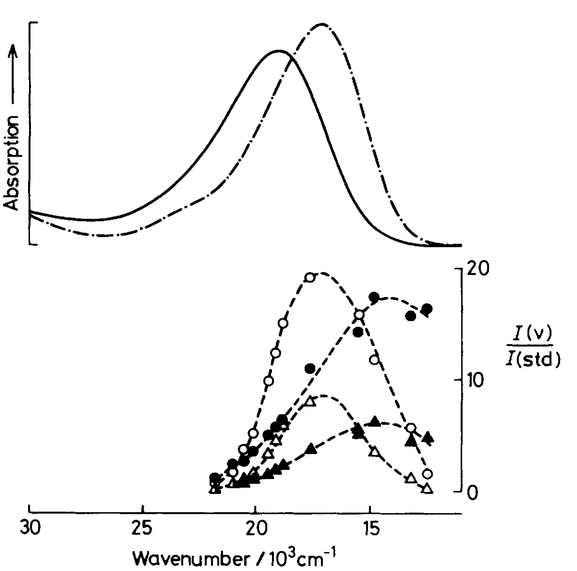


Figure 2. Electronic spectra (——, red; —·—·—, blue) (suspension in $CHCl_3$ at 295 K) and excitation profiles (*ca.* 80 K) of the ν_1 (○, ●) and $2\nu_1$ (△, ▲) bands of $[Pt(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$ [○ and △ refer to red (small) particles and ● and ▲ refer to blue (large) particles]

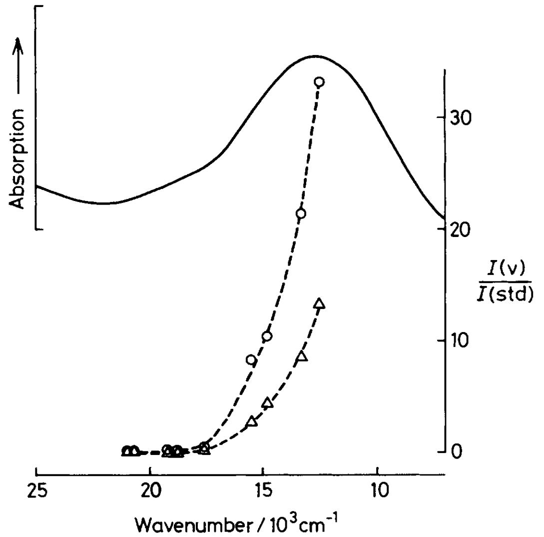


Figure 3. Electronic spectrum ($K[ClO_4]$ disc at 295 K) and excitation profiles (*ca.* 80 K) of the ν_1 (○) and $2\nu_1$ (△) bands of $[Pt(pn)_2][Pt(pn)_2I_2][ClO_4]_4$

The electronic spectra of the complexes have been recorded at room temperature by transmission through pressed discs or suspensions in chloroform. The spectra are shown in Figures 1—3. We observed that, after grinding the complexes for a long period of time, the electronic spectra by transmission through discs were reproducible and had full widths at half maximum larger than those obtained from suspensions. The intervalence band maxima are included in Table 2.

Resonance-Raman Spectra.—In previous work [5-17] we have demonstrated that the r.R. spectra of linear-chain, halogen-bridged platinum complexes are dominated by long overtone progressions, $v_1\nu_1$, where ν_1 is the totally symmetric chain stretching mode, $\nu_{sym}(X-Pt^{IV}-X)$. By contrast, the i.r. spectra of such complexes (Table 3) are essentially the superposition of the spectra of the constituent species. The same observations were made in the present study.

