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Electronic and Vibrational Studies of Mixed-Valence Complexes. The Resonace Raman Spectra of the Bromine-bridged Platinum Complexes $[Pt(LL)_2][Pt(LL)_2Br_2]Br_4$, where L L = 1,2-Diaminoethane, -propane, -butane, and -pentane

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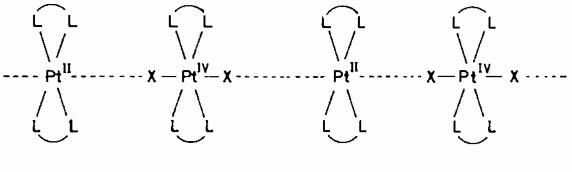
Electronic, infrared and resonance Raman (RR) spectra of the mixed-valence, bromine-bridged platinum complexes $[Pt(LL)_2][Pt(LL)_2Br_2]Br_4$, where LL = 1,2-diaminoethane, -propane, -butane, or -pentane, have been recorded. The electronic spectra are characterised by strong, broad bands in the visible region, attributable to $Pt^{II} \rightarrow Pt^{IV}$ charge transfer. The RR spectra, obtained on resonance with this band, display long overtone progressions, $v_1\nu_1$, in the totally symmetric chain mode, $\nu(Br–Pt^{IV}–Br)$, reaching v_1 = 11, 7, 8, an d8 for the 1,2-diaminoethane, -propane, -butane, and -pentane complexes, respectively. The harmonic wavenumber, ω_1, and the anharmonicity, x_{11}, are both independent of the mass of the amine, the average values being $\omega_1 = 171.2 \pm 0.6$ cm^{-1}, and $x_{11} = -0.35 \pm 0.09$ cm^{-1}; this result demonstrates the highly one-dimensional nature of the complexes. The excitation profiles of the ν_1, $2\nu_1$ and $3\nu_1$ bands all maximise on the low wavenumber side of the intervalence transition maximum.

Introduction

The chemistry and spectroscopy of mixed-valence species have been the subject of many studies in recent years [1, 2]. In particular, resonance Raman (RR), infrared and electronic spectral studies of one-dimensional linear-chain complexes of platinum have attracted considerable interest [3]. These complexes, which consist of stacks of $[Pt^{II}(LL)_2]^{2+}$ and $[Pt^{IV}(LL)_2X_2]^{2+}$ entities, *viz.*



form halogen (X)-bridged linear chains, and are intensely coloured as a consequence of the axially polarized $Pt^{II} \rightarrow Pt^{IV}$ intervalence band lying typically in the 450–750 nm region. Irradiation within the contour of this band leads to the observation of progressions in the totally symmetric chain mode, $\nu(X–Pt^{IV}–X)$ [3–6]. Both the intervalence band, as well as the ν_1 band have been established to decrease in wavenumber (for any given halogen) with decrease in the $Pt^{II}\cdots Pt^{IV}$ chain separation [7]. The present study is concerned with elucidating the role of the equatorially substituted amine ligands (in particular, their mass) in determining the electronic and vibrational properties of a closely related set of bromine-bridged complexes of this sort, *viz.* $[Pt(LL)_2][Pt(LL)_2Br_2]Br_4$, where LL = 1,2-diaminoethane (en), 1,2-diaminopropane (pn), 1,2-diaminobutane (bn) and 1,2-diaminopentane (ptn). The only one of these complexes whose structure has been determined by X-ray diffraction techniques is the pn complex, which apparently has a slightly bent chain with ∠Pt–Br–Pt = 173.7° [8].

Experimental

The complexes were prepared by standard literature methods [2].

The electronic spectra of the complexes, dispersed in KBr pressed discs, were recorded using a Cary 14 spectrometer. The infrared spectra of the complexes, as CsBr and polythene discs, were recorded on a Perkin-Elmer 225 spectrometer and on a Nicolet 7199 interferometer (to 50 cm^{-1}).

