The Synthesis, *X*-Ray Crystal Structure, and Electronic and Vibrational Characterisation of the Mixed-valence, Iodine-bridged Complex $[\mathrm{Pt^{II}(dien)I}][\mathrm{Pt^{IV}(dien)I_3}]\mathrm{I_2}$ †

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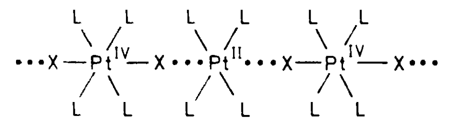
The complex $[\mathrm{Pt(dien)I}][\mathrm{Pt(dien)I_3}]\mathrm{I_2}$ (dien = diethylenetriamine) can be obtained as bronze crystals by partial oxidation of [Pt(dien)Cl]Cl with iodine in dilute hydroiodic acid. *X*-Ray structure analysis of the complex shows it to belong to the orthorhombic space group *Pmcn*, with a = 8.797(1), b = 12.028(2), c = 22.863(3) Å, and Z = 4. Refinement on 1 635 reflections yielded final discrepancy indices R = 0.043 and R' = 0.060. The structure consists of ordered $\mathrm{I{-}[Pt^{IV}(dien)I]{-}I} \cdots [\mathrm{Pt^{II}(dien)I}] \cdots$ chains, with significant bending (*ca.* 21°) about the bridging iodine atom. Pairs of equatorial $\mathrm{Pt^{IV}}$(dien)I and $\mathrm{Pt^{II}}$(dien)I units are oppositely oriented when viewed along the chain direction. The equatorial Pt–N bonds *cis* to the equatorial Pt–I bond in the $\mathrm{Pt^{II}}$ unit have lengths essentially equal to those of the corresponding bonds in the $\mathrm{Pt^{IV}}$ unit (*ca.* 2.09 Å), but the Pt–N bond *trans* to the equatorial Pt–I bond is significantly shorter in the $\mathrm{Pt^{II}}$ unit [1.97(1) Å] than in the $\mathrm{Pt^{IV}}$ unit [2.03(1) Å]. Likewise, the equatorial $\mathrm{Pt^{II}{-}I}$ bond length [2.596(1) Å] is less than the equatorial $\mathrm{Pt^{IV}{-}I}$ bond length [2.650(1) Å]. The electronic spectrum of the complex is dominated by an intense, broad $\mathrm{Pt^{IV}}(d_{z^2}) \longleftarrow \mathrm{Pt^{II}}(d_{z^2})$ intervalence band, centred at 15 500 cm^{-1}, together with other bands at higher energies. The resonance Raman spectrum of the complex displays a long overtone progression, $v_1\nu_1$ to v_1 = 7, and a combination band progression ($v_1\nu_1 + \nu_2$) to v_1 = 4, where ν_1 and ν_2 are the symmetric $\nu(\mathrm{Pt{-}I})_{\mathrm{ax.}}$ and $\nu(\mathrm{Pt{-}I})_{\mathrm{eq.}}$ modes, respectively. The complex represents the first halogen-bridged mixed-valence chain complex to be fully characterised in which each unit carries a +1 charge only, and the first to be characterised in which each platinum ion is co-ordinated to a tridentate ligand.

Of the many classes of mixed-valence complex,[1-4] that which has been most intensively studied spectroscopically is the 'class II', or 'localised valence' type, especially that typified by the halogen-bridged platinum(II,IV) complexes as shown



above, where L is usually a monodentate amine and X = Cl, Br, or I. In some cases, bidentate amines (L–L) have occupied the equatorial positions.[1-5] So far, all the known and fully characterised complexes of this type have carried +2, 0, −1, or −2 charges per $[\mathrm{Pt^{IV}L_4X_2}]$ or $[\mathrm{Pt^{II}L_4}]$ unit (depending on the charge type of L), the appropriate number of counter ions being present and occupying positions between the chains.[6-10] Curiously, however, only two complexes have been reported for which each platinum unit carries a +1 charge only, namely $[\mathrm{Pt(NH_3)_3Br}][\mathrm{Pt(NH_3)_3Br_3}]\mathrm{Br_2}$ and $[\mathrm{Pt(en)(NH_3)I}][\mathrm{Pt(en)(NH_3)I_3}]\mathrm{I_2}$ (en = 1,2-diaminoethane), for neither of which is any *X*-ray structural or spectroscopic evidence available with which to support the formulation.[5] In the course of our studies of complexes of this type we now report the preparation of $[\mathrm{Pt(dien)I}][\mathrm{Pt(dien)I_3}]\mathrm{I_2}$ (dien = diethylenetriamine), together with the results of *X*-ray structural, electronic, i.r. and resonance Raman studies. These studies identify this complex as the first, definitively characterised, mixed-valence platinum complex of the +1 charge type and also, the first such chain complex to be characterised in which a tridentate ligand occupies three equatorial positions on each platinum atom.

