Electronic, Raman, and Resonance Raman Spectra of Mixed-valence Anion-chain Complexes of Platinum

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Electronic, Raman, and resonance Raman (r.R.) spectra of the mixed-valence anion-chain complexes $M_2[Pt(L)X_3][Pt(L)X_5]$ (M = K or NH_4, L = NH_3 or pyridine, and X = Cl, Br, or I) have been recorded at *ca.* 80 K. The electronic spectra are characterised by strong bands in the visible region, attributable to the intervalence transition $Pt^{IV} \leftarrow Pt^{II}$. The r.R. spectra display long overtone progressions ($v_1\nu_1$), ν_1 being the totally symmetric axial breathing mode, $\nu_{sym.}(X\text{–}Pt^{IV}\text{–}X)_{ax.}$, together with combination band progressions $v_1\nu_1 + \nu_2$ and $v_1\nu_1 + \nu_3$, where ν_2 and ν_3 are the totally symmetric stretching modes of the equatorial halogen atoms, $\nu_{sym.}(Pt\text{–}X)_{eq.}$. The excitation profiles of the fundamentals, ν_1, ν_2, ν_3, and in some cases of $2\nu_1$, have been measured and all found to maximise on the low-energy side of the intervalence band maximum. The r.R. results indicate a substantial change in the $Pt\text{–}X_{ax.}$ bond length on excitation from the ground to the intervalence state for each complex, together with other smaller changes in the $Pt\text{–}X_{eq.}$ bond lengths.

The appearance of unusual crystallites formed either during the cooling of $K[Pt(NH_3)Cl_3]$ to which a lesser quantity of $K[Pt(NH_3)Cl_5]$ had been added, or by oxidation of $K[Pt(NH_3)Cl_3]$ with halogens was described by Werner [1] in 1896. Soon afterwards Jorgensen [2] observed crystals with red sections upon prolonged crystallisation of $K[Pt(NH_3)Cl_3]\cdot H_2O$. Fanwick and Martin [3] reinvestigated the red crystals and concluded, on the basis of single-crystal electronic spectra and elemental analyses, that they contained mixed-valence anion chains of the type $M^{II} \cdots X\text{–}M^{IV}\text{–}X \cdots M^{II}$. They quoted a $Pt^{II}\text{–}Pt^{IV}$ distance of 5.22 Å. Since then the syntheses of several analogous complexes have been published; a value of 5.61 Å for the $Pt^{II}\text{–}Pt^{IV}$ distance for the analogous bromide has been established.[4]

Resonance Raman (r.R.) spectroscopy has been shown [5–8] to be a valuable technique for identifying new linear-chain halogen-bridged complexes and can provide information about excited-state geometries. The r.R. spectra of cationic [9–11] and neutral chain [11–13] complexes of platinum have been well characterised. However, few studies of related anion-chain complexes [4,14–16] have yet been made.

The present study is therefore concerned with the electronic and r.R. spectra, and with the excitation profiles of resonance-enhanced bands of a series of anion-chain complexes at *ca.* 80 K. The complexes studied are $M_2[Pt(L)X_3][Pt(L)X_5]$ [M = K or NH_4, X = Br, L = NH_3; M = K, X = I, L = NH_3; M = K, X = Br or Cl, L = pyridine (py)].

The objectives of this study are (*i*) to establish the relationships between anionic, neutral, and cationic chain complexes and (*ii*) to find out whether enhancement of equatorial modes, as observed for the anion-chain complexes [14,15] $Cs_2[Pt(NO_2)(NH_3)X_2][Pt(NO_2)(NH_3)X_4]$ (X = Br or I), is due to the anionic character of the chain or to the π-acceptor properties of the NO_2 group.

Experimental

Preparations.—$K_2[Pt(py)Cl_3][Pt(py)Cl_5]$ was obtained by two methods. First, by co-crystallisation from aqueous solution of equimolar amounts of $K[Pt(py)Cl_3]$ and $K[Pt(py)Cl_5]$ in the presence of some KCl and second, by the oxidation of $K[Pt(py)Cl_3]$ with $[NH_4]_2[S_2O_8]$. Red microcrystals with a green metallic sheen were obtained in both cases.

