The Syntheses, Structures, and Electronic and Resonance-Raman Spectroscopy of Halogen-bridged Platinum(II,IV) Chain Complexes involving Equatorially Co-ordinated Terdentate Amines: *X*-Ray Crystal Structure of $[Pt^{II}(Me\text{-}dien)I][Pt^{IV}(Me\text{-}dien)I_3]I_2$, and Spectroscopy of $[Pt^{II}(dien)(NO_2)][Pt^{IV}(dien)(NO_2)Br_2]Br_2$ †,‡

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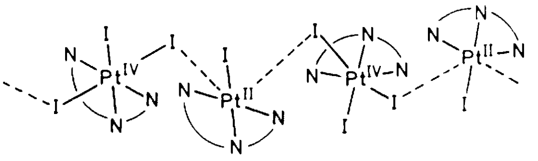
Three chain platinum(II,IV) complexes of the type $[PtL_3X][PtL_3XY_2]Z_2$ (L_3 = terdentate ligand, X = halogen or NO_2^-, Y = halogen, Z = monoanion) have been synthesised. Two of these have been studied in detail, one by *X*-ray and the other by spectroscopic methods. The first, $[Pt(Me\text{-}dien)I][Pt(Me\text{-}dien)I_3]I_2$ (Me-dien = *N*-methyldiethylenetriamine), has been found to crystallize in the monoclinic space group $P2_1/n$, with a = 19.830(8), b = 12.220(5), c = 11.079(6) Å, β = 96.49(4)°, and Z = 4. Refinement on 1 543 independent reflections led to a final R value of 0.043. The Pt–I chain distances are 2.679(3) and 2.691(3) Å (Pt^{IV}) and 3.443(3) and 3.560(3) Å (Pt^{II}), the chain deviating substantially at iodine and platinum(II) from linearity [Pt^{IV}–I–Pt^{II} = 150.5(1) and 149.1(1)°; I–Pt^{II}–I = 162.8(1)°], but not at platinum(IV) [I–Pt^{IV}–I = 179.4(1)°]. The second complex studied in detail, $[Pt(dien)(NO_2)][Pt(dien)(NO_2)Br_2]Br_2$ (dien = diethylenetriamine), was found to yield a very intense resonance-Raman spectrum, the principal observed progression being $v_1\nu_1$, where ν_1 (181.5 cm^{-1}) is the symmetric stretching mode of the chain, $\nu_{sym}(Br\text{–}Pt^{IV}\text{–}Br)$. Analysis of these data yields ω_1 and x_{11} values of 181.9 and −0.2 cm^{-1}, respectively. Further, much weaker, progressions of the sorts $v_1\nu_1 + \nu_{sym}(NO_2)$ (to v_1 = 5) and $v_1\nu_1 + \delta_{sym}(NO_2)$ (to v_1 = 4) were also detected. The results add substantially to the few previously known data on halogen-bridged mixed-valence chain complexes of platinum in which each unit carries a single positive charge.

The synthetic and structural chemistry, as well as the electronic and vibrational spectroscopy of mixed-valence chain complexes of platinum and palladium of most possible charge types have now been broadly established.[1,2] However, studies on complexes of the +1 charge type, *viz.* $[Pt^{II}L_3X][Pt^{IV}L_3XY_2]Z_2$, where L = a monodentate ligand (or L_3 = a terdentate ligand), X = a halogen or NO_2^-, Y = a halogen, and Z = a singly charged anion, remain poorly developed.[2] The only complex of this type which has yet been characterised crystallographically involves the terdentate ligand diethylenetriamine, $NH_2CH_2CH_2NHCH_2CH_2NH_2$ (dien); this occupies three of the four equatorial positions around each platinum atom in $[Pt(dien)I][Pt(dien)I_3]I_2$ as shown below.[3] The two unusual features of this complex as compared to those of the +2, 0, −1, or −2 charge types are (*a*) that the $Pt^{II}\cdots I\text{–}Pt^{IV}$ bridges are not linear, the angles at the iodine atoms being 158.4(1) and 153.1(1)°, and (*b*) that the terdentate ligands appear alternatively to be eclipsed in pairs when viewed down the chain direction. In order to study further this type of complex, we have embarked on a programme of research into the possibility of synthesising complexes of this sort with the more sterically hindered ligand *N*-methyldiethylenetriamine, $MeNHCH_2CH_2NHCH_2CH_2NH_2$ (Me-dien).[4] Two complexes of this sort have now been synthesised and the *X*-ray crystal structure of one of them, $[Pt^{II}(Me\text{-}dien)I][Pt^{IV}(Me\text{-}dien)I_3]I_2$, has been solved. In addition, the electronic, Raman, and resonance-Raman spectra of the dien complex $[Pt^{II}(dien)(NO_2)][Pt^{IV}(dien)(NO_2)Br_2]Br_2$ have been studied in detail; in particular, the Raman spectra of this complex at resonance with the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence band are found to be very rich in features and amenable to interpretation.