Experimental

Preparation.—[Pt(dien)Cl]Cl was prepared by the method of Bailey and Johnson.[11] To an aqueous solution of [Pt(dien)-Cl]Cl, a solution of iodine in hydroiodic acid was added, which resulted in the formation of a black precipitate. This was dissolved in water and allowed to stand for about a fortnight, to give bronze crystals of $[\mathrm{Pt(dien)I}][\mathrm{Pt(dien)I_3}]\mathrm{I_2}$. The crystals were filtered off, washed with a small amount of cold water and acetone, and dried in air (Found: C, 7.1; H, 1.8; I, 55.6; N, 6.2. $\mathrm{C_4H_{13}I_3N_3Pt}$ requires C, 7.1; H, 1.95; I, 56.05; N, 6.2%). Attempts to prepare the chloro- or bromo-analogues have so far been unsuccessful.

Structure Determination.—The quality of the crystals was checked photographically. The crystal used for the collection of the intensity data was mounted in a Lindemann capillary, the crystal dimensions being 0.2 × 0.1 × 0.1 mm.

Crystal data. $\mathrm{C_8H_{26}I_6N_6Pt_2}$, M = 1 357.95, Orthorhombic, a = 8.797(1), b = 12.028(2), c = 22.863(3) Å, U = 2 419.2 Å^3, space group *Pmcn* (alternative setting of *Pnma*), Z = 4, D_c = 3.727 g cm^{-3}, D_m not measured, $\mu(\text{Mo-}K_\alpha)$ = 182.62 cm^{-1}, $F(000)$ = 2 360.

Data collection. A Nonius CAD4 diffractometer was used, with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å), ω—2θ scan mode; 2 464 data were measured ($1.5 \leqslant \theta \leqslant 25°$), of which 1 635 were considered observed [$I > 1.5\sigma(I)$]; the data were corrected for absorption empirically.

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† *catena*-(Diethylenetriamine)-μ-iodo-iodoplatinum(II, IV) diiodide.

Supplementary data available (No. SUP 23610, 17 pp.): observed and calculated structure factors, anisotropic thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt(1)	0.250	0.239 3(1)	0.303 13(6)	N(11)	0.250	0.080(2)	0.273(1)
Pt(2)	0.250	0.166 2(1)	0.553 14(6)	C(11)	0.406(3)	0.060(2)	0.240(1)
I(12)	0.250	0.327 5(2)	0.193 8(1)	C(12)	0.520(3)	0.105(2)	0.282(1)
I(21)	0.250	0.150 1(2)	0.411 2(1)	N(12)	0.485(2)	0.224(2)	0.297 4(8)
I(11)	0.250	0.443 5(2)	0.346 6(1)	N(21)	0.250	0.170(3)	0.049(2)
I(22)	0.750	0.049 1(2)	0.439 1(1)	C(21)	0.407(3)	0.130(2)	0.021(2)
I(1)	0.750	0.368 6(2)	0.392 3(1)	C(22)	0.519(3)	0.194(3)	0.048(2)
I(2)	0.750	0.304 4(2)	0.176 3(1)	N(22)	0.486(2)	0.317(2)	0.051(1)

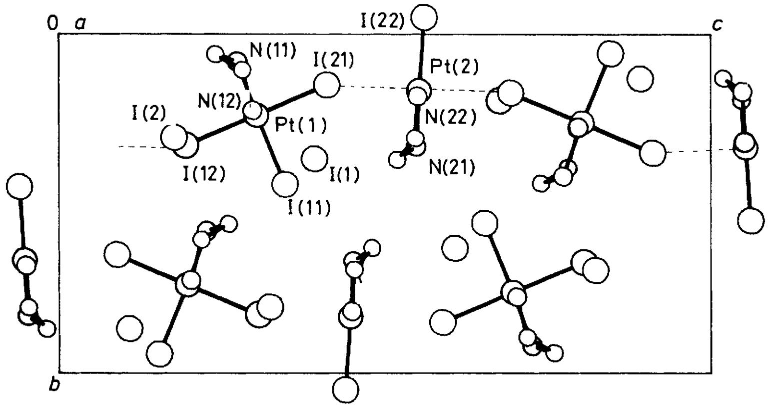

Figure 1. Packing diagram for the complex $[Pt^{II}(dien)I][Pt^{IV}(dien)I_3]I_2$, showing the atom-numbering scheme