Raman spectra were recorded using a Spex 1401 double monochromator, equipped with Bausch and Lomb gratings (1200 line mm^{-1}). Detection was by photon counting, employing an RCA C31034 photomultiplier. Radiation was provided by Coherent Ltd. models 52 Ar^+ and Kr^+ lasers. All spectra were recorded at ~80 K and in conjunction with a cylindrical lens to line-focus the excitation beam; thermal

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TABLE I. Summary of data on $[Pt(LL)_2][Pt(LL)_2Br_2]Br_4$ Complexes.

L L	Colour		Mixed-valence[b] Max/cm^{-1}	Excitation Profile Max/cm^{-1}	ω_1/cm^{-1}	x_{11}/cm^{-1}	Progression (ν_1) at *ca.* 80 K	I($2\nu_1$)/I(ν_1) max.	(Pt^{II}–Pt^{IV})/Å
	Crystal[a]	Powder[b]							
1,2-diaminoethane	Green Gold	Mauve	18000	13500 ~16500[c]	170.7 ± 0.3	0.26 ± 0.03	11ν_1	0.62	5.338
1,2-diaminopropane	Gold	Blue	14400	≤12500	171.2 ± 0.3	0.42 ± 0.04	7ν_1	0.55	–
1,2-diaminobutane	Gold	Blue	14600	13700	171.8 ± 0.3	0.36 ± 0.02	8ν_1	0.63	–
1,2-diaminopentane	–	Light Blue	16400	13300 ~16500[c]	171.2 ± 0.3	0.36 ± 0.03	8ν_1	0.69	–

[a] By reflection. [b] By transmission. [c] Shoulder.

TABLE II. Wavenumbers/cm^{-1}, FWHM, Relative Intensities and Assignments of Bands Observed in the Resonance Raman Spectrum of $[Pt(en)_2][Pt(en)_2Br_2]Br_4$.

$\tilde{\nu}$/cm^{-1} [a]	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	I(ν)/I(ν_1)	Assignment
88.2			
169.6	8.7	1.00	ν_1, ν_s(Br–Pt^{IV}–Br)
204.1			
231.1			ν_2, ν_{as} (Br–Pt^{IV}–Br)
339.5	15.8	0.62	$2\nu_1$
371.3			ν_1 + 204
400.2			$\nu_1 + \nu_2$
508.8	23	0.39	$3\nu_1$
538.9			$2\nu_1 + \nu_2$
676.6	32	0.28	$4\nu_1$
743.5			$3\nu_1 + \nu_2$
845.5	35	0.17	$5\nu_1$
1012.5	39	0.13	$6\nu_1$
1180	43	0.08	$7\nu_1$
1345	51	0.06	$8\nu_1$
1510	57	0.05	$9\nu_1$
1666	>60	0.04	$10\nu_1$
1830	>60	~0.03	$11\nu_1$

[a] Obtained as a KBr disc with 647.1 nm excitation at *ca.* 80 K.

TABLE III. Wavenumbers/cm^{-1}, FWHM, Relative Intensities and Assignments of Bands Observed in the Resonance Raman Spectrum of $[Pt(pn)_2][Pt(pn)_2Br_2]Br_4$.

$\tilde{\nu}$/cm^{-1} [a]	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	I(ν)/I(ν_1)	Assignment
94.1			
150.4			
169.9	15.0	1.00	ν_1, ν_s(Br–Pt^{IV}–Br)
209.6			
244.3			ν_2, ν_{as}(Br–Pt^{IV}–Br)
339.5	27.5	0.55	$2\nu_1$
381.7			ν_1 + 209.6
418.4			$\nu_1 + \nu_2$
509.2	39	0.28	$3\nu_1$
585			$2\nu_1 + \nu_2$
677.2	51	0.16	$4\nu_1$
751			$3\nu_1 + \nu_2$
841.8	59	0.09	$5\nu_1$
920			$4\nu_1 + \nu_2$
1004	67	0.05	$6\nu_1$
1170	>80	<0.03	$7\nu_1$

[a] Obtained as a KBr disc with 647.1 nm excitation at *ca.* 80 K.

decomposition of the sample was thus avoided. Spectral calibration was made with reference to the emission lines of neon. Band intensities were measured with reference to that of the $\nu_1(a_1)$ band of $[SO_4]^{2-}$, and corrected for the spectral response of the instrument.

