Electronic and Resonance-Raman Spectra of the Linear-chain Mixed-valence Platinum Complexes $\{[Pt(en)_2][Pt(en)_2X_2]\}_3[CuX_4]_4$ [X = Cl (1) or Br (2)] and $[Pt(pn)_2][Pt(pn) Br_2][Cu_3Br_5]_2$ (3)† (en = ethane-1,2-diamine and pn = propane-1,2-diamine)

By **Robin J. H. Clark*** and **Mohamedally Kurmoo**, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ
Heimo J. Keller, **Bernt Keppler**, and **Ulrich Traeger**, Anorganisch Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D6900, Heidelberg, W. Germany

Electronic, infrared, and resonance-Raman (r.r.) spectra of the title complexes have been recorded, as well as single-crystal polarised specular-reflectance spectra of complex (2) in the region 5 000—25 000 cm^{-1}. The r.r. spectra have been obtained with exciting lines whose wavenumbers fall within the contours of the intense, axially polarised, intervalence bands observed in the 15 000—20 000 cm^{-1} region of the transmission and specular-reflectance spectra of each complex. The r.r. spectra are characterised by the appearance of an intense progression, $v_1\nu_1$ (reaching at most $v_1 = 17$) where ν_1 is the symmetric ($X-Pt^{IV}-X$) stretching mode. Weak subsidiary progressions, $\nu_n + v_1\nu_1$, also appear in the spectra, where ν_n is another Raman-active mode. The spectroscopic constants ω_1 and x_{11} are calculated. The excitation profiles of the Stokes ν_1 band and additionally, in the case of the two bromo-complexes, of the Stokes $2\nu_1$, $3\nu_1$, and anti-Stokes ν_1 bands, have been measured, and all found to reach maxima on the low-energy side of the electronic band maximum. The present results are compared with previous ones on related linear-chain complexes.

RECENT resonance-Raman (r.r.) spectroscopic studies on mixed-valence complexes have been focused on the linear-chain halogen-bridged complexes of platinum and palladium, $[Pt(C_2H_5NH_2)_4][Pt(C_2H_5NH_2)_4X_2]X_4\cdot nH_2O$,[1,2] $n = 4$ (X = Cl or Br), $n = 0$ (X = Br or I); $[Pt(en)X_2][Pt(en)X_4]$; $[Pt(en)_2][Pt(en)_2X_2][ClO_4]_4$,[3,4] en = ethane-1,2-diamine, X = Cl, Br, or I; $[Pt(pn)_2][Pt(pn)_2X_2]Y_4$,[5] pn = propane-1,2-diamine, X = Cl, Br, or I and Y = ClO_4, X = Y = Br or I; and $[Pt(tn)_2][Pt(tn)_2X_2][ClO_4]_4$,[4] tn = propane-1,3-diamine and X = Cl, Br, or I.

These complexes contain relatively small anions such as Cl, Br, I, ClO_4, or BF_4. The present paper develops this subject further with a detailed electronic, i.r., and r.r. study of three platinum complexes with large polymeric anions. The complexes are: $\{[Pt(en)_2][Pt(en)_2X_2]\}_3[CuX_4]_4$, where X = Cl (1) or Br (2) and $[Pt(pn)_2][Pt(pn)_2Br_2][Cu_3Br_5]_2$ (3). The crystal structures of complexes (1) and (2) are known to contain $Pt^{II}\cdots X-Pt^{IV}-X\cdots$ chains, the $Pt^{II}\cdots Pt^{IV}$ distances being 5.261 Å [6] and 5.617 Å [7] respectively. The polymeric copper-containing anions contain, in each case, $\cdots CuX_3\cdots X-CuX_3-X\cdots$ linear chains running parallel to the $Pt^{II}\cdots Pt^{IV}$ chains, the co-ordination about the copper being trigonal bipyramidal; in the case of the $[Cu_3Br_5]_2$ salt, however, the chain described is also coupled to a parallel chain of tetrahedrally co-ordinated copper ions.[7] Crystallographic data on complex (2), reported herein, indicate that the crystal structure of this complex is analogous to that of (1).