Structure determination and refinement. The Patterson and heavy-atom method was used, with full-matrix least-squares refinement, all atoms being assigned anisotropic thermal parameters. Hydrogen atoms were not included. Final R $(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and R' $(= [\Sigma||F_o| - |F_c||^2/\Sigma F_o^2]^{\frac{1}{2}})$ values were 0.043 and 0.060, respectively. Unit weights were used throughout. Final atomic fractional co-ordinates are given in Table 1. Computers, programs, and sources of scattering factor data are as given elsewhere.[12]

Spectroscopic Studies.—Electronic spectra were recorded on a Cary 14 spectrometer (CsI disc, by transmission, at room temperature). Infrared spectra were recorded using a Perkin-Elmer 225 spectrometer (4 000—200 cm^{-1}, CsI disc) and a Nicolet 7199 interferometer (400—40 cm^{-1}, Nujol mull between Polythene plates).

Raman spectra were recorded with a Spex 1401 double monochromator with 1 200 line mm^{-1} Bausch and Lomb gratings and a Spex 14 018 (R6) double/triple monochromator with 1 800 line mm^{-1} Jobin-Yvon holographic gratings. Coherent Radiation CR3 Ar^+ and Kr^+ lasers provided the excitation radiation. Detection was by photon-counting techniques, employing cooled RCA C31034 photomultipliers. All spectra were recorded at *ca.* 80 K using a Dewar assembly, from samples of the complex dispersed in CsI or K_2SO_4 discs.

Band wavenumbers were measured by reference to emission lines of neon. All band intensities [full-height × full-width at half-maximum (f.w.h.m.)] were corrected for the response of the instruments. The a_1 band of SO_4^{2-} at 986 cm^{-1} was used as internal standard for excitation profile measurements.

Results and Discussion

Description of the Structure.—The structure of the complex consists of long parallel chains, each being made up of alternate $I-[Pt^{IV}(dien)I]-I$ and $[Pt^{II}(dien)I]$ units linked together by iodine bridges (Figures 1 and 2). Each of the [Pt(dien)I] units lies across a mirror plane which bisects the tridentate ligand, with the three nitrogen atoms occupying meridional positions in the equatorial square planes. The platinum and bridging iodine atom sites are ordered, this having the consequence that each metal atom is designated as being either Pt^{II} or Pt^{IV}. Although ordered chains have been established for certain other related chain complexes, namely $[Pt^{II}(NH_3)_4][Pt^{IV}(NH_3)_4I_2][HSO_4]_3[OH]\cdot H_2O$,[7] it is more generally the case for this sort of complex that the metal atom sites behave as though they are disordered ($\frac{1}{2}Pt^{II} + \frac{1}{2}Pt^{IV}$).[10]

Although the $I-Pt^{IV}-I$ and $I-Pt^{II}-I$ groups are essentially linear (179.5 and 177.9°, respectively), the $Pt^{II} \cdots I-Pt^{IV}$ angles deviate markedly from linearity (there being two different such angles, of 158.4 and 153.1°). There are also two different $Pt^{II} \cdots Pt^{IV}$, $Pt^{II} \cdots I$, and $Pt^{IV}-I$ distances in the complex (Table 2). Although several halogen-bridged chain complexes of platinum have non-linear chains, the present complex displays the greatest known deviation from linearity. This is probably a consequence of the fact that pairs of $Pt^{II}(dien)I$ and $Pt^{IV}(dien)I$ units have opposite orientations when viewed along the chain direction.