Results and Discussion

Electronic Spectra

Large crystals of the complexes appear metallic with gold reflection and are very dichroic, ranging from mauve to blue with the electric vector of the incident beam parallel to chain axis and almost colourless with it perpendicular to this axis. The crystals lose their metallic sheen on being ground. The colours of the crystals and of their powders are listed in Table I. The electronic transmission spectra of the complexes all show a broad band in the 18000–14400 cm^{-1} region, assigned to the $Pt^{II} \rightarrow Pt^{IV}$ intervalence transition.

Resonance Raman Spectra

The resonance Raman spectra of the four complexes are shown in Figs. 1–4. The wavenumbers, full width at half maximum, ($\Delta\tilde{\nu}_{1/2}$), relative band intensities and assignments of bands observed are listed in Tables II–V. The RR spectra are characterised by long overtone progressions in the axial symmetric stretching mode (ν_1) of the Pt^{IV} moiety, $\nu(Br-Pt^{IV}-Br)$. The progressions were observed to reach v_1 = 11 (cn), v_1 = 7 (pn), v_1 = 8 (bn), and v_1 = 8 (ptn). A second progression of the sort $v_1\nu_1 + \nu_2$ was also observed in the case of the en, pn, and bn complexes, based upon ν_2 values of 231, 244, and 247 cm^{-1} respectively. As is common for RR spectra of this sort, the $\Delta\tilde{\nu}_{1/2}$ values increase and the intensities decrease monotonically with increase in vibrational quantum number.

The observation of a large number of overtones makes it possible by standard procedures to calculate approximate values for the harmonic wavenumber (ω_1) and accurate values for the anharmonicity constant (x_{11}) in each case; the results are given in Table I. Both the ω_1 and x_{11} values are found to be independent of the mass of the amine, the average values being ω_1 = 171.2 ± 0.6 cm^{-1} and x_{11} = –0.35 ± 0.09 cm^{-1}. This result clearly shows that the amines, mainly since they lie in the planes normal to the chain axis, are effectively decoupled from the chain stretching mode, ν_1.

Infrared Spectra and Vibrational Analysis

The wavenumbers of the bands observed in the infrared spectra of the complexes are listed in Table VI together with band assignments made on the basis of published results on related complexes [9 10]. In the case of the en, pn and bn complexes, the totally symmetric mode ν_1, $\nu(Br-Pt^{IV}-Br)$, gives rise to an infrared band, (strong, shoulder, and shoulder, respectively), thus indicating that these complexes behave as though they do not have a centre of symmetry; however, the rule of mutual exclusion applies in the case of the ptn complex since no band attributable to ν_1 appears in this case. Thus, the complexes appear to approach the line group D_{2h} as the size of the ligand increases. The ν_2 mode, the asymmetric $Br-Pt^{IV}-Br$ stretching mode of the linear chain, is clearly observed to give rise to a very strong infrared band in the 241–252

TABLE IV. Wavenumbers/cm^{-1}, FWHM, Relative Intensities and Assignments of Bands Observed in the Resonance Raman Spectrum of $[Pt(bn)_2][Pt(bn)_2Br_2]Br_4$.

$\tilde{\nu}$/cm^{-1} a	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	$I(\nu)/I(\nu_1)$	Assignment
95			
170.5	15.0	1.00	$\nu_1, \nu_s(Br-Pt^{IV}-Br)$
247.0			$\nu_2, \nu_{as}(Br-Pt^{IV}-Br)$
341.6	29	0.63	$2\nu_1$
417.5			$\nu_1 + \nu_2$
521.0	40	0.35	$3\nu_1$
588.4			$2\nu_1 + \nu_2$
681.3	47	0.16	$4\nu_1$
758			$3\nu_1 + \nu_2$
849.2	55	0.10	$5\nu_1$
1014	63	0.05	$6\nu_1$
1179	>70	~0.03	$7\nu_1$
1337	>70	<0.03	$8\nu_1$

^{a}Obtained as a KBr disc with 647.1 nm excitation at *ca.* 80 K.

TABLE V. Wavenumbers/cm^{-1}, FWHM, Relative Intensities and Assignments of Bands Observed in the Resonance Raman Spectrum of $[Pt(ptn)_2][Pt(ptn)_2Br_2]Br_4$.