$K_2[Pt(py)Br_3][Pt(py)Br_5]$ was obtained by the reaction of $K[Pt(py)Cl_3]$ and $K[Pt(py)Cl_3Br_2]$ in equimolar amounts in HBr containing some KBr. Gold plates were obtained.

$M_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$ (M = K or NH_4) were obtained as gold needles by the oxidation of $K[Pt(NH_3)Cl_3]$ [17] in HBr containing some MBr (M = K or NH_4).

$K_2[Pt(NH_3)I_3][Pt(NH_3)I_5]$ was obtained as bronze microcrystals by the reaction of the bromo-analogue with KI in aqueous solution.

Instrumental Details.—Electronic spectra were recorded by transmission using a Cary 14 spectrometer, at both room temperature and at liquid-nitrogen temperature, from pressed discs of the complexes dispersed in alkali halide.

Raman spectra were recorded using a Spex 1401 or 14018 (R6) double monochromator equipped with Bausch and Lomb gratings (1 200 line mm^{-1}) and Jobin-Yvon holographic gratings (1 800 line mm^{-1}), respectively. Radiation was provided by Coherent Radiation model 52 Ar^+ and Kr^+ lasers. Detection was by photon-counting techniques using cooled RCA C31034 photomultipliers. Spectra were recorded from pressed discs of the complexes dispersed in $K_2[SO_4]$, held at liquid-nitrogen temperature. A cylindrical lens was used to line-focus the beam, thus preventing heating and consequent decomposition of the samples.

Band wavenumbers were calibrated by reference to the emission lines of neon. Band intensities were measured relative to that of the band attributed to the a_1 mode of the sulphate ion and corrected for the response of the instrument in each case.

Infrared spectra were recorded using a Perkin-Elmer 225 spectrometer.

Results and Discussion

Electronic Spectra.—All complexes studied are dichroic and appear metallic with gold reflection. However, the crystals lose their metallic sheen on being ground. The colours of the crystals and their powders are listed in Table 1.

Electronic transmission spectra of pressed discs, which are effectively the sums of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in each case, show broad bands in the visible and near-i.r. regions (Figure 1). The spectrum of $K_2[Pt(py)Cl_3][Pt(py)Cl_5]$ contains a broad band with a maximum at 20 800 cm^{-1} whereas those of the (yellow) constituent ions, $K[Pt(py)Cl_3]$ and $K[Pt(py)Cl_5]$, do not show a

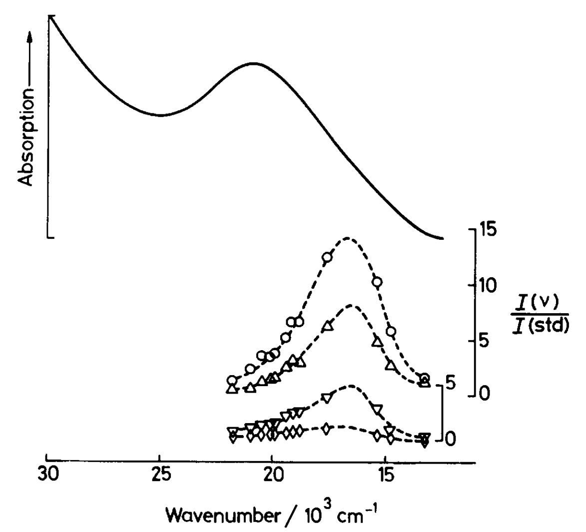

Figure 1. Electronic spectrum and excitation profiles of the ν_1 (○), $2\nu_1$ (△), ν_2 (▽), and ν_3 (◇) bands of $K_2[Pt(py)Cl_3][Pt(py)Cl_5]$ at *ca.* 80 K