The $Pt^{II}N_3I$ and $Pt^{IV}N_3I$ units are nearly planar with the greatest distortion from true square-planar geometry occurring in-plane, with $N-Pt^{II}-N$ and $N-Pt^{IV}-N$ angles of 168.6 and 167.5°, respectively. The $I-Pt^{II}-N'$ and $I-Pt^{IV}-N'$ angles are 179.2 and 177.6°, respectively (N' is the bridgehead nitrogen atom); the $Pt^{II}N_3I$ unit thus appears to be the less distorted {*cf.* the structures of the complexes [Pt(dien)Cl]Cl [13] and [Pt(dien)Br]Br [14]}. As for other *mer* complexes of diethylenetriamine, each ring adopts the *gauche* form and the ligand either the $\lambda\delta$ or $\delta\lambda$ configuration, depending on which molecule in the cell is considered (λ is the mirror image of δ, and each dien lies across a mirror plane). The dihedral

Table 2. Bond lengths (Å) and interbond angles (°) for $[Pt(dien)I][Pt(dien)I_3]I_2$

Pt(1)–I(12)	2.715(1)	C(12)–N(12)	1.503(9)	I(11)–Pt(1)–N(12)	96.1(2)	N(21)–Pt(2)–N(22)	84.4(2)
Pt(1)–I(21)	2.693(1)	N(21)–C(21)	1.590(10)	N(11)–Pt(1)–N(12)	84.0(2)	N(22)–Pt(2)–N(22)	168.6(4)
Pt(1)–I(11)	2.650(1)	C(21)–C(22)	1.393(14)	N(12)–Pt(1)–N(12)	167.5(3)	Pt(1)–I(12)–Pt(2)	158.4(1)
Pt(1)–N(11)	2.032(7)	C(22)–N(22)	1.510(13)	I(12)–Pt(2)–I(21)	177.9(1)	Pt(1)–I(21)–Pt(2)	153.1(1)
Pt(1)–N(12)	2.084(6)	I(12)–Pt(1)–I(21)	179.5(1)	I(12)–Pt(2)–I(22)	87.4(1)	Pt(1)–N(11)–C(11)	107.9(4)
Pt(2)–I(12)	3.217(1)	I(12)–Pt(1)–I(11)	89.1(1)	I(12)–Pt(2)–N(21)	91.7(3)	N(11)–C(11)–C(12)	102.2(5)
Pt(2)–I(21)	3.252(1)	I(12)–Pt(1)–N(11)	93.3(2)	I(12)–Pt(2)–N(22)	91.1(2)	C(11)–C(12)–N(12)	111.1(6)
Pt(2)–I(22)	2.596(1)	I(12)–Pt(1)–N(12)	88.7(2)	I(21)–Pt(2)–I(22)	90.5(1)	Pt(1)–N(12)–C(12)	107.5(4)
Pt(2)–N(21)	1.974(10)	I(21)–Pt(1)–I(11)	91.4(1)	I(21)–Pt(2)–N(21)	90.4(3)	Pt(2)–N(21)–C(21)	108.6(5)
Pt(2)–N(22)	2.090(6)	I(21)–Pt(1)–N(11)	86.2(2)	I(21)–Pt(2)–N(22)	89.1(2)	N(21)–C(21)–C(22)	106.1(8)
N(11)–C(11)	1.590(8)	I(21)–Pt(1)–N(12)	91.3(2)	I(22)–Pt(2)–N(21)	179.2(3)	C(21)–C(22)–N(22)	115.0(8)
C(11)–C(12)	1.496(11)	I(11)–Pt(1)–N(11)	177.6(2)	I(22)–Pt(2)–N(22)	95.6(2)		

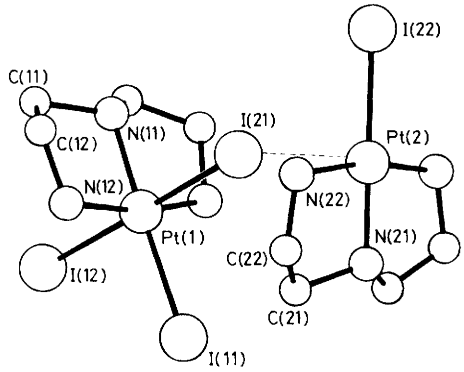

Figure 2. Co-ordination environment of the $I[Pt^{IV}(dien)I]I\cdots[Pt^{II}(dien)I]$ entity, illustrating the geometry of the dien ligand at Pt(1) and Pt(2)