Table 2. Summary of data on 1,2-diaminopropane complexes

Complex	Crystal [a]	Powder [b]	Mixed-valence max./cm^{-1}	Excitation profile (ν_1) max./cm^{-1}	ω_1/cm^{-1}	x_{11}/cm^{-1}	$\frac{I(2\nu_1)}{I(\nu_1)}$ [c]	Progression [c] (ν_1) at *ca.* 80 K	λ_0 [d]/nm
$[Pt(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$	Red	Orange-yellow	25 000 [e]	20 500	315.9 ±0.5	−0.85 ±0.05	0.86	$16\nu_1$	457.9
$[Pt(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$	Gold-green	Blue	16 950 [f]	14 500	174.8 ±0.3	−0.27 ±0.03	0.67	$11\nu_1$	568.2
		Red	19 600 [g,f]	17 300	174.5 ±0.3	−0.25 ±0.03	0.64	$9\nu_1$	
$[Pt(pn)_2][Pt(pn)_2Br_2][BF_4]_4$	Gold-green	Purple	20 500 [e]	—	179.4 ±0.5	−0.33 ±0.03	0.56	$7\nu_1$	568.2
$[Pt(pn)_2][Pt(pn)_2I_2][ClO_4]_4$	Gold	Blue	12 800 [e]	⩽12 500	121.4 ±0.5	−0.56 ±0.05	0.40	$7\nu_1$	752.5

[a] By reflection. [b] By transmission. [c] Maximum observed value. [d] Excitation line for which longest progression in ν_1 is observed. [e] By transmission through $K[ClO_4]$ or $Cs[BF_4]$ disc. [f] By transmission through suspension in chloroform. [g] As measured for a $K[ClO_4]$ disc.

Table 3. Wavenumbers (cm^{-1}) of bands observed in the i.r. spectra of the complexes $[Pt(pn)_2][Pt(pn)_2X_2]Y_4$

X = Cl Y = ClO_4	X = Br Y = ClO_4	X = Br Y = BF_4	X = I Y = ClO_4	Assignment
935w	936w		930w	$\nu_1(ClO_4)$
835w	834w	835w	826w	
806w	804m	801m	808m	
		771m		$\nu_1(BF_4)$
	722m	720m	724w	
628s	628s	628s	626s	
618s	617s	618s	616s	
	560w, br	575w	560m, br	ν(Pt–N)
		533s		$\nu_4(BF_4)$
		522s		
470s	472s	473s	468m	
455m	454m, br	456m, br	450m	
448w	448w			
429vw	427vw			
391w, br	387w, br		385w, br	
		328m		
356vs	255vs	254s	185s	$\nu_{asym}(X\text{–}Pt^{IV}\text{–}X)$
303m		302m	304m	
287m	299s, br	291m	291s	
255s	259vs	279m	266s	δ(N–Pt–N)
		235s		
162ms		149vs	138s	
122ms	114s	112s	108s	
99ms			91s	

The r.R. spectrum of the chloro-complex depends strongly on the excitation wavelength, temperature, and particle size. The strongest and most detailed spectrum is obtained with the blue line (457.9 nm) at *ca.* 80 K. The spectrum (Figure 4) is dominated by the long overtone progression $v_1\nu_1$ (up to $v_1 = 16$) and by combination tones $v_1\nu_1 + \delta$(N–Pt–N) (up to $v_1 = 3$) and $v_1\nu_1 + \nu_2$ (up to $v_1 = 1$), where ν_2 is the asymmetric chain-stretching mode, $\nu_{asym}(Cl\text{–}Pt^{IV}\text{–}Cl)$. The other bands observed (at 585 and 171.5 cm^{-1}) are attributable to the symmetric stretching mode ν(Pt–N) and, tentatively, to the $\delta(Cl\text{–}Pt^{IV}\text{–}Cl)$ mode. The intensities of the overtones relative to that of the ν_1 mode depended on particle size and could not be reproduced to better than *ca.* ±10% on different occasions. The wavenumbers of the bands observed in the r.R. spectrum and their assignments are listed in Table 4.