The particular interest in the complexes studied lies in the possibility that vibrational modes of the chain anions might become involved in the r.r. process. However, the results obtained clearly indicate that this is not the case, the r.r. spectra being shown to arise exclusively from chain cation vibrations.

EXPERIMENTAL

The complexes $\{[Pt(en)_2][Pt(en)_2X_2]\}_3[CuX_4]_4$ (X = Cl or Br) and $[Pt(pn)_2][Pt(pn)_2Br_2][Cu_3Br_5]_2$ were obtained by the method of Kurnakov [7,8] by the oxidation of $[Pt(en)_2]X_2$ or $[Pt(pn)_2]Br_2$, as appropriate, with an aqueous approximately equimolar solution of CuX_2 at *ca.* 90 °C; on evaporating the solution to *ca.* $\frac{1}{5}$ volume, and allowing the solution to cool, long needles appeared. The products were recrystallised from aqueous solution. All three complexes were characterised by elemental analyses.

Instrumental Details.—Raman spectra were recorded using a Spex 1401 double monochromator equipped with 1 200 line mm^{-1} Bausch and Lomb gratings and a standard photon-counting detection system. Exciting radiation was provided by Coherent Radiation models 52 Ar^+ and Kr^+ lasers. Raman spectra at room temperature were obtained using a rotating sample holder and at *ca.* 80 K from pressed discs of the complex dispersed in alkali halide. Excitation profiles were measured at room temperature with respect to the 986 cm^{-1} band of $K_2[SO_4]$ as internal standard.

Absorption spectra were recorded on alkali halide discs of the complexes using a Cary 14 spectrometer, and i.r. spectra were recorded on Nujol mulls of the complexes using a Perkin-Elmer 225 spectrometer. The specular-reflectance spectrum of complex (2) was recorded on a single crystal grown from a standard preparation and with approximate dimensions of 3 × 0.2 × 0.2 mm.

Rotating crystal and Weissenburg photographs (Cu-K_α radiation) showed the crystal to be hexagonal and yielded approximate lattice constants. The Weissenberg photographs of complex (2) are identical in form with those of (1), and the complexes are thus isostructural. Exact lattice constants [$a = 15.917(8)$, $b = 15.917(8)$, $c = 10.895(4)$ Å, $\gamma = 120°$] were determined by least squares [9] from the θ values of 22 reflections, measured on a single-crystal diffractometer (Siemens AED). Thus the $Pt^{II}\cdots Pt^{IV}$ distance is 5.448 Å.

RESULTS

The electronic spectra of all three complexes show broad, featureless bands in the visible near-i.r. region which, on the basis of previous studies,[10] are readily assignable to intervalence $Pt^{II}\rightarrow Pt^{IV}$ transitions of the cation chain. The axial polarisation of this transition is demonstrated

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† Bis(propane-1,2-diamine)platinum(II) Dibromobis(propane-1,2-diamine)platinum(IV) Bis[pentabromotricuprate(2—)].

by a polarised, specular-reflectance spectrum of a single crystal of complex (2) (Figure 1); the intense band at 15 870 cm^{-1} is seen to be completely polarised along the needle axis. The electronic spectra of the three complexes are included in Figures 2—4.

The r.r. spectra of the complexes at *ca.* 80 K are shown in Figures 5—7 and the wavenumbers and assignments of the bands observed are listed in Table 1. As observed in previous studies on these sorts of complexes, excitation with radiation whose wavenumber falls within the contour of the axially polarised mixed-valence $Pt^{II} \rightarrow Pt^{IV}$ transition gives rise to r.r. spectra which are dominated by a progression in ν_1, the symmetric $X-Pt^{IV}-X$ stretching mode of the chain halogen atoms. This progression is very extensive in each case, being observed to reach as far as $14\nu_1$ for (1), $12\nu_1$ for (2), and $17\nu_1$ for complex (3). These observations imply that in the resonant excited state the geometry of the molecule is considerably displaced along the ν_1 co-ordinate.