$\tilde{\nu}$/cm^{-1} a	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	Assignment
95			
170.1	8.7	1.00	$\nu_1, \nu_s(Br-Pt^{IV}-Br)$
340.9	18.1	0.69	$2\nu_1$
509.7	26	0.44	$3\nu_1$
678.1	35	0.33	$4\nu_1$
847.4	43	0.23	$5\nu_1$
1014.5	47	0.13	$6\nu_1$
1176	55	0.07	$7\nu_1$
1337	>60	~0.03	$8\nu_1$

^{a}Obtained as a KBr disc with 676.4 nm excitation at *ca.* 80 K.

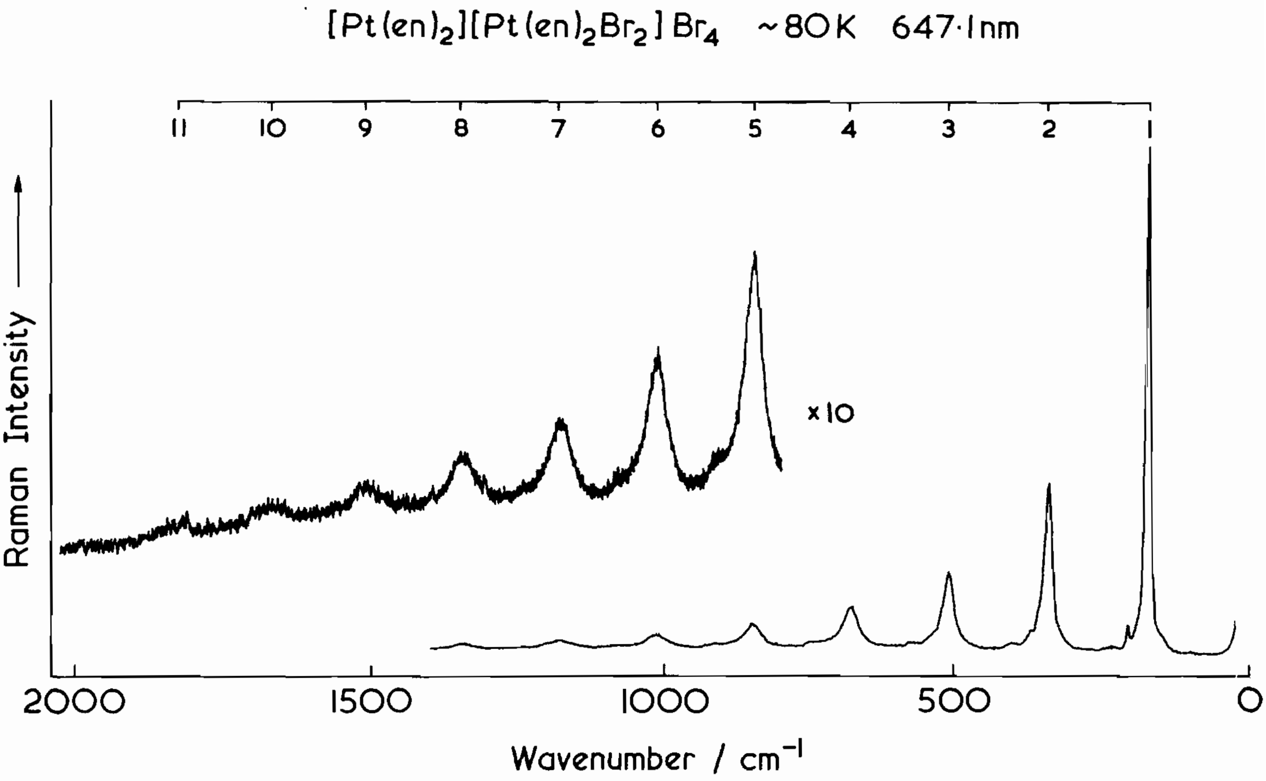

Fig. 1. RR Spectrum of [Pt(en)$_2$] [Pt(en)$_2$Br$_2$] Br$_4$ at ~80 K λ_0 = 647.1 nm. Slit ≅ 1.5 cm^{-1}.