In the case of the complex $[Pt(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$, two samples of different particle size have been studied (see Experimental section). The small and large particles (approximately spheres, diameter *ca.* 150 Å and needles *ca.* 900 Å long)[23] are here referred to by their colours, red and blue, respectively. The r.R. spectra of the two samples are similar to one another except for the relative intensities of the overtones and for the fact that some additional features are discernible in the spectrum of the red sample. This spectrum consists of the $v_1\nu_1$ progression (up to $v_1 = 9$), combination tones $v_1\nu_1 + \delta$(N–Pt–N) (up to $v_1 = 2$), $v_1\nu_1 + \nu_2$ (up to $v_1 = 1$), where $\nu_2 = \nu_{asym}(Br\text{–}Pt^{IV}\text{–}Br)$, and $v_1\nu_1 + \delta$(H–C–H) (up to $v_1 = 1$). One other mode at *ca.* 150 cm^{-1} (referred to as ν_x) which is unassigned, forms a progression up to the second harmonic and combination tones $v_1\nu_1 + v_x\nu_x$, up to $v_1 = 2$ and $v_x = 2$. The spectrum of the blue sample consists of the $v_1\nu_1$ progression (up to $v_1 = 11$) and a combination tone $v_1\nu_1 + \nu_x$. The wavenumbers and assignments of bands observed are given in Table 5 and a typical spectrum is shown in Figure 5. The spectrum of the tetrafluoroborate salt (Table 6) is similar to that of the perchlorate salt.

The iodo-complex shows the same characteristics as those

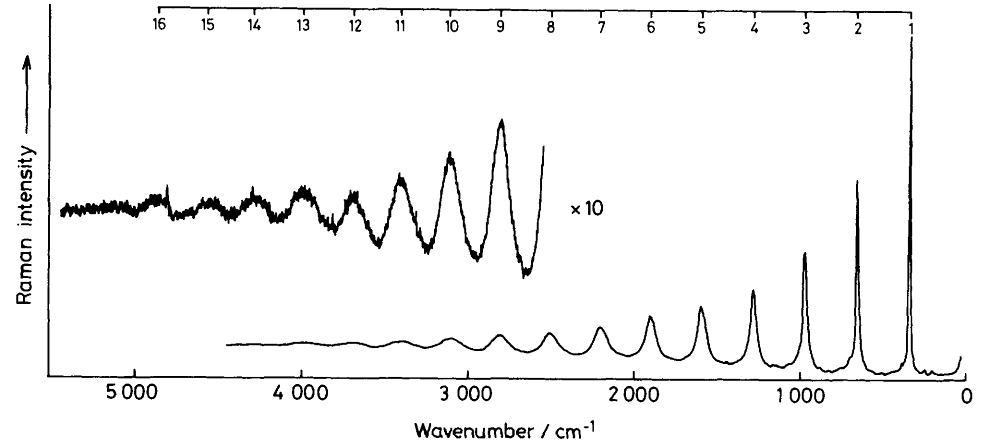


Figure 4. Resonance-Raman spectrum of $[Pt(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$ as a $K[ClO_4]$ disc at *ca.* 80 K with 457.9 nm excitation (spectral slit width *ca.* 2.5 cm^{-1}). The upper scale represents the vibrational quantum numbers for the ν_1 mode

Table 4. Wavenumbers * and assignments of bands observed in the r.R. spectrum of $[Pt(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$

$\tilde{\nu}$/cm^{-1}	Assignment	$\tilde{\nu}$/cm^{-1}	Assignment
171.5	$\delta(Cl-Pt^{IV}-Cl)$?	1 555	$5\nu_1$
216.1	$\delta(N-Pt-N)$	1 859	$6\nu_1$
295		2 160	$7\nu_1$
313.2	ν_1, $\nu_{sym}(Cl-Pt^{IV}-Cl)$	2 462	$8\nu_1$
357.2	ν_2, $\nu_{asym}(Cl-Pt^{IV}-Cl)$	2 764	$9\nu_1$
530	$\nu_1 + \delta(N-Pt-N)$	3 066	$10\nu_1$
585	$\nu(Pt-N)$	3 359	$11\nu_1$
627.5	$2\nu_1$	3 650	$12\nu_1$
672	$\nu_1 + \nu_2$	3 950	$13\nu_1$
844	$2\nu_1 + \delta(N-Pt-N)$	4 240	$14\nu_1$
937.7	$3\nu_1$	4 530	$15\nu_1$
1 155	$3\nu_1 + \delta(N-Pt-N)$	4 820	$16\nu_1$
1 246	$4\nu_1$		

* Obtained from a $K[ClO_4]$ disc with 457.9 nm excitation at *ca.* 80 K.