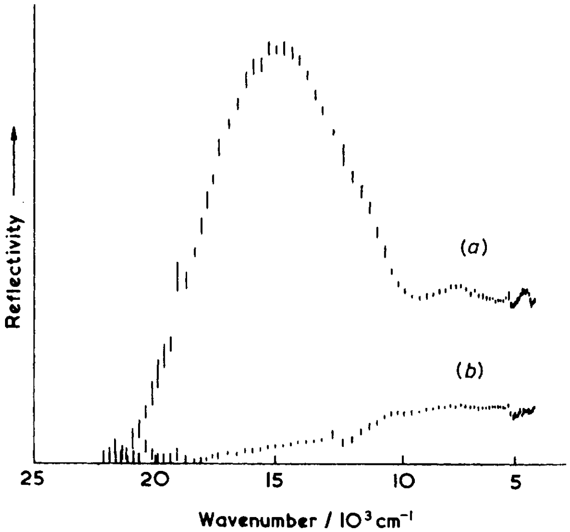

FIGURE 1 Specular-reflectance spectra of a single crystal of $\{[Pt(en)_2][Pt(en)_2Br_2]\}_3[CuBr_4]_4$ with the electric vector of the incident beam parallel, (*a*), and perpendicular, (*b*), to the chain axis

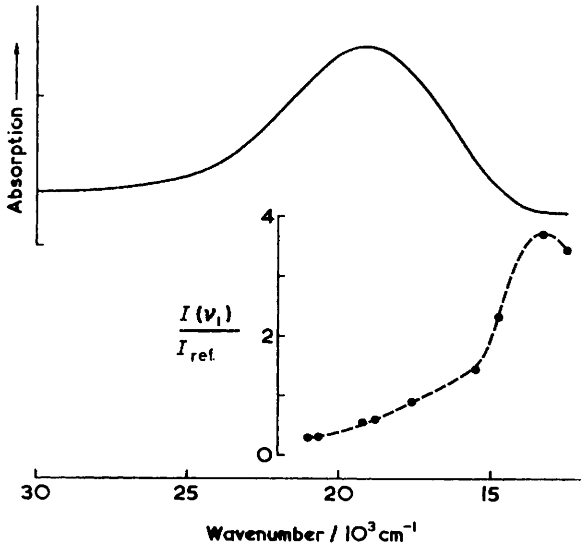

FIGURE 2 Electronic transmission spectrum and excitation profile of the Stokes ν_1 band of $\{[Pt(en)_2][Pt(en)_2Cl_2]\}_3[CuCl_4]_4$

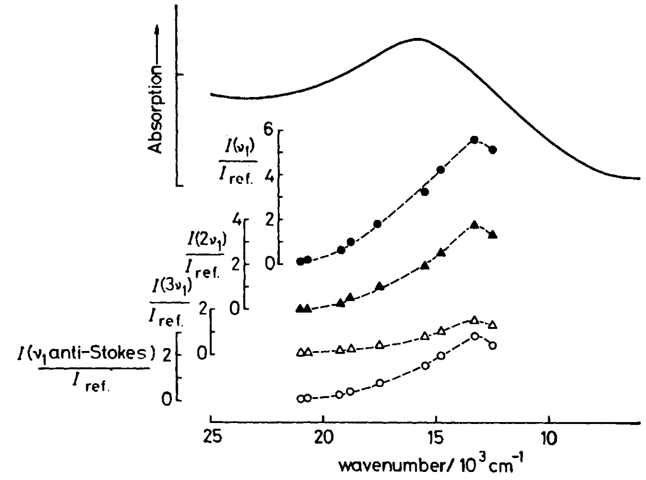

FIGURE 3 Electronic transmission spectrum and excitation profiles of the Stokes ν_1 (●), $2\nu_1$ (▲), $3\nu_1$ (△), and anti-Stokes ν_1 (○) bands of $\{[Pt(en)_2][Pt(en)_2Br_2]\}_3[CuBr_4]_4$