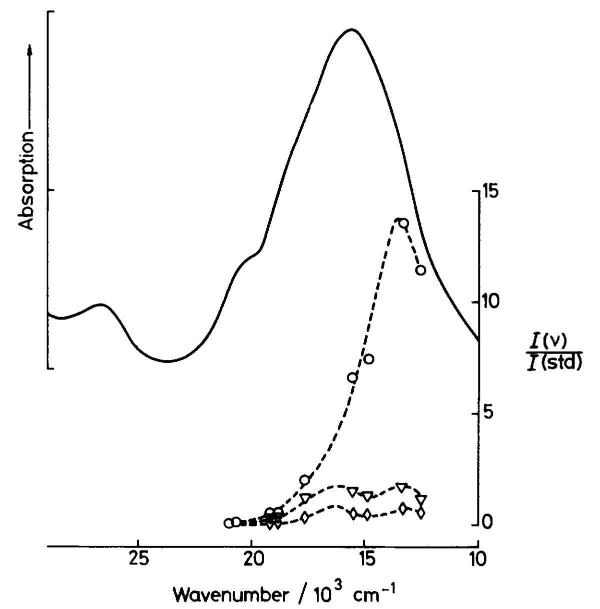

Figure 2. Electronic spectrum and excitation profiles of the ν_1 (○), ν_2 (▽), and ν_3 (◇) bands of $K_2[Pt(py)Br_3][Pt(py)Br_5]$ at *ca.* 80 K

band below 30 000 cm^{-1}. The band at 20 800 cm^{-1} is thus assigned [8–14] to the intervalence transition $Pt^{IV} \leftarrow Pt^{II}$.

The bromo-analogue, $K_2[Pt(py)Br_3][Pt(py)Br_5]$, has a strong band at 15 600 cm^{-1}, assigned to the intervalence band, and two other weak bands at 20 500 and 26 500 cm^{-1} (Figure 2) which could arise from halogen-to-metal charge-transfer transitions. These results are similar to those found for $Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]$.[14]

The ammine complexes $M_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$ show similar characteristic absorption bands at 16 800 cm^{-1} ($M = K$) and 15 800 cm^{-1} ($M = NH_4$), each with poorly defined shoulders on the high-frequency side (Figures 3 and 4). The spectrum of the iodide complex shows a very strong and very broad band with a maximum in the near-i.r. region at 11 000 cm^{-1}.

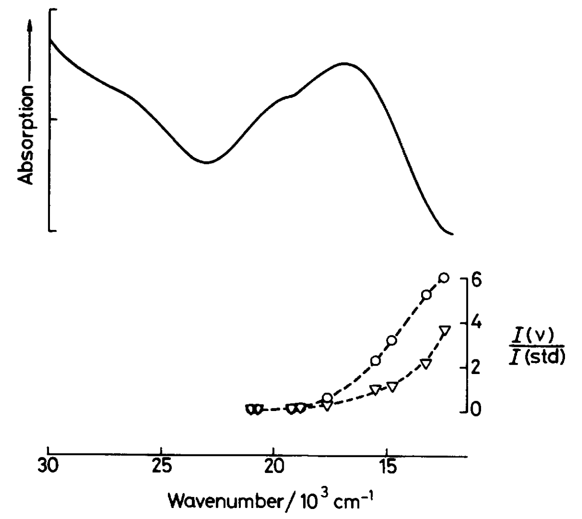

Figure 3. Electronic spectrum and excitation profiles of the ν_1 (○) and ν_2 (▽) bands of $K_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$ at *ca.* 80 K

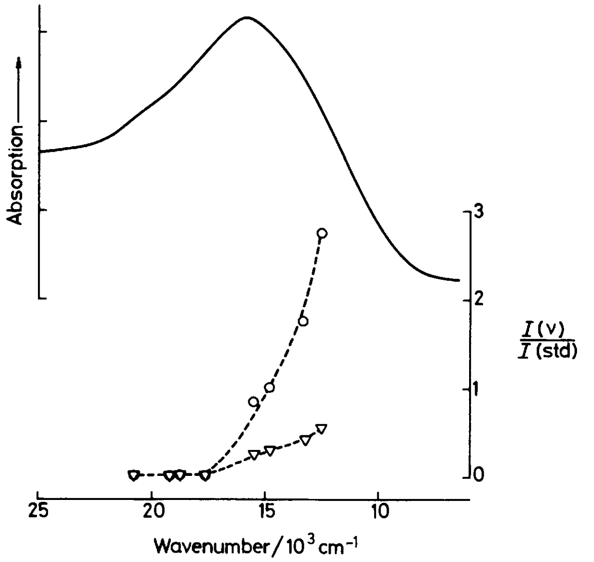

Figure 4. Electronic spectrum and excitation profiles of the ν_1 (○) and ν_2 (▽) bands of $[NH_4]_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$ at *ca.* 80 K