Table 5. Wavenumbers [a] and assignments of bands observed in the r.R. spectrum of $[Pt(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$

$\tilde{\nu}$ [b]/cm^{-1}		$\tilde{\nu}$ [c]/cm^{-1}		Assignment
149.9 [d]	149.8 [e]	152.0 [d]	149.4 [e]	
173.5	172.3	173.9	171.9	ν_1, $\nu_{sym}(Br-Pt^{IV}-Br)$
210.5	212.2	211.0	209.5	$\delta(N-Pt-N)$
250.1	251.0			ν_2, $\nu_{asym}(Br-Pt^{IV}-Br)$
299.9	299.5			2 × 149.9
325.8	322.8	327	324.5	ν_1 + 149.9
347.6	344.5	348.1	343.7	$2\nu_1$
386.6	385	387.2		$\nu_1 + \delta(N-Pt-N)$
425				$\nu_1 + \nu_2$
472.8	472.5			ν_1 + 2 × 149.9
500.6	497.1			$2\nu_1$ + 149.9
520.4	516.3	520.7	514.6	$3\nu_1$
645	645			$2\nu_1$ + 2 × 149.9
693.0	686.2	693.3	684.2	$4\nu_1$
864.6	856.2	865.7	852.3	$5\nu_1$
1 036.5	1 021.6	1 037.5	1 020	$6\nu_1$
1 206	1 192	1 209.3	1 186	$7\nu_1$
1 263				$\delta(H-C-H)$
1 381	1 360	1 378	1 358	$8\nu_1$
1 440				$\nu_1 + \delta(H-C-H)$
1 550	1 525	1 550	1 525	$9\nu_1$
		1 720	1 690	$10\nu_1$
		1 890	1 850	$11\nu_1$

[a] Obtained from a $K_2[SO_4]$ disc at *ca.* 80 K. [b] Red sample. [c] Blue sample. [d] λ_0 = 568.2 nm. [e] λ_0 = 647.1 nm.

of the chloro- and bromo-complexes. The r.R. spectrum obtained with 752.5 nm at *ca.* 80 K shows a $v_1\nu_1$ progression consisting of seven harmonics (Figure 6); the wavenumbers and assignments of the bands observed in this spectrum are given in Table 7.

Although the wavenumbers of the ν_1 mode and of its overtones are independent of particle size (Table 5), they do depend slightly on the excitation wavelength, λ_0. The wavenumbers of the equatorial modes such as $\delta(N-Pt-N)$ on the other hand, are, as expected, independent of both particle size and excitation wavelength. The dispersion of the ν_1 band of each complex is shown in Figure 7, from which it is evident that the effect increases in the order chloride < bromide < iodide. Clearly, as argued elsewhere for other linear-chain complexes,[25] the dispersion depends on the extent of valence-electron delocalisation along the chain direction and is related to the semi-conductor properties of the complexes. The results bear some similarity to those observed for some lattice modes of the semi-conductors [26] Cu_2O, CdS, and CdSe.

The observation of long overtone progressions allows the determination, for each complex, of the harmonic wavenumber, ω_1 (approximately) and of the anharmonicity constant, x_{11}. The results of the present analyses are given in Table 2. The mode displaying the overtone progression behaves as a near harmonic oscillator in each case with an average x_{11}/ω_1 value of 0.0026. Due to the ν_1 band dispersion with ν_0, the ω_1 values are different for different ν_0, but the x_{11} values are independent thereof.