Experimental

Preparation of Complexes.—Commercial reagents were used without further purification.

$[Pt(Me\text{-}dien)I]I$ *and* $[Pt(Me\text{-}dien)I][Pt(Me\text{-}dien)I_3]I_2$. The new complexes $[Pt(Me\text{-}dien)I]I$ and $[Pt(Me\text{-}dien)I][Pt(Me\text{-}dien)I_3]I_2$ were prepared by methods similar to those already reported for the preparations of the analogous complexes of dien[5,6] [Found: C, 10.4; H, 2.6; I, 44.6; N, 7.1. $C_5H_{15}I_2N_3Pt$ requires C, 10.60; H, 2.65; I, 44.85; N, 7.40%. Found: C, 8.2; H,

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† *catena*-μ-Iodo-iodo(*N*-methyldiethylenetriamine)platinum(II,IV) iodide and *catena*-μ-bromo-[(diethylenetriamine)nitroplatinum(II)]-[dibromo(diethylenetriamine)nitroplatinum(IV)] dibromide respectively.

Supplementary data available (No. SUP 56360, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

‡ See ref. 4.

Table 1. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt(1)	1 307(1)	2 456(1)	1 307(1)
Pt(2)	3 717(1)	2 949(1)	−1 354(1)
I(1)	279(1)	1 632(2)	2 415(2)
I(2)	918(1)	4 475(2)	1 679(3)
I(3)	2 332(1)	3 293(3)	222(2)
I(4)	3 542(1)	5 045(2)	−1 286(2)
I(5)	3 875(1)	3 041(3)	3 637(2)
I(6)	1 690(1)	3 612(3)	5 659(2)
N(1)	1 991(12)	2 331(23)	2 852(21)
N(2)	1 632(13)	901(25)	1 037(23)
N(3)	687(13)	2 211(27)	−321(24)
N(4)	3 338(14)	2 857(27)	−3 121(25)
N(5)	3 858(13)	1 302(23)	−1 402(23)
N(6)	4 155(15)	2 793(29)	417(26)
C(1)	2 208(17)	1 142(36)	3 004(31)
C(2)	2 281(19)	694(33)	1 755(33)
C(3)	1 567(20)	621(35)	−292(34)
C(4)	805(18)	1 051(37)	−696(32)
C(5)	738(18)	2 978(35)	−1 406(32)
C(6)	3 299(19)	1 604(34)	−3 398(33)
C(7)	3 886(17)	967(34)	−2 708(31)
C(8)	4 464(20)	1 031(39)	−534(36)
C(9)	4 318(21)	1 599(41)	615(37)
C(10)	4 839(16)	3 448(31)	681(28)

1.7; I, 53.0; N, 5.4. $C_5H_{15}I_3N_3Pt$ requires C, 8.65; H, 2.20; I, 54.95; N, 6.00%].

[Pt(Me-dien)I][Pt(Me-dien)I_3][I_5]$_2$. To a suspension of [Pt(Me-dien)I]I (0.150 g, 0.25 mmol) in water (20 cm^3) was added iodine (0.125 g, 0.5 mmol) and the heterogeneous mixture stirred at 60 °C for 5 h. As the iodine dissolves it reacts with the [Pt(Me-dien)I]I to form a black precipitate which was separated, washed first with a solution of NaI (to remove excess of iodine) and then with water, and dried in air. [This method is similar to that used by Chernyaev *et al.*[7] for the preparation of $Pt(NH_2CH_2CH_2NH_2)(CN)_2I$.] The product was dissolved in the minimum volume of *NN*-dimethylformamide and the solution placed in a test tube in contact with a layer of three times its own volume of water. After being allowed to stand for two weeks, metallic black crystals separated out. These were collected, washed with water, and dried in air [Found: C, 5.4; H, 1.3; I, 70.0; N, 3.5. $C_5H_{15}I_7N_3Pt$ requires C, 5.00; H, 1.25; I, 74.0; N, 3.50%] (the low value found for iodine may be due to partial substitution of I_5^- by I_3^- or I^-; it is to be noted that replacement of an I^- and I_5^- by two I_3^- ions would give the same analytical results).