Resonance Raman Spectra.—The Raman spectra of the complexes show strong dependence on the wavenumber of the exciting line and on the sample temperature. At room temperature the spectrum of $K_2[Pt(py)Cl_3][Pt(py)Cl_5]$ with blue or red lines consists mainly of bands due to fundamentals and weak overtone and combination tones, whereas with yellow or green lines, overtones and combination tones become stronger and long progressions are observed. The bromo- and iodo-complexes, by contrast, give the more detailed and intense spectra with red lines. On cooling the samples to liquid-nitrogen temperature, the bands become sharper and stronger and an increase in the number of overtones and combination tones is observed. The wavenumbers of the bands observed in the spectra at *ca.* 80 K together with

Table 1. Summary of data on complexes studied

Complex	Crystal colour	Powder colour	Mixed-valence band max./cm^{-1}	Excitation profile (ν_1) max./cm^{-1}	$\tilde{\nu}_1$/cm^{-1}	$\tilde{\nu}_2$/cm^{-1}	$\tilde{\nu}_3$/cm^{-1}
$K_2[Pt(py)Cl_3][Pt(py)Cl_5]$	Green	Red	20 800	16 700	300.5	325.4	345.4
$K_2[Pt(py)Br_3][Pt(py)Br_5]$	Gold	Blue	15 600	13 500	170.8	200.0	216.5
$K_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$	Gold	Blue	16 800	$\leqslant$12 500	169.1	205.1	233.4
$[NH_4]_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$	Gold	Blue	15 800	$\leqslant$12 500	168.6	205.1	235.3
$K_2[Pt(NH_3)I_3][Pt(NH_3)I_5]$	Bronze	Black	*ca.* 11 000	<12 500	113.0	142.0	

Table 2. Wavenumbers and assignments of bands observed in the r.R. spectrum of $K_2[Pt(py)Cl_3][Pt(py)Cl_5]$ *

$\tilde{\nu}$/cm^{-1}	Assignment	$\tilde{\nu}$/cm^{-1}	Assignment
180.1		926	$2\nu_1 + \nu_2$
203.0		950	$2\nu_1 + \nu_3/\nu_1 + 2\nu_2$
240.8	ν_4, (Pt–N)	1 060	C–H deformation
300.5	ν_1	1 100	
325.4	ν_2	1 120	
345.4	ν_3	1 160	
541.3	ν_1 + 240.8	1 230	4th harmonic
603.2	$2\nu_1$	1 560	5th harmonic
625.9	$\nu_1 + \nu_2$	1 880	6th harmonic
648.0	$2\nu_2/\nu_1 + \nu_3$	2 170	7th harmonic
676.7	$\nu_2 + \nu_3$ (?)	2 480	8th harmonic
901	$3\nu_1$	2 760	9th harmonic

* Obtained as a $K_2[SO_4]$ disc at *ca.* 80 K with 520.8 nm excitation.

Table 3. Wavenumbers and assignments of bands observed in the r.R. spectrum of $K_2[Pt(py)Br_3][Pt(py)Br_5]$ *

$\tilde{\nu}$/cm^{-1}	Assignment	$\tilde{\nu}$/cm^{-1}	Assignment
85		679.2	$4\nu_1$
170.8	ν_1	710	$3\nu_1 + \nu_2$
200.0	ν_2	732.8	$3\nu_1 + \nu_3$
216.5	ν_3	762	$3\nu_1 + \nu_4$
238.3	ν_4, (Pt–N)	827	ν_1 + 654.1
248.3			
340.9	$2\nu_1$	851	$5\nu_1$
370.5	$\nu_1 + \nu_2$	879	$4\nu_1 + \nu_2$
389.5	$\nu_1 + \nu_3$	903	$4\nu_1 + \nu_3$
395.8	$2\nu_2$	1 025	C–H deformation
416	$\nu_1 + \nu_4$	1 040	6th harmonic
510.4	$3\nu_1$	1 050	C–H deformation
540.7	$2\nu_1 + \nu_2$	1 220	7th harmonic
561.8	$2\nu_1 + \nu_3$	1 370	8th harmonic
589	$2\nu_1 + \nu_4$		
654.1	ring deformation		

* Obtained as a $K_2[SO_4]$ disc at *ca.* 80 K with 647.1 nm excitation.