Excitation Profiles.—The excitation profiles (e.p.) of the ν_1 and $2\nu_1$ bands of the three perchlorate salts have been measured at *ca.* 80 K. The chloro-complex shows an e.p. maximum for both ν_1 and $2\nu_1$ at 20 500 cm^{-1}, some 4 500 cm^{-1} on the low-energy side of the intervalence band maximum (Figure 1). The iodo-complex, on the other hand, does not show any maximum in its e.p. and still shows increasing intensity for the ν_1 and $2\nu_1$ bands with the lowest energy exciting line available (799.3 nm ≡ 12 510 cm^{-1}, Figure 3).

The excitation profiles of the two bromo-samples (Figure 2) show particle-size effects. The red sample has a maximum in its e.p. at 17 300 cm^{-1} and the blue sample at 14 500 cm^{-1}.

Table 6. Wavenumbers * and assignments of bands observed in the r.R. spectrum of $[Pt(pn)_2][Pt(pn)_2Br_2][BF_4]_4$

$\tilde{\nu}$/cm^{-1}	Assignment
156.9	
178.8	ν_1, ν_{sym}(Br–Pt^{IV}–Br)
213.4	δ(N–Pt–N)
248.9	ν_2, ν_{asym}(Br–Pt^{IV}–Br)
314.2	2 × 156.9
331.6	ν_1 + 156.9
357.1	$2\nu_1$
395.7	ν_1 + δ(N–Pt–N)
426.5	$\nu_1 + \nu_2$
494.1	ν_1 + 2 × 156.9
534.7	$3\nu_1$
575.9	$2\nu_1$ + δ(N–Pt–N)
710.3	$4\nu_1$
757.2	$3\nu_1$ + δ(N–Pt–N)
887	$5\nu_1$
1 064	$6\nu_1$
1 240	$7\nu_1$

* Obtained as a $Cs[BF_4]$ disc with 568.2 nm excitation at *ca.* 80 K.

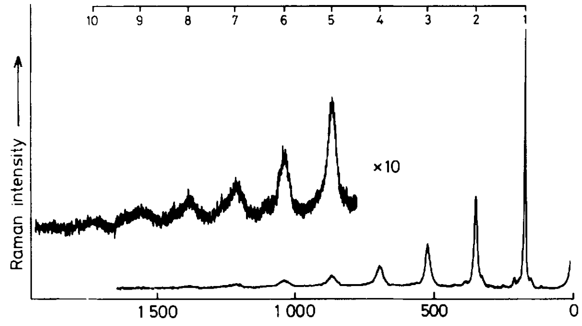


Figure 5. Resonance-Raman spectrum of $[Pt(pn)_2][Pt(pn)_2Br_2]$-$[ClO_4]_4$ as $K[ClO_4]$ disc at *ca.* 80 K with 568.2 nm excitation (spectral slit width *ca.* 1.5 cm^{-1}). The upper scale represents the vibrational quantum numbers for the ν_1 mode

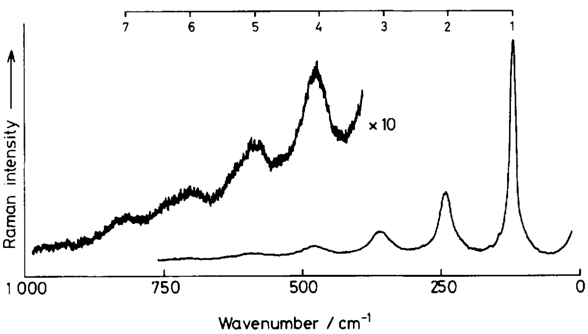


Figure 6. Resonance-Raman spectrum of $[Pt(pn)_2][Pt(pn)_2I_2]$-$[ClO_4]_4$ as a $K[ClO_4]$ disc at *ca.* 80 K with 752.5 nm excitation (spectral slit width *ca.* 2.5 cm^{-1}). The upper scale represents the vibrational quantum numbers for the ν_1 mode