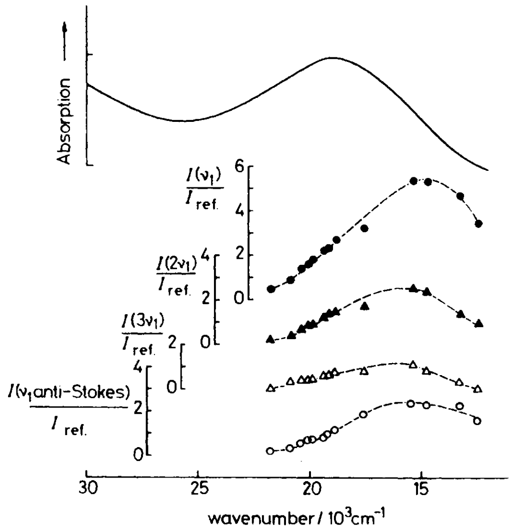

FIGURE 4 Electronic transmission spectrum and excitation profiles of the Stokes ν_1 (●), $2\nu_1$ (▲), $3\nu_1$ (△), and anti-Stokes ν_1 (○) bands of $[Pt(pn)_2][Pt(pn)_2Br_2][Cu_3Br_5]_2$

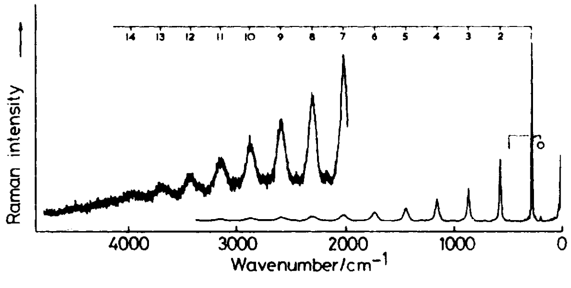

FIGURE 5 Resonance-Raman spectrum of $\{[Pt(en)_2][Pt(en)_2Cl_2]\}_3[CuCl_4]_4$ in a KCl disc at *ca.* 80 K. $\lambda_0 = 568.2$ nm. Slit ≈ 1.5 cm^{-1}

The observation of a large number of overtones of a totally symmetric fundamental under r.r. conditions makes it possible to determine the harmonic frequency (ω_1) and anharmonicity constant (x_{11}) by standard procedures.

TABLE 1

Wavenumbers (cm^{-1}) and assignments of bands observed in the resonance Raman spectra at *ca.* 80 K

$\{[Pt(en)_2][Pt(en)_2X_2]\}_3[CuX_4]_4$ X = Cl		$\{[Pt(en)_2][Pt(en)_2X_2]\}_3[CuX_4]_4$ X = Br		$[Pt(pn)_2][Pt(pn)_2Br_2][Cu_3Br_5]_2$	
				175.8	ν_1, $\nu(Br–Pt^{IV}–Br)$
		38.9		214.9	
84.9		166.8	ν_1, $\nu(Br–Pt^{IV}–Br)$	250.0	
117.1		207.4		351.7	$2\nu_1$
181.0		236.8		386.8	$\nu_1 + 214.9$
214.0		333.0	$2\nu_1$	425.9	$\nu_1 + 250.0$
		499.5	$3\nu_1$	527.3	$3\nu_1$
298.0	$\nu_1,\nu(Cl–Pt^{IV}–Cl)$	577.1	$\nu(Pt–N)$	568.5	$2\nu_1 + 214.9$
		665.0	$4\nu_1$	601.8	$2\nu_1 + 250.0$
512.5	$\nu_1 + 214.0$	743.9	$\nu_1 + \nu(Pt–N)$	701.8	$4\nu_1$
593.6	$2\nu_1$	830.4	$5\nu_1$	876.2	$5\nu_1$
886.4	$3\nu_1$	910.7	$2\nu_1 + \nu(Pt–N)$	1 047.3	$6\nu_1$
1 176.9	$4\nu_1$	994.0	$6\nu_1$	1 220.4	$7\nu_1$
1 466.8	$5\nu_1$	1 077.0	$3\nu_1 + \nu(Pt–N)$	1 259.3	$\delta(H–C–H)$
1 754.7	$6\nu_1$	1 154.0	$7\nu_1$	1 392.5	$8\nu_1$
2 041	$7\nu_1$	1 244.0	$4\nu_1 + \nu(Pt–N)$	1 432.3	$\nu_1 + \delta(H–C–H)$
2 323	$8\nu_1$	1 271.7	$\delta(H–C–H)$	1 565.2	$9\nu_1$
2 608	$9\nu_1$	1 311.7	$8\nu_1$	1 613.2	$2\nu_1 + \delta(H–C–H)$
2 878	$10\nu_1$	1 410.5	$5\nu_1 + \nu(Pt–N)$	1 739.5	$10\nu_1$
3 153	$11\nu_1$	1 437	$\nu_1 + \delta(H–C–H)$	1 785.2	$3\nu_1 + \delta(H–C–H)$
3 428	$12\nu_1$	1 470	$9\nu_1$	1 909	$11\nu_1$
3 703	$13\nu_1$	1 577	$6\nu_1 + \nu(Pt–N)$	1 958	$4\nu_1 + \delta(H–C–H)$
3 980	$14\nu_1$	1 623	$10\nu_1$	2 079	$12\nu_1$
		1 781	$11\nu_1$	2 249	$13\nu_1$
		1 939	$12\nu_1$	2 413	$14\nu_1$
				2 581	$15\nu_1$
				2 743	$16\nu_1$
				2 910	$17\nu_1$