Table 4. Wavenumbers and assignments of bands observed in the r.R. spectra of $M_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$

M = K $\tilde{\nu}$/cm^{-1}	M = NH_4 $\tilde{\nu}$/cm^{-1}	Assignment
100	100	
169.1	168.6	ν_1
205.1	205.1	ν_2
233.4	235.3	ν_3
336.4	336.2	$2\nu_1$
374.8	373.2	$\nu_1 + \nu_2$
405.4	406.1	$\nu_1 + \nu_3$
502.1	502	$3\nu_1$
542.6	541	$2\nu_1 + \nu_2$
559.7	560	$2\nu_1 + \nu_3$
668	665	$4\nu_1$
710		$3\nu_1 + \nu_2$
832		$5\nu_1$

* Obtained as $K_2[SO_4]$ discs at *ca.* 80 K with 676.4 nm excitation.

Table 5. Wavenumbers and assignments of bands observed in the r.R. spectrum of $K_2[Pt(NH_3)I_3][Pt(NH_3)I_5]$ *

$\tilde{\nu}$/cm^{-1}	Assignment
55	
113.0	ν_1
142.0	ν_2
226	$2\nu_1$
256	$\nu_1 + \nu_2$
345	$3\nu_1$

* Obtained as a $K_2[SO_4]$ disc at *ca.* 80 K with 752.5 nm excitation.

the assignments are listed in Tables 2—5. The spectra are shown in Figures 5—9.

The spectra of all five complexes consist of bands due to the fundamentals ν_1, ν_2, and ν_3, to overtones $v_1\nu_1$, and to combination tones $v_1\nu_1 + \nu_2$ and $v_1\nu_1 + \nu_3$, where ν_1 and ν_2 are assigned to the axial and equatorial totally symmetric stretching modes $\nu_{sym.}(X{-}Pt{-}X)_{ax.}$ and $\nu_{sym.}(X{-}Pt{-}X)_{eq.}$ and ν_3 is assigned to the Pt–X stretching mode of the halogen atom *trans* to the amine. The wavenumber order $\nu_1 < \nu_2$ is consistent with the fact that $\nu(MX)_{bridging} < \nu(MX)_{terminal}$ for a wide variety of inorganic complexes.[18] The ν_2 values {200.0 and 205.1 cm^{-1} for the complexes $K_2[Pt(L)Br_3][Pt(L)Br_5]$, L = py and NH_3, respectively} are close to those for other related bromine-bridged chain complexes, *viz.* 206.9 cm^{-1} for $Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]$ [14,15] and 206.3 cm^{-1} for $[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$.[13] The near independence of ν_2 for different complexes on the nature of the amine is also consistent with its assignment to the symmetric stretch of *trans*-equatorial halogen atoms. Moreover, the substantial dependence of ν_3 on the nature of the amine {216.5, 229.7, 233.4, and 235.3 cm^{-1} for $K_2[Pt(py)Br_3][Pt(py)Br_5]$, $[Pt(en)Br_2][Pt(en)Br_4]$ [11] (en = 1,2-diaminoethane), $K_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$, and $[NH_4]_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$, respectively} is consistent with its assignment, made above, to the PtX stretching mode of the halogen atom *trans* to the amine. It is improbable, as previously suggested,[16] that the band in this region of the Raman spectra of the bromo-complexes could be attributed to the asymmetric stretching mode of the chain, $\nu_{asym.}(X{-}Pt^{IV}{-}X)$, since the latter is known for a large number of bromo-bridged complexes of aliphatic amines to occur in a relatively narrow and rather higher wavenumber region (241—252 cm^{-1}).[19]

The weak bands at 240.8 cm^{-1} in the Raman spectrum of $K_2[Pt(py)Cl_3][Pt(py)Cl_5]$ and at 238.3 and 248.3 cm^{-1} in that of the bromo-analogue may arise from the Pt–py stretching modes (referred to as ν_4 in Table 2), since these are known to occur in this region for a wide variety of complexes.[20] Likewise, the bands at 507.1 and 518.7 cm^{-1} for $K_2[Pt(NH_3)Br_3]$-