[Pt(dien)(NO_2)][Pt(dien)(NO_2)Br_2]Br_2. The complex [Pt(dien)(NO_2)][Pt(dien)(NO_2)Br_2]Br_2 was first reported by Badar-Ud-Din and Bailar,[8] and has been prepared both by their method as well as by the more general one of mixing equimolar solutions of the constituent species [Pt(dien)(NO_2)]Br and [Pt(dien)(NO_2)Br_2]Br, the latter having been obtained from the former by oxidation with bromine [Found: C, 9.4; H, 2.7; Br, 31.4; N, 10.7. $C_4H_{13}Br_2N_4O_2Pt$ requires C, 9.55; H, 2.60; Br, 31.70; N, 11.10%].

X-Ray Crystallography.—*Crystal data.* [Pt($C_5H_{15}N_3$)I][Pt($C_5H_{15}N_3$)I_3]I_2, M = 1 385.99, monoclinic, a = 19.830(8), b = 12.220(5), c = 11.079(6) Å, β = 96.49(4)°, U = 2 667(2) Å^3 (by least-squares refinement from the θ values of 28 reflections accurately measured), space group $P2_1/n$, Z = 4, D_c = 3.451 g cm^{-3}, μ(Mo-K_α) = 174.73 cm^{-1}, $F(000)$ = 2 424. Crystal dimensions: 0.15 × 0.20 × 0.20 mm.

Data collection and processing. Siemens AED diffractometer, niobium-filtered Mo-K_α radiation (λ = 0.710 69 Å), θ/2θ scan mode, 3 801 independent reflections measured ($3 \leqslant \theta \leqslant 23°$), 1 543 observed [$I \geqslant 2\sigma(I)$], data corrected for absorption[9] (max. and min. transmission factors on F, 1.2943 and 0.8190 respectively) using ASSORB.[10]

Structure analysis and refinement. Patterson and heavy-atom methods were used, full-matrix least-squares refinement with anisotropic thermal parameters for Pt and I atoms in the last cycles. Hydrogen atoms were not included. The weighting scheme used in the last cycle was $w = 0.2907/[\sigma^2(F_o) + 0.0032F_o^2]$. The final R ($= \Sigma\Delta/\Sigma F_o$, $\Delta = |F_o - F_c|$) and R' [$= (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$] values were 0.043 and 0.051 respectively. Calculations were performed on the CYBER-76 computer of the Centro di Calcolo Elettronico Interuniversitario dell' Italia Nord-Orientale, Bologna, using the SHELX[11] system of programs. Atomic scattering factors, corrected for anomalous dispersion of Pt and I were from ref. 12. Final atomic co-ordinates are given in Table 1.

Spectroscopy.—The electronic spectra of the complexes as Nujol mulls were recorded by transmission on a Cary 14 spectrometer. The Raman spectra were recorded on a Spex 14018 (R6) spectrometer with 1 800 line mm^{-1} gratings (Jobin-Yvon, holographic). Coherent Radiation CR 3000 K and CR12 lasers provided the exciting lines. Detection was by photon counting using a cooled RCA C 31034 photomultiplier. Raman spectra were recorded on samples dispersed in K[ClO_4] or KBr discs held at *ca.* 80 K using a Dewar assembly. The a_1 band of $[ClO_4]^-$ at 936 cm^{-1} was used as internal intensity standard. Band wavenumbers were measured by reference to emission lines of mercury. Excitation profiles relate to band intensities calculated as the products of peak height and full-width half-maximum for each exciting line.

Results and Discussion

General Description of the Complexes.—The iodide complexes are black with a metallic reflection and, from their method of preparation and general appearance, are considered to be chain iodide-bridged complexes. Their electronic spectra possess a very broad absorption band beginning in the i.r. region and with no definable maximum. The Raman spectra of the iodide complexes are of poor quality and no conclusive assignments could be made in the low-wavenumber region owing to overlap between bands due to $\nu(Pt\text{–}I)_{ax.}$ and $\nu(Pt\text{–}I)_{eq.}$, as well as to bands possibly attributable to I_3^- or I_5^- modes. However, the complex [Pt(Me-dien)I][Pt(Me-dien)I_3]I_2 could be prepared as well formed crystals from which the *X*-ray crystal structure was determined. This confirms that the complex is a chain iodide-bridged species, and has allowed a careful evaluation of the effects of the methyl group on the nature of the ··· I–Pt–I ··· chain. In particular, a structural comparison of this complex with [Pt(dien)I][Pt(dien)I_3]I_2[3] is possible.

Attempts to solve the *X*-ray crystal structure of the polyiodide complex were unsuccessful. Thus its formulation can only be speculated upon, but a reasonable guess would be [Pt(Me-dien)I][Pt(Me-dien)I_3][I_5]$_2$; however, the anion has not been identified for certain.

