Syntheses, Crystal Structures, and Raman and Resonance Raman Spectroscopy of Platinum(II), Platinum(IV), and Halogen-bridged Chain Platinum(II,IV) Complexes involving the Terdentate Ligand 3-Methyl-3-azapentane-1,5-diamine (4Me-dien)†

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The effect of introducing a methyl substituent onto the central nitrogen atom of the ligand dien (dien = diethylenetriamine or 3-azapentane-1,5-diamine) on the ease of formation of mixed-valence chain complexes of platinum has been investigated. The chain complex prepared by partial oxidation of [Pt(4Me-dien)I]I, *viz.* [Pt(4Me-dien)I][Pt(4Me-dien)I$_3$]I$_2$ (**4**) (4Me-dien = 3-methyl-3-azapentane-1,5-diamine), breaks down on recrystallisation to yield separate crystals of [Pt(4Me-dien)I]X [X = I$_3^-$ (**1**) or I$^-$ (**2**)] and [Pt(4Me-dien)I$_3$]I (**3**). *X*-Ray structural investigation of (**1**)—(**3**) and of similar discrete complexes of platinum reported previously indicate that dien co-ordinates in the planar (pseudo-*mer*) conformation in four-co-ordinate platinum(II) but in the bent (*fac*) conformation in six-co-ordinate platinum(IV) complexes. However, in mixed-valence chain complexes, dien is forced to co-ordinate to the platinum(IV) centre in the *mer* conformation. In the case of 4Me-dien the *mer* conformation around platinum(IV) is severely hindered; hence unless this species is trapped quickly between two platinum(II) entities it isomerises from *mer* to *fac*, thereby preventing the assembly of the mixed-valence chain complex. Complex (**4**) has a very intense Raman spectrum at resonance with the intervalence band, the principal observed progression being $v_1\nu_1$ [ν_1 (116.5 cm^{-1}) is the symmetric stretching mode of the chain, ν_{sym}(I–Pt^{IV}–I)]. The wavenumber of ν_1 found for this complex is lower than that of the analogous species with unsubstituted dien in accord with a lengthening of the Pt^{IV}–I linkage on N-methyl substitution of the ligand. Crystallographic data: (**1**), monoclinic, space group *P*2$_1$/*n*, *a* = 15.433(3), *b* = 7.856(5), *c* = 13.327(4) Å, β = 102.24(2)°, and *Z* = 4; (**2**), monoclinic, space group *P*2$_1$/*c*, *a* = 20.434(7), *b* = 8.267(2), *c* = 15.571(1) Å, β = 110.67(2)°, and *Z* = 8; (**3**), monoclinic, space group *P*2$_1$/*m*, *a* = 8.960(6), *b* = 10.561(4), *c* = 7.651(4) Å, β = 103.10(2)°, and *Z* = 2.

The syntheses, structures, and spectroscopy of mixed-valence chain complexes of platinum containing the terdentate ligands dien and 1Me-dien (dien = diethylenetriamine or 3-azapentane-1,5-diamine, 1Me-dien = *N*-methyl-3-azapentane-1,5-diamine) have been reported.[1,2] These complexes, [Pt(dien)I][Pt(dien)I$_3$]I$_2$ and [Pt(1Me-dien)I][Pt(1Me-dien)I$_3$]I$_2$, are the only ones of the relatively rare +1 charge type yet to have been structurally characterised[3] and they display interesting structural features. The dien ligands are eclipsed in alternate pairs along the chain; the puckering of the two condensed rings of each dien or 1Me-dien makes them slightly concave, the concavity being oriented in the same sense throughout the chain. The deviation from linearity of the iodide-bridged chain is larger than that observed for any other type of chain complex of platinum or palladium. We also observed that the introduction of a methyl substituent onto a terminal nitrogen atom of dien causes yet further bending of the chain centred on the I $\cdots$ Pt^{II} $\cdots$ I junctions and an overall increase of the Pt^{II} $\cdots$ Pt^{IV} distance. Moreover the ligands were arranged in such a way as to bring the methyl substituents into staggered rather than eclipsed positions as viewed along the chain direction.

It was considered of value to investigate what structural features would arise by the introduction of a methyl substituent onto the central rather than a terminal nitrogen atom of the dien ligand. The results of this study are reported herein.