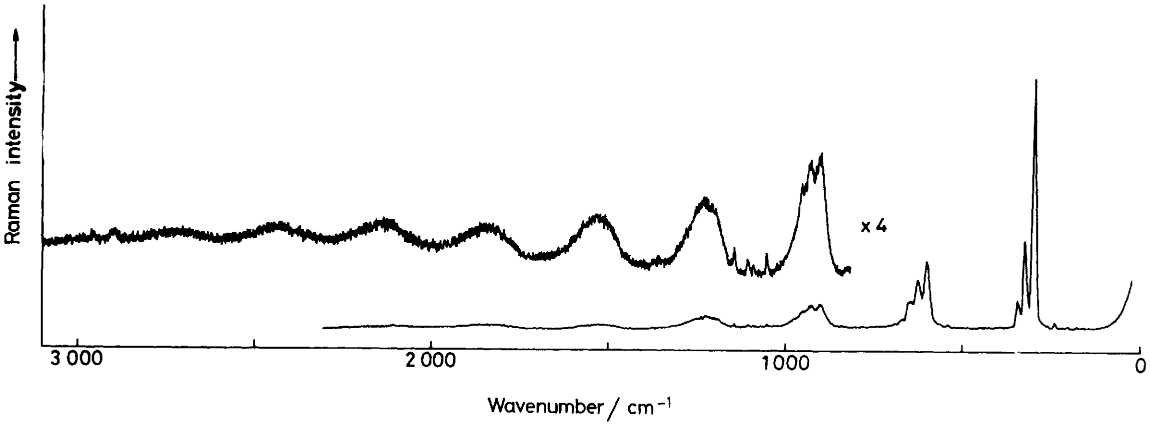

Figure 5. Resonance Raman spectrum of $K_2[Pt(py)Cl_3][Pt(py)Cl_5]$ as a $K_2[SO_4]$ disc recorded with 520.8 nm excitation at *ca.* 80 K; slit width 3 cm^{-1}

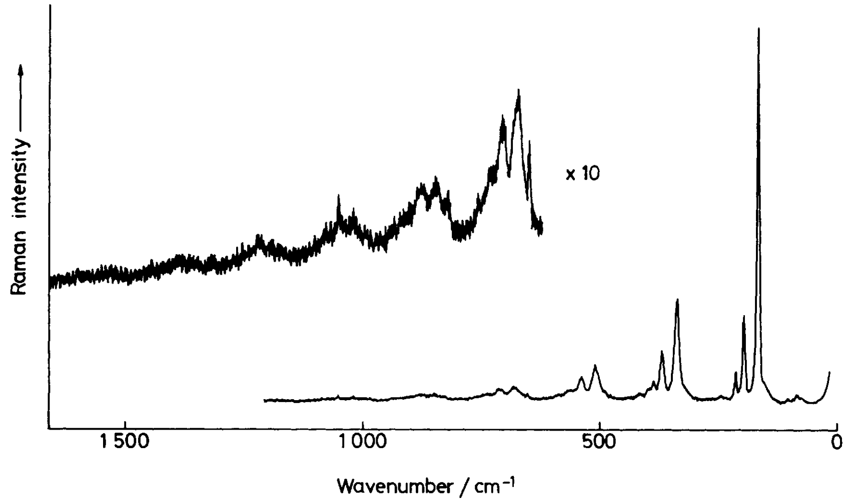

Figure 6. Resonance Raman spectrum of $K_2[Pt(py)Br_3][Pt(py)Br_5]$ as a $K_2[SO_4]$ disc recorded with 647.1 nm excitation at *ca.* 80 K; slit width *ca.* 2 cm^{-1}

$[Pt(NH_3)Br_5]$, and at 505.9 and 517.4 cm^{-1} for the analogous ammonium salt, are assigned as $Pt-NH_3$ stretching modes, as is the band at 457.6 cm^{-1} in the spectrum of the iodo-complex. These metal–ammonia bands are only observed clearly in off-resonance spectra since near resonance they are obscured by the very intense ν_1 band progression. The metal–ammonia bands, as well as the ν_2 and ν_3 bands, all increase in intensity relative to that of ν_1 on lowering the temperature from *ca.* 300 to *ca.* 80 K.