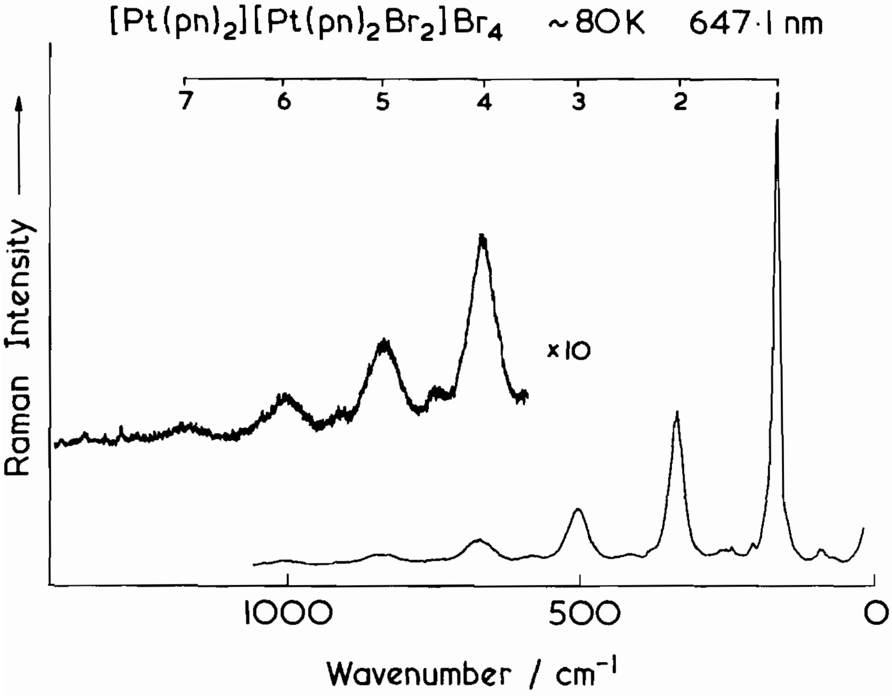

Fig. 2. RR Spectrum of [Pt(pn)$_2$] [Pt(pn)$_2$Br$_2$] Br$_4$ at ~80 K λ_0 = 647.1 nm. Slit ≅ 1 cm^{-1}.

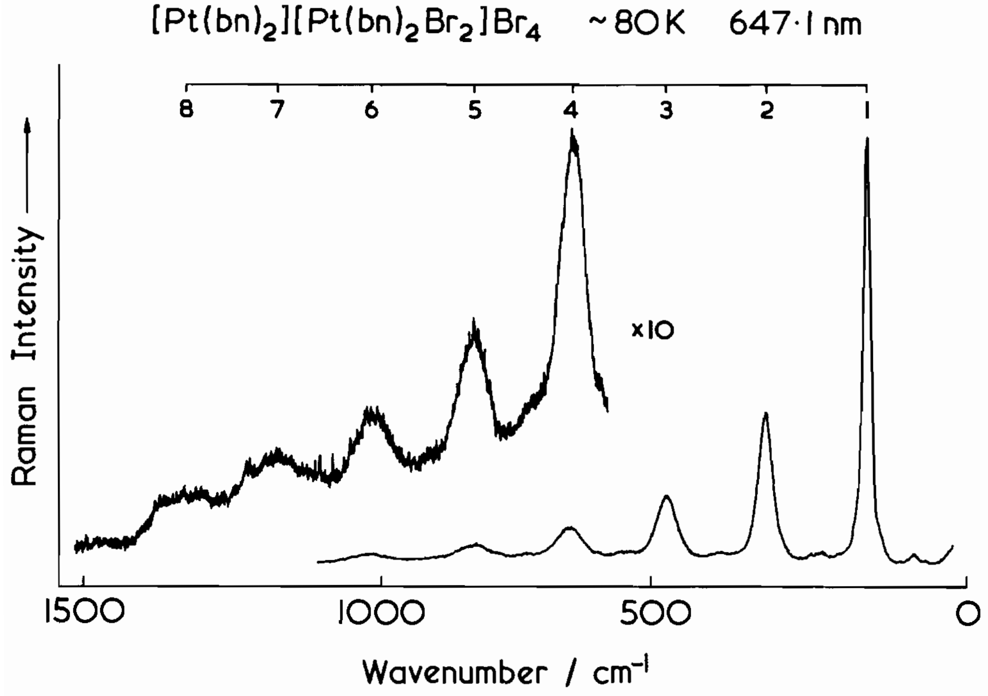

Fig. 3. RR Spectrum of $[Pt(bn)_2][Pt(bn)_2Br_2]Br_4$ at ~80 K λ_0 = 647.1 nm. Slit ≅ 1 cm^{-1}.