TABLE 2

Summary of results on complexes studied

Complex	$\{[Pt(en)_2][Pt(en)_2X_2]\}_3[CuX_4]_4$ X = Cl	$\{[Pt(en)_2][Pt(en)_2X_2]\}_3[CuX_4]_4$ X = Br	$[Pt(pn)_2][Pt(pn)_2Br_2][Cu_3Br_5]_2$
Crystal colour	Green needles	Gold needles	Green-gold needles
Powder colour	Mauve	Blue	Mauve
Mixed-valence band max./cm^{-1}	19 100	15 870	19 000
Excitation profile max./cm^{-1} (Stokes ν_1)	13 300	13 300	15 000
ω_1/cm^{-1}	300.5 ± 0.4	168.6 ± 0.3	176.6 ± 0.2
x_{11}/cm^{-1}	−1.16 ± 0.05	−0.52 ± 0.04	−0.27 ± 0.02
Progression (ν_1) at *ca.* 80 K	$14\nu_1$	$12\nu_1$	$17\nu_1$
$(Pt^{II}–X)$/Å	2.933		3.07
$(Pt^{IV}–X)$/Å	2.331		2.55
$(Pt^{II}–Pt^{IV})$/Å	5.264	5.448	5.62
$I(2\nu_1)/I(\nu_1)$ (maximum)	0.46	0.46	0.51

The results of such analyses on the present data are given in Table 2 and Figure 8. In all cases the mode which displays the r.r. effect is close to behaving as a simple harmonic oscillator.

The r.r. spectra of the complexes also display weak subsidiary progressions, $\nu_n + v_1\nu_1$, in which ν_1 is the progression-forming mode and ν_n is another Raman-active mode. The wavenumbers and assignments of these enabling modes, which include ν(PtN) and δ(HCH), are

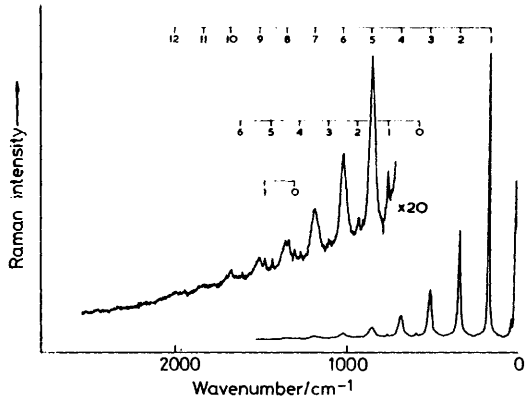

FIGURE 6 Resonance-Raman spectrum of $\{[Pt(en)_2][Pt(en)_2Br_2]\}_3[CuBr_4]_4$ in a KBr disc at *ca.* 80 K. λ_0 = 647.1 nm. Slit ≈ 1.5 cm^{-1}