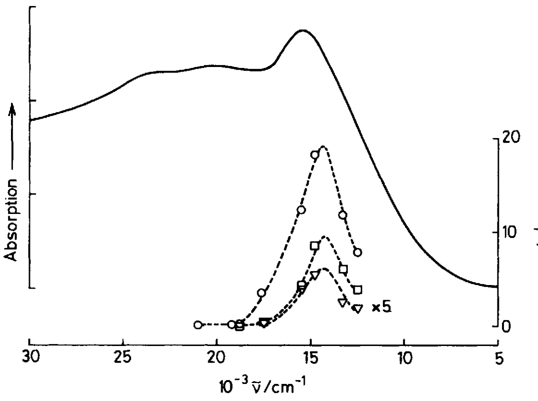

Figure 3. Electronic spectrum (CsI disc, 295 K, transmission) of $[Pt^{II}(dien)I][Pt^{IV}(dien)I_3]I_2$, together with the excitation profiles of the ν_1 (○), $2\nu_1$ (□), and ν_2 bands (▽) of the $Pt^{II}\cdots I-Pt^{IV}-I\cdots$ chain (K_2SO_4 intensity reference)

(torsion) angles N–C–C–N are ±56° for the dien on Pt(1) and ±46.7° for that on Pt(2).

As expected for a ' class II ', or ' localised valence ', complex the chain Pt^{IV}–I bond lengths (2.693 and 2.715 Å) are substantially less than the chain Pt^{II}–I distances (3.217 and 3.252 Å). There are also small differences between related equatorial bond lengths, namely the equatorial Pt^{II}–I bond length (2.596 Å), which is less than the equatorial Pt^{IV}–I distance (2.650 Å) and, where N′ is the bridgehead nitrogen atom, the Pt^{II}–N′ bond length (1.97 Å) is less than the Pt^{IV}–N′ bond length (2.03 Å). The equatorial Pt–N bonds *cis* to the equatorial Pt–I bond in the Pt^{II} unit have lengths essentially equal to those in the related Pt^{IV} unit (*ca.* 2.09 Å).

Table 3. Wavenumbers (cm^{-1}) of bands observed in the i.r. spectrum of $[Pt(dien)I][Pt(dien)I_3]I_2$

$\tilde{\nu}/cm^{-1}$	Assignment	$\tilde{\nu}/cm^{-1}$	Assignment
3 210vs	$\nu(NH_2)$	877m	$\rho(CH_2)$
3 170vs		836s	$\nu(C-N)$
3 105		780m	$\rho(NH_2)$
3 050vs	$\nu(NH)$	758m	
2 880w	$\nu(CH)$	596m	$\nu(Pt-N)$
2 750w		565w	
1 570vs	$\delta(NH_2)$	510m	
1 440s	$\delta(CH_2)$	500 (sh)	
1 425s	$\delta(NH)$	466m	$\delta(NCC)$
1 367w	$\omega(CH_2)$	402w	
1 352w		386w	$\delta(NCC)$
1 337s		284m	$\delta(N-Pt-N)$
1 290s	$\gamma(CH_2)$	262ms	
1 280s		253w	
1 252s		235w	
1 165s (sh)		187w	$\nu(Pt-I)$
1 153vs	$\gamma(NH_2)$	178s	
1 125w	$\omega(NH_2)$	169s	
1 077vs	$\nu(CC)$	152m	
1 070 (sh)	$\nu(CN)$	124m	
1 050s		105w	
1 030w			
1 015w			
992s	$\gamma(NH_2)$	89w	$\delta(I-Pt-I)$ + lattice
980 (sh)		84m	
919ms	$\nu(CN)$	78m	
		63vw	
		55vw	

Electronic and Infrared Spectra.—The crystals of the complex appear metallic, with a bronze reflection. They are pleochroic, appearing black, red, or orange as the polarisation of the incident beam is changed. The transmission spectrum of the complex (Figure 3) displays three bands, at 15 500, 20 000, and 23 500 cm^{-1}, that at lowest energy being assigned to the $Pt^{IV} \longleftarrow Pt^{II}$ intervalence transition.