Experimental

Preparation of Complexes.—Commercial reagents were used without further purification. 3-Methyl-3-azapentane-1,5-diamine (4Me-dien) was prepared according to the reported procedure.[4]

[Pt(4Me-dien)I]I (**2**). The salt K$_2$[PtCl$_4$] (500 mg, 1.2 mmol) was dissolved in water (7.5 cm^3) and treated with 4Me-dien·3HCl (633 mg, 2.79 mmol). The resulting solution was partially neutralised by addition of KOH (190 mg dissolved in 3 cm^3 of water) and then stirred for 24 h at 60 °C. During this time the colour changed from red to yellow. After being cooled to room temperature the solution was filtered, an excess of NaI (450 mg, 3 mmol) was added, and the solution stirred for 3 h. The brown precipitate which formed was separated and recrystallised from hot water to give pale yellow needles of the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Experimental data for the *X*-ray diffraction studies on complexes (**1**)—(**3**)

	(1)	(2)	(3)
Molecular formula	$C_5H_{15}I_4N_3Pt$	$C_5H_{15}I_2N_3Pt$	$C_5H_{15}I_4N_3Pt$
M	819.90	566.09	819.90
Space group	$P2_1/n$	$P2_1/c$	$P2_1/m$
a/Å	15.433(3)	20.434(7)	8.960(6)
b/Å	7.856(5)	8.267(2)	10.561(4)
c/Å	13.327(4)	15.571(1)	7.651(4)
β/°	102.24(2)	110.67(2)	103.10(2)
U/Å^3	1 579(1)	2 461(1)	705.2(7)
Z	4	8	2
D_c/g cm^{-3}	3.45	3.06	3.86
F(000)	1 424	2 000	712
Crystal dimensions/mm	0.15 × 0.17 × 0.20	0.20 × 0.25 × 0.25	0.15 × 0.20 × 0.33
Linear absorption/cm^{-1}	167.0	164.5	187.0
2θ range/°	6—46	6—50	6—54
Reflections measured	$\pm h, k, l$	$h, k, \pm l$	$\pm h, k, l$
Unique total data	2 138	4 322	1 639
Unique observed data $[I > 2\sigma(I)]$	1 416	1 922	1 237
R	0.0373	0.0349	0.0545
R'	0.0284	0.0436	0.0706

* Details common to all three complexes: crystal system, monoclinic; diffractometer, Siemens AED; scantype, θ—2θ; scan speed, 3—12° min^{-1}; scan width, $(\theta - 0.55)$ to $(\theta - 0.55 + 0.346 \tan\theta)$; radiation, niobium-filtered Mo-K_α (λ = 0.710 73 Å); standard reflections, 1 every 50.

pure product. Yield 415 mg, 61% (Found: C, 10.5; H, 2.7; I, 43.3; N, 7.3. $C_5H_{15}I_2N_3Pt$ requires C, 10.6; H, 2.7; I, 44.8; N, 7.4%).

[Pt(4Me-dien)I][Pt(4Me-dien)I_3]I_2 (**4**). Complex (**2**) (328 mg, 0.58 mmol) was dissolved in the minimum amount of water and treated with half the stoicheiometric amount of I_2 (73.5 mg, 0.29 mmol) and concentrated HI (0.15 cm^3). The suspension was stirred for 24 h in the dark, the black solid was separated, washed several times with water, and dried. Yield 350 mg, 87% (Found: C, 9.0; H, 2.3; I, 53.3; N, 5.8. $C_5H_{15}I_3N_3Pt$ requires C, 8.7; H, 2.2; I, 54.9; N, 6.1%).

All attempts to obtain crystals of this complex were unsuccessful. For instance it dissolves in hot water but, when the solution is cooled, [Pt(4Me-dien)I_3]I (**3**) precipitates in a pure form. Concentration of the solution afforded separate crystals of the square-planar complex (**2**) and the octahedral species (**3**). Complex (**4**) is a highly absorbing, black solid with no discernible electronic band maximum.

[Pt(4Me-dien)I_3]I_3 (**5**). Complex (**2**) (300 mg, 0.52 mmol), dissolved in the minimum amount of cold water, was treated with twice the stoicheiometric amount of I_2 (350 mg, 1.1 mmol) in aqueous solution (10 cm^3) containing some KI. The brown precipitate was stirred in an ice-bath for 15 min, filtered off, washed several times with water, and dried. Yield 390 mg, 90% (Found: C, 5.8; H, 1.4; N, 4.0. $C_5H_{15}I_6N_3Pt$ requires C, 5.6; H, 1.4; N, 3.9%).

If the reaction is carried out using the stoicheiometric amount of I_2 (Pt:I_2 = 1:1) the same product precipitates, while unreacted [Pt(4Me-dien)I]I is left in solution.