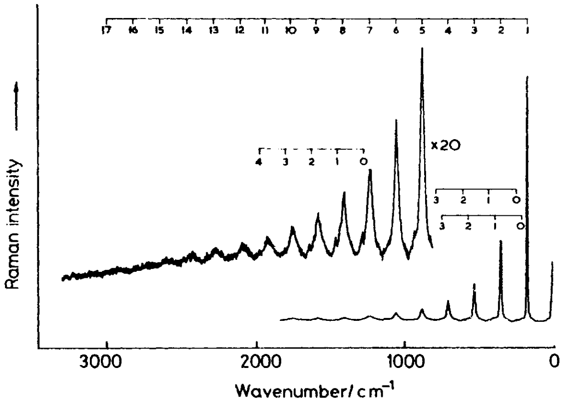

FIGURE 7 Resonance-Raman spectrum of $[Pt(pn)_2][Pt(pn)_2Br_2][Cu_3Br_5]_2$ in a KBr disc at *ca.* 80 K. λ_0 = 568.2 nm. Slit ≈ 1.5 cm^{-1}

also included in Table 1. No bands attributable to the copper-containing anion chains could be identified.

The excitation profiles of the Stokes ν_1 bands and, in the case of the bromo-complexes, also those of the $2\nu_1$ and $3\nu_1$ bands and of the anti-Stokes ν_1 bands, are included in Figures 2—4. The maxima of all the profiles (Table 2) are shifted to the low-energy side of the electronic band maxima, as is typical for linear-chain complexes.[2-4]

The bands observed in the i.r. spectra in the region 200—450 cm^{-1} are at 260s, 298m, and 359s for complex (1), at 237s, 254m, 296m, and 353s for complex (2), and at 233m, 285w, and 325m for complex (3). The bands at 359, 237, and 233 cm^{-1} are assigned to the antisymmetric (X–Pt^{IV}–X) stretching mode of the chain platinum–halogen bonds of (1), (2), and (3) respectively.

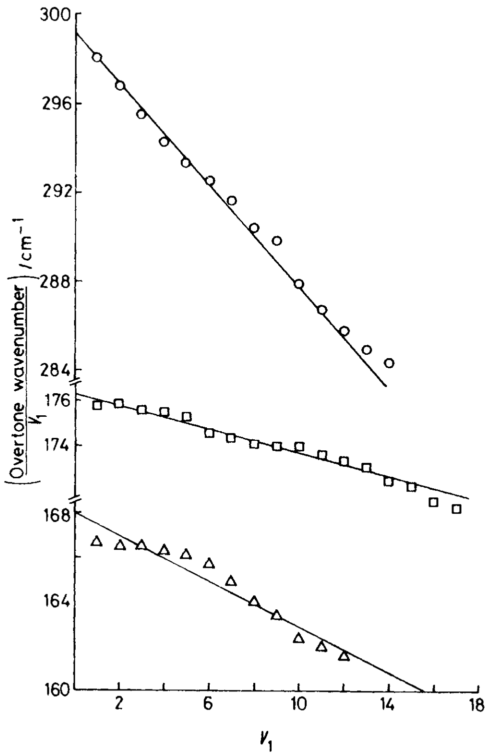

FIGURE 8 Plot of the ν_1 overtone wavenumber divided by the vibrational quantum number, v_1, against v_1, for {[Pt(en)$_2$][Pt(en)$_2$Cl$_2$]}$_3$[CuCl$_4$]$_4$ (○), [Pt(pn)$_2$][Pt(pn)$_2$Br$_2$][Cu$_3$Br$_5$]$_2$ (□), and {[Pt(en)$_2$][Pt(en)$_2$Br$_2$]}$_3$[CuBr$_4$]$_4$ (△)