The related complex [Pt(dien)(NO_2)][Pt(dien)(NO_2)Br_2]Br_2, in which the equatorially co-ordinated halogen is replaced by a nitro-group, has also been studied. It readily yields very detailed resonance-Raman spectra, similar to that of Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]. This suggests a structural similarity between the complexes, the latter being known from crystallographic work to possess a chain structure with equatorially co-ordinated nitro-groups.[13]

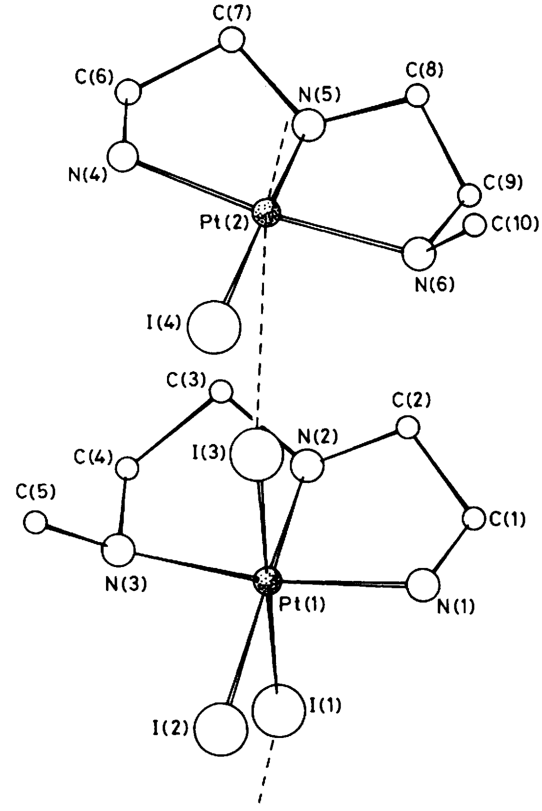

Figure 1. Chain of alternating $[Pt^{IV}(Me\text{-}dien)I_3]^+$ and $[Pt^{II}(Me\text{-}dien)I]^+$ cations with the atomic numbering scheme

Table 2. Selected bond distances (Å) and angles (°)

Pt(1)–I(1)	2.691(3)	N(2)–C(2)	1.46(4)
Pt(1)–I(2)	2.631(3)	N(2)–C(3)	1.50(5)
Pt(1)–I(3)	2.679(3)	C(3)–C(4)	1.61(5)
Pt(1)–N(1)	2.07(2)	N(3)–C(4)	1.50(6)
Pt(1)–N(2)	2.04(3)	N(3)–C(5)	1.54(5)
Pt(1)–N(3)	2.09(2)	N(4)–C(6)	1.56(5)
Pt(2)–I(4)	2.587(3)	C(6)–C(7)	1.53(5)
Pt(2)–N(4)	2.02(3)	N(5)–C(7)	1.51(4)
Pt(2)–N(5)	2.03(3)	N(5)–C(8)	1.49(5)
Pt(2)–N(6)	2.06(3)	C(8)–C(9)	1.51(6)
N(1)–C(1)	1.52(5)	N(6)–C(9)	1.51(6)
C(1)–C(2)	1.51(5)	N(6)–C(10)	1.57(4)
I(1)–Pt(1)–I(2)	91.6(1)	Pt(1)–N(1)–C(1)	108(2)
I(1)–Pt(1)–I(3)	179.4(1)	N(1)–C(1)–C(2)	107(3)
I(2)–Pt(1)–I(3)	87.9(1)	C(1)–C(2)–N(2)	106(3)
I(1)–Pt(1)–N(1)	93.1(7)	C(2)–N(2)–C(3)	118(3)
I(1)–Pt(1)–N(2)	89.2(8)	C(2)–N(2)–Pt(1)	111(2)
I(1)–Pt(1)–N(3)	86.4(7)	C(3)–N(2)–Pt(1)	111(2)
I(2)–Pt(1)–N(1)	96.7(7)	N(2)–C(3)–C(4)	100(3)
I(2)–Pt(1)–N(2)	178.6(7)	C(3)–C(4)–N(3)	114(3)
I(2)–Pt(1)–N(3)	96.6(8)	C(4)–N(3)–C(5)	109(3)
I(3)–Pt(1)–N(1)	86.5(7)	C(4)–N(3)–Pt(1)	106(2)
I(3)–Pt(1)–N(2)	91.2(7)	C(5)–N(3)–Pt(1)	120(2)
I(3)–Pt(1)–N(3)	94.0(7)	Pt(2)–N(4)–C(6)	104(2)
N(1)–Pt(1)–N(2)	82.2(11)	N(4)–C(6)–C(7)	112(3)
N(1)–Pt(1)–N(3)	166.7(12)	C(6)–C(7)–N(5)	103(3)
N(2)–Pt(1)–N(3)	84.5(11)	C(7)–N(5)–C(8)	116(3)
I(4)–Pt(2)–N(4)	92.7(9)	C(7)–N(5)–Pt(2)	108(2)
I(4)–Pt(2)–N(5)	179.8(7)	C(8)–N(5)–Pt(2)	108(2)
I(4)–Pt(2)–N(6)	96.2(9)	N(5)–C(8)–C(9)	103(3)
N(4)–Pt(2)–N(5)	87.5(12)	C(8)–C(9)–N(6)	112(4)
N(4)–Pt(2)–N(6)	171.0(13)	C(9)–N(6)–C(10)	107(3)
N(5)–Pt(2)–N(6)	83.6(11)	C(9)–N(6)–Pt(2)	107(2)
		C(10)–N(6)–Pt(2)	113(2)