Approximate values for the harmonic wavenumber (ω_i) and anharmonicity constant (x_{ii}) may be deduced when long overtone progressions ($v_i\nu_i$) are observed in r.R. spectra.[21] If, in addition to the progression $v_i\nu_i$, combination band progressions $v_i\nu_i + \nu_j$ are observed, then the cross terms x_{ij} can also be deduced. Analysis of the present data was only possible for the complex $K_2[Pt(py)Br_3][Pt(py)Br_5]$ because in this case there is less overlapping of bands than for the others. The results are $\omega_1 = 171.4 \pm 0.3$ cm^{-1}, $x_{11} = -0.46 \pm 0.1$ cm^{-1}, $x_{12} = -0.7 \pm 0.2$ cm^{-1}, and $x_{13} = -2.1 \pm 0.5$ cm^{-1}. These results are similar to those obtained for $Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]$ [14,15] and they indicate that the band which displays the r.R. progression behaves almost as a simple harmonic oscillator.

Excitation Profiles.—The excitation profiles (e.p.s) of ν_1, ν_2, ν_3, and $2\nu_1$ bands for $K_2[Pt(py)Cl_3][Pt(py)Cl_5]$ are included in Figure 1. The e.p.s all maximise about 4 500 cm^{-1} to the low-wavenumber side of the intervalence band maximum; this result is typical of those for other mixed-valence halogen-bridged platinum complexes.[8,16,19] Similarly, for $K_2[Pt(py)Br_3][Pt(py)Br_5]$, the e.p. of ν_1 reaches a maximum at 13 500 cm^{-1}, some 2 100 cm^{-1} to the low-wavenumber side of the intervalence band maximum. However, in this case, the e.p.s of the two equatorial modes ν_2 and ν_3 both display two weak maxima, at *ca.* 16 500 and *ca.* 13 500 cm^{-1}; this could imply the presence of equatorially polarised ligand-field bands in this region.

In the case of the ammine complexes, the e.p.s of ν_1 and ν_2 do not reach a maximum even for excitation with laser lines of the lowest available wavenumber (799.3 nm, 12 500 cm^{-1}), Figures 3 and 4.

As for all linear-chain complexes studied so far, the band most enhanced at resonance is ν_1, the totally symmetric axial stretching mode $\nu_{sym.}(X-Pt^{IV}-X)$. This implies that, in all cases, the structural change on going from the ground to the intervalence state is primarily along the axial Pt–X bonds. However, the ν_1 progression at resonance is, in general, shorter for

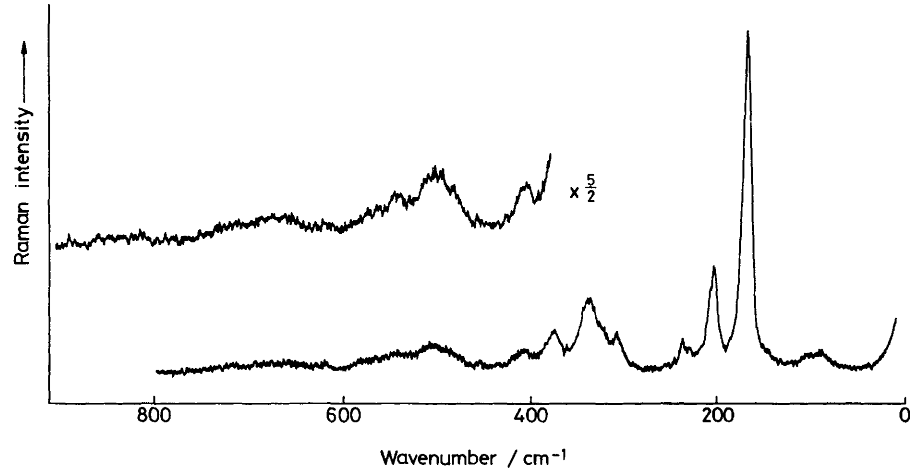

Figure 7. Resonance Raman spectrum of $K_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$ as a $K_2[SO_4]$ disc recorded with 676.4 nm excitation at *ca.* 80 K; slit width *ca.* 2 cm^{-1}