DISCUSSION

The most immediately remarkable features of linear-chain mixed-valence complexes of platinum are their colours. Nearly all such chloro-complexes previously studied form as red crystals (green when large) which remain red when ground to fine powders. Complex (1) forms as mauve crystals (by transmission) with a greenish reflection; these crystals also appear mauve when ground to a fine powder. The consequence of these slight colour differences between complex (1) and previously studied chloro-complexes of this sort is that whereas (1) has its Pt^{II}→Pt^{IV} intervalence transition maximum at 19 100 cm^{-1}, those for previously studied chloro-complexes occur in the 20 000—25 000 cm^{-1} region.[5,10] This result is evidently a consequence of the fact that the Pt$^{II}\cdots$Pt^{IV} distance in complex (1) (5.264 Å) is less than that for all other such chloro-complexes yet studied (5.39—5.48 Å).

Complex (2) shows similar trends when compared with other bromo-complexes of this sort previously studied. It forms as gold needles (dark blue by transmitted light, gold by reflection, blue as a powder), whereas related bromo-complexes form as green-gold needles. In consequence, the Pt^{II}→Pt^{IV} intervalence transition of complex (2) maximises at 15 870 cm^{-1}, significantly lower than for eight other such complexes studied (18 250—23 600 cm^{-1}).[5,10] This result also appears to be a consequence of the shortness of the Pt$^{II}\cdots$Pt^{IV} distance in complex (2) (5.448 Å) as compared with that for other related bromo-complexes (5.462—6.095 Å).

One further bromo-complex still under study displays a similar correlation between the Pt^{II}→Pt^{IV} transition maximum and the Pt$^{II}\cdots$Pt^{IV} distance, *viz.* [Pt(pn)$_2$][Pt(pn)$_2$Br$_2$]Br$_4$; it shows an even shorter Pt$^{II}\cdots$Pt^{IV} distance (5.338 Å) and an even lower intervalence transition maximum (14 300 cm^{-1}) than reported above for complex (2). Thus there can be little doubt that these two properties are closely interrelated.

A further consequence of the shortness of the Pt$^{II}\cdots$Pt^{IV} distance in complexes (1) and (2) is the relatively low value observed for the symmetric X–Pt^{IV}–X, ν_1, vibration. The ω_1 value (300.5 cm^{-1} for the chloride, 168.6 cm^{-1} for the bromide) is less in each case than the range of all previously observed ω_1 values for this type of chain complex, *viz.* 306.0—319.5 cm^{-1} for the chlorides, 169.8—182.5 cm^{-1} for the bromides.*

Although several factors might be expected to affect the intervalence band maximum, the Pt$^{II}\cdots$Pt^{IV} distance, and the ν_1 band wavenumber (such as steric effects and electronic requirements of both the amines as well as the counter ions), the conclusion seems inescapable that a low value for the intervalence band maximum is associated with a short Pt$^{II}\cdots$Pt^{IV} distance and also with a low ν_1 band wavenumber. What factor is responsible for the short Pt$^{II}\cdots$Pt^{IV} distances in chain complexes of this sort remains, however, obscure. Possibly the copper–halogen anion chains impose a compression on the Pt$^{II}\cdots$X–Pt^{IV} chains, and thus make the platinum atoms approach the situation of a Pt^{III}–X–Pt^{III} chain, *i.e.* one containing formally equivalent platinum(III) atoms.

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* The complex [Pt(NH$_3$)$_2$Br$_2$][Pt(NH$_3$)$_2$Br$_4$] appears exceptional in that both the intervalence transition maximum (< 13 000 cm^{-1}) as well as the ν_1 value (165.4 cm^{-1}) are low, suggesting a rather shorter Pt$^{II}\cdots$Pt^{IV} distance than actually reported (5.54 Å). The rather early *X*-ray data on this complex would bear restudy, J. Wallén, C. Brosset, and N.-G. Vannenberg, *Arkiv Kemi*, 1961, **18**, 541.

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