Description of the Structure of $[Pt(Me\text{-}dien)I][Pt(Me\text{-}dien)I_3]I_2$.—The crystal structure of the title compound consists of iodide anions and of alternating $[Pt^{IV}(Me\text{-}dien)I_3]^+$ and $[Pt^{II}(Me\text{-}dien)I]^+$ cations, Pt^{IV} [Pt(1)] having distorted octahedral, and Pt^{II} [Pt(2)] square-planar co-ordination (Figure 1); the bond distances and angles are listed in Table 2. The two types of complex cation are linked together in chains by iodine bridges (Figure 2). In each chain the platinum and iodine atoms occupy ordered positions so that each metal atom is either Pt^{II} or Pt^{IV} [Pt^{IV}–I bond distances 2.679(3) and 2.691(3), $Pt^{II} \cdots$ I distances 3.443(3) and 3.560(3) Å]; moreover the chain deviates substantially from linearity as indicated by the values of the Pt^{IV}–I–Pt^{II} [150.5(1) and 149.1(1)°] and I–Pt^{II}–I angles [162.8(1)°]. The I–Pt^{IV}–I group is, on the other hand, essentially linear [179.4(1)°]. It is worth noting that the methyl groups on successive ligands occupy staggered rather than eclipsed positions as viewed along the chain direction.

The $Pt^{IV}N_3I$ and $Pt^{II}N_3I$ units are practically planar, the maximum deviation from the mean plane being 0.03 Å for N(2) and N(6). The Pt^{II}–N [2.02(3), 2.03(3), and 2.06(3) Å] and Pt^{II}–I bond distances [2.587(3) Å] are slightly shorter than the corresponding ones in the Pt^{IV} unit [Pt^{IV}–N = 2.04(3), 2.07(2), and 2.09(2) Å; Pt^{IV}–I = 2.631(3) Å]. The N–Pt–N and N′–Pt–I angles (N′ being the bridgehead nitrogen atom) are respectively 171.0(13) and 179.8(7)° in the Pt^{II} unit, 166.7(12) and 178.6(7)° in the Pt^{IV} unit, so that the former appears to be the less distorted. The Pt^{II} unit is also less distorted than the Pt^{IV} unit in $[Pt(dien)I][Pt(dien)I_3]I_2$.[3]

The structure of the present complex (with a methyl substituent at a terminal nitrogen atom of the dien ligand) is similar to that of the complex with unsubstituted dien.[3] The most significant differences concern the $Pt^{II} \cdots$ I distances [3.443(3) and 3.560(3), *versus* 3.217(1) and 3.252(1) Å for the Me-dien and dien complexes, respectively], the Pt^{II}–I–Pt^{IV} angles [150.5(1) and 149.1(1) *versus* 158.4(1) and 153.1(1)°], the I–Pt^{II}–I angles [162.8(1) *versus* 177.9(1)°], and the $Pt^{II} \cdots Pt^{IV}$ distance in the chain [5.923(4) and 6.029(4) Å in the Me-dien complex *versus* 5.783(2) and 5.827(2) Å in the dien complex].

The longer and more dissimilar $Pt^{II} \cdots$ I distances and the more marked deviations from linearity of the Pt^{II}–I–Pt^{IV} and I–Pt^{II}–I groups in the Me-dien derivative are probably due to the steric hindrance of the methyl group and to alterations in the extent of hydrogen bonding as a consequence of a methyl group replacing one hydrogen atom at a terminal nitrogen atom of the dien ligand. The Me-dien complex thus has more localised valences than has its dien analogue. In both cases the packing of the chains is determined by the network of hydrogen bonds which the hydrogen atoms of the $-NH_2$ and –NH– groups form with the iodide ions.