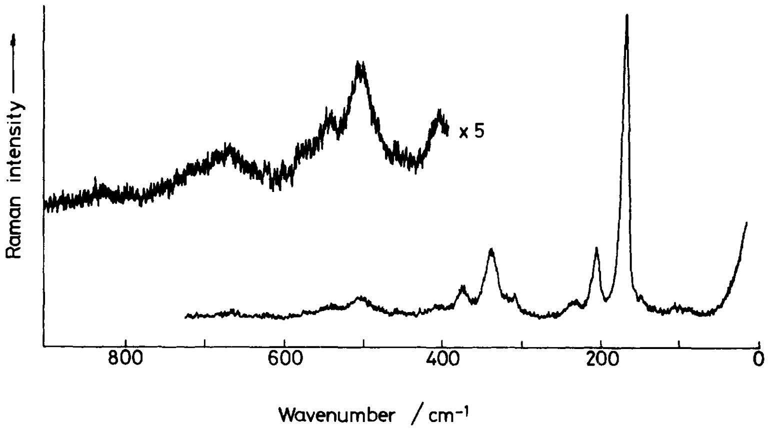

Figure 8. Resonance Raman spectrum of $[NH_4]_2[Pt(NH_3)Br_3][Pt(NH_3)Br_5]$ as a $K_2[SO_4]$ disc recorded with 676.4 nm excitation at *ca.* 80 K; slit width *ca.* 2 cm^{-1}

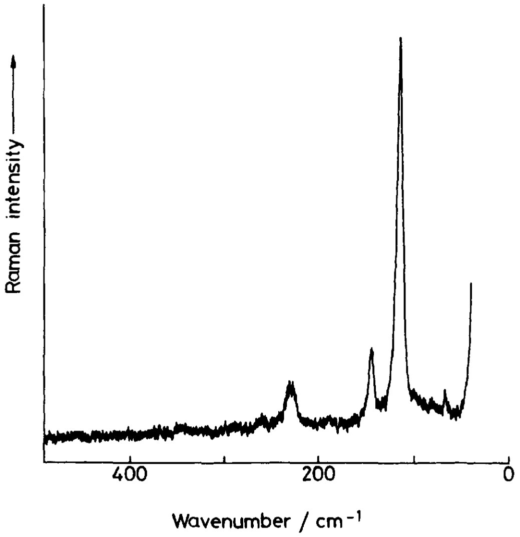

Figure 9. Resonance Raman spectrum of $K_2[Pt(NH_3)I_3][Pt(NH_3)I_5]$ as a $K_2[SO_4]$ disc recorded with 752.5 nm excitation at *ca.* 80 K; slit width *ca.* 3 cm^{-1}

anion-chain complexes than it is for neutral- or cation-chain ones, implying that the change in Pt–X$_{ax.}$ bond length on excitation is the less extensive for anion-chain complexes. It is also clear that the two equatorial modes, ν_2 and ν_3, are significantly enhanced at resonance for the anion-chain complexes studied, implying some small changes along the equatorial Pt–X bonds on excitation. The involvement of the equatorial modes is much more pronounced for the anion-chain complexes studied here and elsewhere, *e.g.* $Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]$,[14,15] than for neutral-chain and cation-chain complexes, suggesting a greater change in Pt–X$_{eq.}$ bond lengths on excitation for anion-chain complexes.

Conclusion

Resonance with the axially polarised $Pt^{IV} \leftarrow Pt^{II}$ intervalence band of the anion-chain complexes studied leads to the development of long r.R. progressions in ν_1, the axial symmetric $\nu_{sym.}(X–Pt^{IV}–X)$ stretching mode, just as has previously been established for cation-chain and neutral-chain complexes. Thus, all types of linear-chain, halogen-bridged complexes distort substantially along the Q_1 co-ordinate on excitation from the ground to the intervalence state. As judged from the lengths of the observed progressions in ν_1 (to $18\nu_1$),[9] cation-chain complexes distort the most on excitation to this state. Equatorial modes may also be enhanced at resonance, especially for anion-chain complexes, implying that there is a more extensive coupling of axial and equatorial modes and a slight change in equatorial Pt^{IV}–X bond lengths when the infinite chains carry negative charge. The metal-ion valences thus appear to be slightly more delocalised for anion-chain than for cation-chain complexes.

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