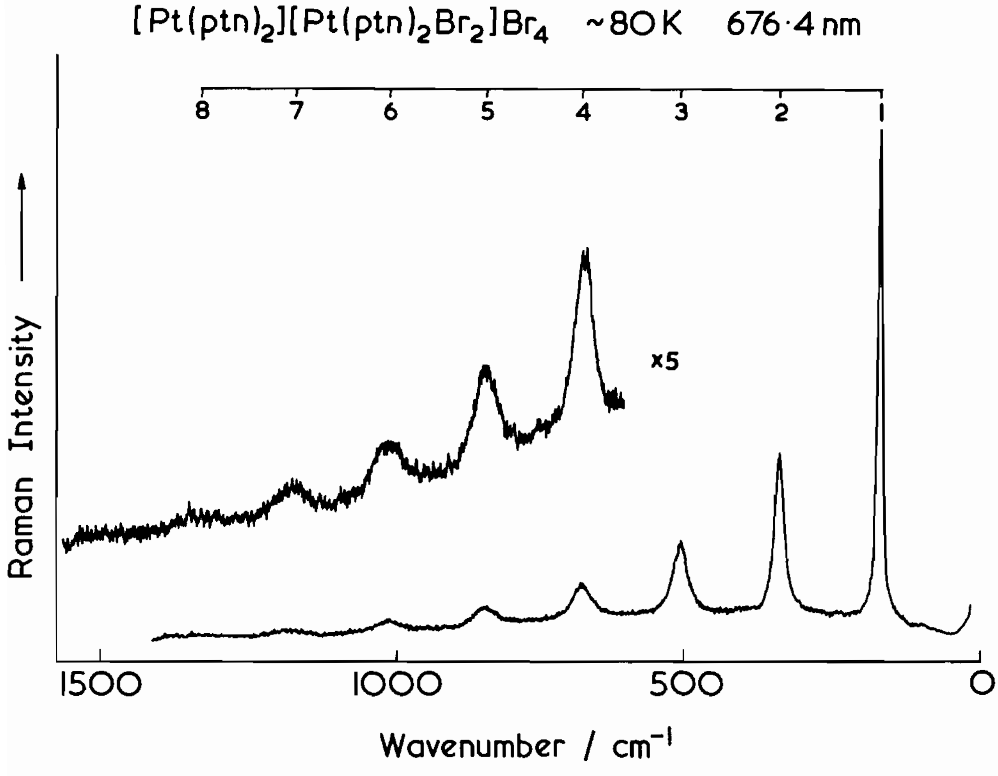

Fig. 4. RR Spectrum of $[Pt(ptn)_2][Pt(ptn)_2Br_2]Br_4$ at ~80 K λ_0 = 676.4 nm. Slit ≅ 1 cm^{-1}.

TABLE VI. Wavenumbers/cm^{-1} and Assignments of Bands Observed in the Infrared Spectra of the Complexes.

en	*pn*	*bn*	*ptn*	
	102 sh	93 sh	93 s	
127 vs	127 vs	120 vs		δ(N–Pt–Br)
	140 s			
	146 sh		152 s	
167 m	170 sh	168 sh		ν_1, ν_s(Br–Pt^{IV}–Br)
182 sh				
241 s	245 s	246 s	252 vs	ν_2, ν_{as}(Br–Pt^{IV}–Br)
249 sh				
277 s	277 m	266 m,br		δ(N–Pt–N)
		286		
312	306	315 m	316 sh	
	316 m,br			ring skeletal
	325			
343 m			349 m	
360 s				
373 w		392 m	387 s	
			393	
472 s	468 m	470 m	450 m	δ(N C C N)
		506 m		
540 s				
560 m,br	560 br	560 br	552 m	ν(Pt–N)
584 m				
	634 m			
804 m		772 m	740 m	ρ(NH$_2$)

cm^{-1} range (with very weak counterparts in the Raman spectra). The asymmetric PtN stretching mode occurs in the 552–560 cm^{-1} range for all four complexes.