In both complexes the dien and Me-dien ligands present δλ or λδ conformation; in the dien complex the N–C–C–N torsion angles are ±56(2)° on Pt^{IV} and ±47(3)° on Pt^{II}, in the Me-dien case the torsion angles are −55(3) and 52(3)° on Pt^{IV} and 53(3) and −53(3)° on Pt^{II}. This conformation of the dien or Me-dien ligand allows them to be slightly concave, the concavity being oriented in the same sense throughout the chain but in the opposite sense in adjacent chains (Figure 2). Adjacent units either have the organic ligand with the same conformation (*e.g.* δλ) and are in all other respects eclipsed (except for the methyl groups) when viewed along the chain direction, or have adjacent ligands with the opposite conformation (*e.g.* δλ and λδ, respectively) in which case they are rotated by about 180°

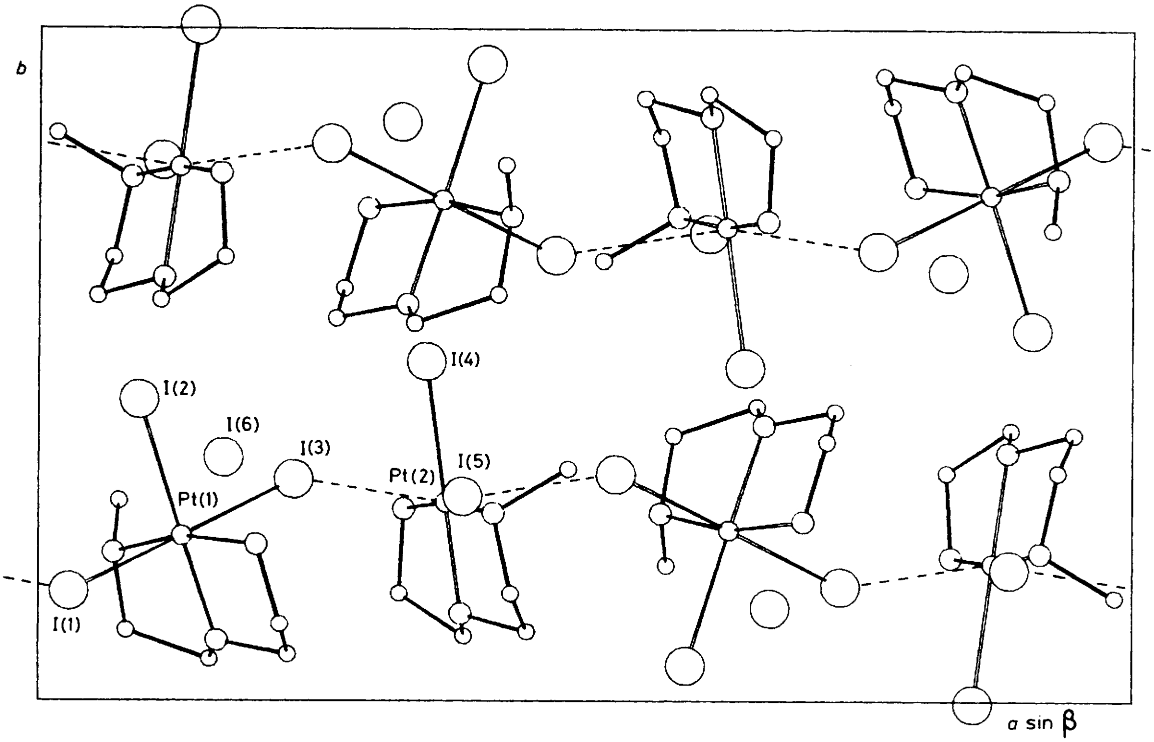

Figure 2. Projection along *c* showing the packing of the chains

around the chain direction. Both arrangements occur alternately within any given chain: probably that with eclipsed ligands allows the Pt^{II} and Pt^{IV} units to come closer to each other, while that with the ligands on opposite sides is required in addition in order to have overall chain linearity.

The introduction of the methyl substituent on the (co-ordinated) dien ligand results in longer Pt ··· Pt distances; in consequence the chain is more free to deviate from linearity and so minimise steric interactions.

Electronic and Vibrational Spectroscopy of $[Pt(dien)(NO_2)][Pt(dien)(NO_2)Br_2]Br_2$.—The complex $[Pt(dien)(NO_2)][Pt(dien)(NO_2)Br_2]Br_2$ is obtained as dark red dichroic crystals which appear dark red and light yellow with the electric vector of the incident beam parallel and perpendicular, respectively, to the chain axis. The electronic spectrum is dominated by a very intense, broad band centred at 21 000 cm^{-1} which is characteristic[1] of a $Pt^{II} \longrightarrow Pt^{IV}$ intervalence transition of a bromine-bridged chain complex, *cf.* that for $Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]$ is centred at 19 000 cm^{-1}.[13] Moreover, the complex displays a very rich resonance-Raman spectrum, similar to that of $Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]$, when irradiated with laser lines whose wavelengths (*e.g.* 476.5, 488.0, or 501.7 nm) fall within the contour of the intervalence band. The observed band maxima are listed, together with the band assignments, in Table 3.