The wavenumbers and assignments of the bands observed in the i.r. spectrum of the complex at 295 K are listed in Table 3. The spectrum is dominated by bands due to ligand modes, these being found to be of similar intensities and wavenumbers to those found for [Pt(dien)Cl]Cl [15] and [Pd(dien)-X]X (X = Cl or Br).[16,17]

Raman and Resonance Raman Spectra.—Since crystals of the complex were too small to permit single-crystal Raman studies, the Raman spectrum could only be obtained for the finely ground powder. Excitation with blue or green lines

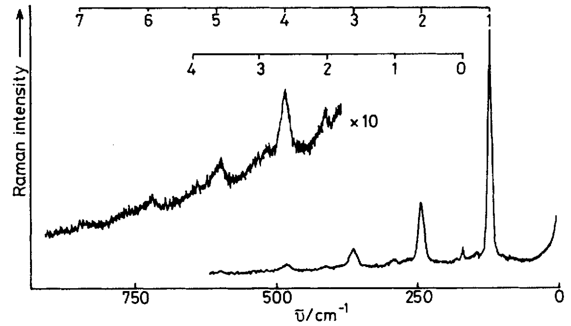

Figure 4. Resonance Raman spectrum of $[Pt^{II}(dien)I][Pt^{IV}(dien)I_3]I_2$ as a K_2SO_4 disc at *ca*. 80 K (λ_0 = 676.4 nm)

Table 4. Wavenumbers (cm^{-1}), relative intensities, f.w.h.m. ($\Delta\bar{\nu}_{\frac{1}{2}}$), and assignments of bands observed in the resonance Raman spectrum * of $[Pt(dien)I][Pt(dien)I_3]I_2$

$\bar{\nu}/cm^{-1}$	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\bar{\nu}_{\frac{1}{2}}/cm^{-1}$	Assignment
120.2	1.00	5.9	$\nu_1,\nu_{sym}(I-Pt^{IV}-I)_{ax.}$
168.9			$\nu_2,\nu(Pt-I)_{eq.}$
241.3	0.49	10.2	$2\nu_1$
289.9			$\nu_1 + \nu_2$
361.0	0.23	13.0	$3\nu_1$
410.9			$2\nu_1 + \nu_2$
480.2	0.12	17	$4\nu_1$
515			$\nu(Pt-N)$
528			$3\nu_1 + \nu_2$
598.7	0.06	21	$5\nu_1$
719	0.03	24	$6\nu_1$
835	<0.03	>25	$7\nu_1$

* Obtained as a K_2SO_4 disc with 676.4 nm excitation at *ca*. 80 K.

(457.9—530.9 nm) gives rise to a simple Raman spectrum consisting essentially of two bands assigned to ν_1, the symmetric $I-Pt^{IV}-I$ axial stretching mode, and ν_2, the Pt–I equatorial stretching mode. However, by use of yellow (568.2 nm) or red (647.1—799.3 nm) lines, overtones $v_1\nu_1$ and combination tones ($v_1\nu_1 + \nu_2$) are observed. The peak heights of these bands increase, and their widths decrease as the temperature of the sample is lowered and, in consequence, longer progressions are observed for samples held at low temperatures. The progressions reach $7\nu_1$ and ($4\nu_1 + \nu_2$) if the sample is held at *ca*. 80 K and 676.4 nm excitation is used (Figure 4). The wavenumbers, full-widths at half-maximum, and relative intensities of the bands are listed in Table 4.

Analysis of the measured band wavenumbers by standard procedures[18] allows an estimate to be made for the harmonic wavenumber ω_1 and for the anharmonicity constant x_{11}; these were found to be 120.6 ± 0.3 cm^{-1} and −0.26 ± 0.03 cm^{-1}, respectively. These values are similar to those of other iodine-bridged chain complexes.[6]

The excitation profiles of the Stokes ν_1, $2\nu_1$, and ν_2 bands (Figure 3) all maximize within the contour of the 15 500 cm^{-1} intervalence band of the complex. This demonstrates that both ν_1 and ν_2, but especially the former (which is the more enhanced), are coupled to the intervalence transition. Both this result and the slight red shift (*ca*. 1 200 cm^{-1}) of the maxima in the excitation profiles with respect to the resonant absorption band maximum are typical of the optical behaviour of halogen-bridged mixed-valence platinum complexes.[10] The result demonstrates that it is mainly the axial $Pt^{IV}-I$ bond which alters its length on excitation to the intervalence $Pt^{III}\cdots X\cdots Pt^{III}$ state, but that a small change also occurs to the equatorial $Pt^{IV}-I$ bond length.

Conclusions

By the synthesis and the spectroscopic and *X*-ray structural characterisation of the title complex, we have established unambiguously, for the first time, the existence of a chain mixed-valence platinum complex in which each platinum unit carries a single positive charge only. The complex is also the first chain complex established in which the platinum atoms are co-ordinated to a tridentate ligand.

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