If one treats complexes such as these as one-dimensional, infinitely long chains

$$---X\text{–}Pt^{IV}\text{–}X---Pt^{II}---X\text{–}Pt^{IV}\text{–}X---$$

|← unit cell length →|

held together by two force constants, f(Pt^{IV}–X) and f(Pt$^{II}\cdots$X), the unit cell containing four masses, then the equation of motion leads to the expectation of four longitudinal lattice modes – one acoustic and three optical. The optical modes consist of ν_1 and ν_2, the symmetric and asymmetric X–Pt^{IV}–X stretching modes, and ν_3 which is the motion of [Pt^{II}(L L)$_2$]$^{2+}$ against [Pt^{IV}(L L)$_2$X$_2$]$^{2+}$. The k ≅ 0 wavenumbers of the three optical modes can be shown to obey the equation [11]:

$$\frac{\nu_2^2 + \nu_3^2}{\nu_1^2} = 1 + 2\left(\frac{m_X}{m_{Pt}}\right)$$

The masses of the ligands have been ignored since the RR results showed the axial modes to be effectively decoupled from the equatorial modes. The above relation, the best currently available, indicates that ν_3 must occur at very low wavenumbers. Taking the ν_1 and ν_2 values of the en complex as typical (170 and 231 cm^{-1}, respectively), ν_3 is found to be (just) imaginary on the above basis. Only a very small change in ν_2 is, however, necessary in order to achieve a real and reasonable solution to ν_3 *viz.* if ν_2 = 229 cm^{-1}, ν_3 = 0 while if ν_2 = 224 cm^{-1}, ν_3 = 50 cm^{-1}. The 0–50 cm^{-1} region is certainly that expected for ν_3, since it involves the relative motion of the heaviest of the chain elements. Unfortunately, it is clear that the published vibrational analysis [11] is too crude to permit a reasonable estimate of the value of ν_3 in linear-chain complexes. Any more detailed treatment of the mechanics of such complexes must take into account the most significant of the force constants ignored to date, *viz.* the stretch-stretch interaction constant of the chain. On the experimental side, no bands attributable with certainty to ν_3 could be detected in the RR spectra, possibly because they were obscured by the Rayleigh wing.

Excitation Profiles

The excitation profiles of the Stokes ν_1, $2\nu_1$ and $3\nu_1$, bands of each complex are given in Figs. 5–8, together with the electronic transmission spectrum in each case. The intervalence band maximum occurs in the 18,000–14,400 cm^{-1} region, (Table I), the difference from one complex to another presumably reflecting the differences in the effectiveness

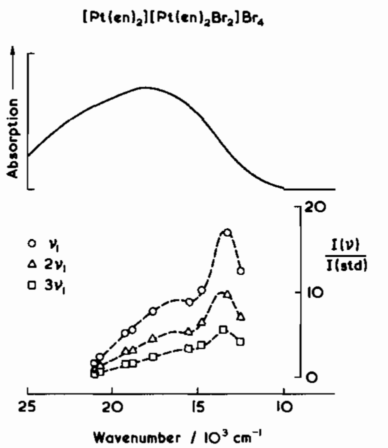

Fig. 5. Electronic Spectrum (in KBr at ~295 K) and excitation profiles (in K_2SO_4 at ~80 K) of $[Pt(en)_2][Pt(en)_2Br_2]Br_4$.