For each sample, the maximum in the e.p. for both ν_1 and $2\nu_1$ is 2 000—3 000 cm^{-1} lower than the intervalence band maximum, a behaviour which is typical of that of one-dimensional semi-conductors.[1-4]

Table 7. Wavenumbers * and assignments of bands observed in the r.R. spectrum of $[Pt(pn)_2][Pt(pn)_2I_2][ClO_4]_4$

$\tilde{\nu}$/cm^{-1}	Assignment
119.9	ν_1, ν_{sym}(I–Pt^{IV}–I)
143.3	
160.6	
187.1	ν_2, ν_{asym}(I–Pt^{IV}–I)
240.1	$2\nu_1$
358.2	$3\nu_1$
475.1	$4\nu_1$
587.1	$5\nu_1$
703	$6\nu_1$
820	$7\nu_1$

* Obtained as a $K[ClO_4]$ disc with 752.5 nm excitation at *ca.* 80 K.

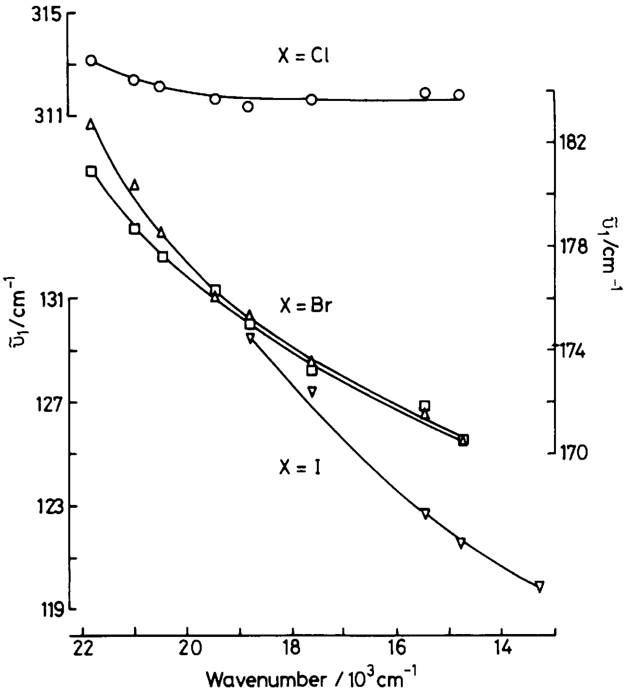


Figure 7. Plot of ν_1 against ν_0 at *ca.* 80 K for the complexes [Pt-$(pn)_2][Pt(pn)_2X_2][ClO_4]_4$: X = Cl (○), X = Br (red particles) (△), X = Br (blue particles) (□), and X = I (▽)

The shape and wavenumber maximum of an electronic absorption band are determined by both the real (ε′) as well as the imaginary (ε″) part of the dielectric constant of a complex, the maximum in ε″ for a strongly absorbing insoluble complex being best determined by a Kramers–Kronig analysis of the specular reflectance spectrum.[21,24] Such analyses for one-dimensional semi-conductors have revealed that the maximum in ε″ lies at lower energies than the maximum in the diffuse reflectance spectrum, and that it coincides with the e.p. maximum of the resonance-enhanced bands (consistent with the fact that this quantity is also determined by ε″). Indeed, it may be argued that e.p.$_{max.}$ are the most readily determined measures of electronic transition energies in such strongly absorbing one-dimensional materials.

Conclusions

The optical and resonance-Raman spectra of the set of linear-chain mixed-valence complexes studied are striking and typical of those of other structurally related amine derivatives of platinum and palladium. Both the unusual size effects on the electronic band maxima and on the excitation profile maxima of the complex $[Pt(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$, as well as the ν_1 band dispersion with ν_0 for all of the complexes (but especially for the bromides and iodides), are indicative of the one-dimensional semi-conductor nature of this intriguing class of complex.

Acknowledgements

The authors thank the S.E.R.C. and the University of London for financial support, and Dr. B. Stewart and Mr. P. Rabin for some initial experimental work.

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Received 2nd September 1982; *Paper* 2/1513