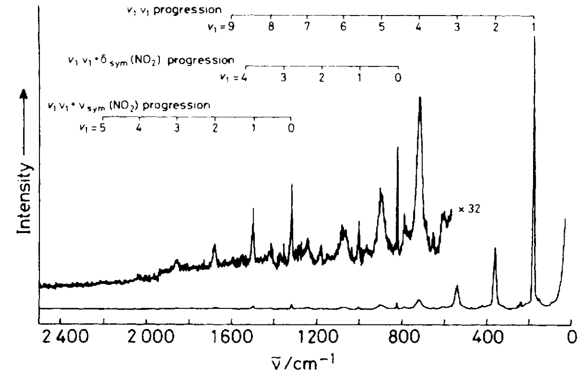

Figure 3. Resonance-Raman spectrum of $[Pt(dien)(NO_2)][Pt(dien)(NO_2)Br_2]Br_2$ as a KBr disc at *ca.* 80 K and 476.5 nm excitation (50 mW). Spectral slit width 1.5 cm^{-1}

The dominant features of the resonance-Raman spectrum of $[Pt(dien)(NO_2)][Pt(dien)(NO_2)Br_2]Br_2$ (Figure 3) are the members of the $v_1\nu_1$ progression (to $9\nu_1$), where ν_1 is the symmetric $Br-Pt^{IV}-Br$ chain mode of the chain bromine atoms. Thus the principal geometric change undergone by the complex on excitation to the intervalence state is an elongation of the axial $Pt^{IV}-Br$ bonds; this is typical of the behaviour of a wide range of other chain mixed-valence complexes of platinum and palladium.[1,2] However, other (albeit much less intense) progressions are also evident in the spectra. These all consist of progressions in ν_1 based on one quantum of another Raman-active mode; in particular, the symmetric stretching and bending modes of the nitro-group are particularly effective in this regard, progressions $v_1\nu_1 + \nu_{sym}(NO_2)$ and $v_1\nu_1 + \delta_{sym}(NO_2)$ each reaching as far as $v_1 = 5$ and 4, respectively. Other fundamentals which so act are ν(PtN) and, in particular, δ(NPtN); however, the involvement of $\nu(PtN)_{eq.}$ is invariably only slight in the resonance-Raman spectra of mixed-valence amine complexes[1] [much less than for $\nu(PtX)_{eq.}$] implying a low $(\partial\alpha/\partial Q)_0$ for this mode and little geometric change on excitation to the intervalence state. The involvement of nitro-group modes suggests that the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence transition alters the effective nuclear charge on each platinum atom, and hence the extent of $Pt(d_{xy}) \longrightarrow NO_2(\pi^*)$ back bonding and the equilibrium geometry of the NO_2 group in the intervalence state. The closely similar spectroscopic behaviour of the NO_2 group

Table 3. Wavenumbers (cm^{-1}), relative intensities, and assignments of bands observed in the resonance-Raman spectrum of [Pt(dien)(NO$_2$)][Pt(dien)(NO$_2$)Br$_2$]Br$_2$[a]

$\tilde{\nu}$/cm^{-1}	$I/I(\nu_1)$[b]	Assignment
96	0.03	
156	0.04	
181.5	1.0	ν_1, ν_{sym}(Br–Pt^{IV}–Br)
218	0.03	δ(NPtN)
243	0.04	δ(NPtN) [or $\rho_r(NO_2)$]
257	0.02	
277	0.02	96 + ν_1
363	0.27	$2\nu_1$
400	0.02	δ(NPtN) + ν_1
424	0.02	243 + ν_1
438	0.02	257 + ν_1
477	0.02	ν(PtN) or possibly δ(NCCN)
512	0.02	ν(PtN)
543	0.10	$3\nu_1$
603	0.02	243 + $2\nu_1$
618	0.02	257 + $2\nu_1$
659	0.02	ν(PtN) + ν_1
692	0.02	ν(PtN) + ν_1
724	0.05	$4\nu_1$
796	0.02	δ(NPtN) + $3\nu_1$
831	0.03	$\delta_{sym}(NO_2)$
905	0.02	$5\nu_1$
975	0.02	δ(NPtN) + $4\nu_1$
1 012	0.02	$\delta_{sym}(NO_2)$ + ν_1
1 084	0.02	$6\nu_1$
1 159	0.01	δ(NPtN) + $5\nu_1$
1 195	0.01	$\delta_{sym}(NO_2)$ + $2\nu_1$
1 259	0.02	$7\nu_1$
1 338	0.02	$\nu_{sym}(NO_2)$
1 380	0.01	$\delta_{sym}(NO_2)$ + $3\nu_1$
1 440	0.01	$8\nu_1$
1 519	0.02	$\nu_{sym}(NO_2)$ + ν_1
1 570	0.01	$\delta_{sym}(NO_2)$ + $4\nu_1$
1 616	0.01	$9\nu_1$
1 699	0.01	$\nu_{sym}(NO_2)$ + $2\nu_1$
1 880	0.01	$\nu_{sym}(NO_2)$ + $3\nu_1$
2 058	<0.01	$\nu_{sym}(NO_2)$ + $4\nu_1$
~2 240	<0.01	$\nu_{sym}(NO_2)$ + $5\nu_1$