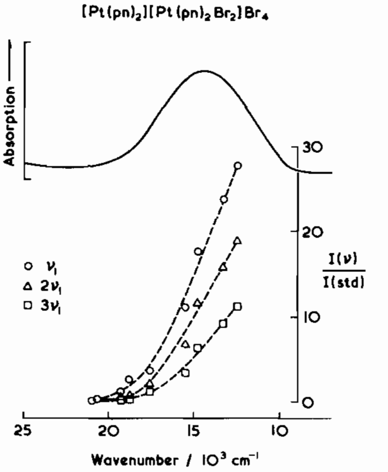

Fig 6. Electronic Spectrum (in KBr at ~295 K) and excitation profiles (in K_2SO_4 at ~80 K) of $[Pt(pn)_2][Pt(pn)_2Br_2]Br_4$.

of packing of the amines and of hydrogen-bonding between the amines and the chain bromine atoms, and therefore in the $Pt^{II}\cdots Pt^{IV}$ distances [7]. The excitation profiles of the ν_1, $2\nu_1$ and $3\nu_1$ bands maximise in the 14000–12000 cm^{-1} region (Table I), *i.e.* typically ~3,000 cm^{-1} below the appropriate intervalence band maximum. This result is common to all linear-chain complexes previously studied, and reasons for it have been outlined [3].

The excitation profiles in two cases (the en and ptn complexes) show weaker additional maxima on the high energy side of the main maxima. The reason for these maxima is unclear, but such maxima have been observed previously in the excitation profiles of other bromine-bridged linear-chain complexes, *viz.* $[Pt(en)Br_2][Pt(en)Br_4]$ [5] and $[Pt(tn)_2][Pt(tn)_2Br_2](ClO_4)_4$ [6], where en = 1,2-diaminoethane and tn = 1,3-diaminopropane.

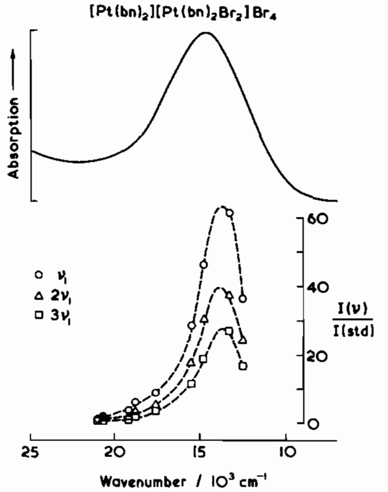

Fig. 7. Electronic Spectrum (in KBr at ~295 K) and excitation profiles (in K_2SO_4 at ~ 80 K) of $[Pt(bn)_2][Pt(bn)_2Br_2]Br_4$.

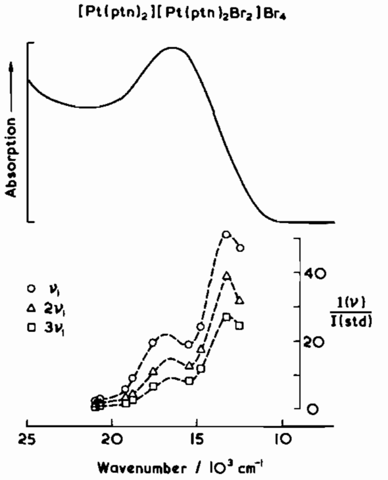

Fig. 8. Electronic Spectrum (in KBr at ~295 K) and excitation profiles (in K_2SO_4 at ~80 K) of $[Pt(ptn)_2][Pt(ptn)_2Br_2]Br_4$.

Conclusion

The close similarity between the RR spectra of all four complexes clearly indicates that they all have bromine-bridged linear-chain structures of the sort established crystallographically for the pn- complex [8]. The wavenumber of the symmetric $Br-Pt^{IV}-Br$ stretching mode, ν_1, is independent of the mass of the amine, averaging 171.2 ± 0.6 cm^{-1}; this indicates that this chain mode is effectively decoupled from the equatorial modes. The ν_1 mode is close to behaving as a simple harmonic oscillator, since the x_{11} value is very small, (the average value for all four complexes is -0.35 ± 0.09 cm^{-1}) ν_3 is thought to lie in the 0–50 cm^{-1} range, but could neither be calculated nor observed at present.

The very effective coupling of the ν_1 mode to the intervalence band in these complexes, as judged both by the long overtone progression in ν_1 at resonance and by the excitation profile of ν_1 in the vicinity of this band, indicates that a very substantial change occurs along the ν_1 coordinate on excitation from the ground to the intervalence state, consistent with the formation of Pt^{III} units in the chain.

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