[a] Obtained as a KBr disc with 476.5, 488.0, and 501.7 nm excitation (power, *ca.* 50 mW), the sample being held at *ca.* 80 K. Spectral slit width 1—1.5 cm^{-1}. [b] Peak heights relative to that of ν_1 = 1.0.

in this complex to that in Cs$_2$[Pt(NO$_2$)(NH$_3$)Br$_2$][Pt(NO$_2$)(NH$_3$)Br$_4$] suggests that as already established crystallographically for the latter,[13] the NO$_2$ group is oriented in the chain direction.

Analysis of the extensive resonance-Raman data on the complex by standard procedures[14] permits the calculation of the harmonic wavenumber, ω_1, and the anharmonicity constant, x_{11}. These are deduced (subject to the usual approximations)[14] to be 181.9 ± 0.3 and -0.2 ± 0.05 cm^{-1}, respectively, *i.e.* very close to the values found[13] for Cs$_2$[Pt(NO$_2$)(NH$_3$)Br$_2$][Pt(NO$_2$)(NH$_3$)Br$_4$], for which the corresponding values are 179.0 ± 0.3 and -0.39 ± 0.04 cm^{-1}, respectively. The ω_1 value found for the cation chain is thus slightly above that found for the anion chain, a typical result for this type of complex.[1]

The excitation profiles of ν_1, $2\nu_1$, $\nu_{sym}(NO_2)$, and $\delta_{sym}(NO_2)$ all mirror the contour of the intervalence band, as measured by transmission spectroscopy, except for a red shift of some 1 000 cm^{-1} and much smaller half-widths (Figure 4). Both of these features are typical of the optical behaviour of halogen-bridged mixed-valence complexes of platinum and palladium. The shoulder on the low-wavenumber side of the excitation profile is ill defined and its occurrence may be associated with the unexplained doubling of ν_1 (component separation 7 cm^{-1}) which develops with red excitation only.[15]

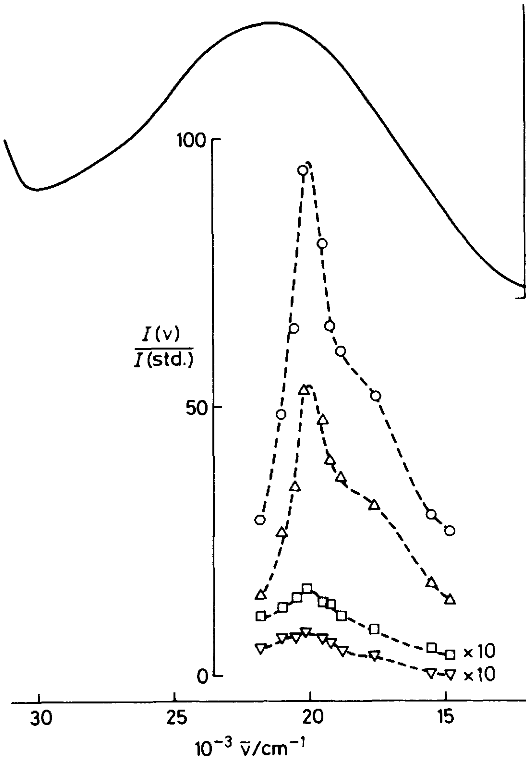

Figure 4. Electronic spectrum (Nujol mull, 295 K, transmission) of [Pt(dien)(NO$_2$)][Pt(dien)(NO$_2$)Br$_2$]Br$_2$, together with the excitation profiles of ν_1(○), $2\nu_1$(△), $\nu_{sym}(NO_2)$ (□), and $\delta_{sym}(NO_2)$ (▽) bands (K[ClO$_4$] disc, *ca.* 80 K)

Conclusions

The two complexes studied in detail are each examples of class II (localised valence) mixed-valence complexes of the relatively rare +1 charge type. Each also involves a terdentate amine co-ordinated in the equatorial positions. The Me-dien ligand imposes the greatest deviation of the ··· I–Pt^{IV}–I ··· Pt^{II} chain from linearity known for a chain complex of platinum or palladium.

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