[Pt(4Me-dien)I_3]I (**3**). Complex (**5**) (350 mg, 0.32 mmol) was suspended in ethanol (50 cm^3) and held under reflux for 4 h. Red crystals of a new complex (**3**) separated; these were collected, washed several times with ethanol, and dried. Yield 240 mg, 91% (Found: C, 7.3; H, 1.8; I, 62.5; N, 5.1. $C_5H_{15}I_4N_3Pt$ requires C, 7.3; H, 1.8; I, 61.8; N, 5.1%).

Dark red crystals of this complex, suitable for *X*-ray diffraction, were obtained by slow concentration of an ethanol solution of complex (**3**) left at room temperature for several days.

[Pt(4Me-dien)I]I_3 (**1**). This complex was obtained in crystalline form together with [Pt(4Me-dien)I]I and [Pt(4Me-dien)I_3]I in an attempt to crystallise complex (**4**) from hot water.

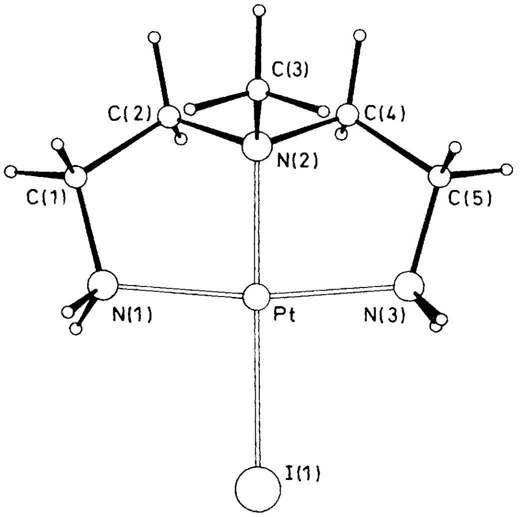

Figure 1. View of the structure of the cation [Pt(4Me-dien)I]$^+$ in (**1**) with the atomic numbering scheme

X-Ray Data Collection, Structure Determination, and Refinement for Complexes (**1**)—(**3**).—The crystallographic data for the three complexes are summarised in Table 1. Unit-cell parameters were determined from the θ values of 30 carefully centred reflections. Data were collected at room temperature, the individual profiles having been analysed following the procedures of Lehmann and Larsen.[5] A correction for absorption was applied [maximum and minimum values for the transmission factors were 1.42 and 0.75 for (**1**), 1.59 and 0.80 for (**2**), and 1.62 and 0.74 for (**3**)][6] using the program ABSORB.[7]

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, first with isotropic and then with anisotropic thermal parameters for all the non-hydrogen atoms in complexes (**1**) and (**2**), and only for the platinum and iodine atoms in (**3**). All the hydrogen atoms of the three complexes were placed at their geometrically calculated positions and introduced into the final structure-

Table 2. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for non-hydrogen atoms of complexes (**1**)—(**3**)

Atom	X/a	Y/b	Z/c
Complex (**1**)			
Pt	4 610(1)	5 589(1)	3 180(1)
I(1)	3 827(1)	3 025(2)	3 800(1)
I(2)	2 367(1)	3 609(2)	292(1)
I(3)	4 272(1)	2 923(2)	722(1)
I(4)	6 155(1)	2 283(2)	1 254(1)
N(1)	3 466(9)	6 738(18)	2 436(13)
N(2)	5 238(9)	7 560(20)	2 656(12)
N(3)	5 839(9)	4 602(20)	3 669(15)
C(1)	3 705(15)	8 269(26)	1 859(17)
C(2)	4 684(13)	8 097(26)	1 649(15)
C(3)	5 469(16)	9 080(23)	3 405(17)
C(4)	6 079(12)	6 983(27)	2 476(15)
C(5)	6 536(14)	5 861(26)	3 444(16)
Complex (**2**)			
Pt(1)	1 209(1)	2 100(1)	3 739(1)
I(11)	1 162(1)	4 570(2)	4 725(1)
I(21)	1 348(1)	−931(2)	6 393(1)
N(11)	527(11)	772(20)	4 156(12)
N(21)	1 221(9)	186(21)	2 959(11)
N(31)	1 959(8)	3 049(23)	3 276(11)
C(11)	428(14)	−830(32)	3 694(17)
C(21)	1 018(21)	−1 223(37)	3 379(26)
C(31)	676(18)	278(35)	2 011(18)
C(41)	1 913(23)	210(53)	2 830(35)
C(51)	2 114(14)	1 848(35)	2 650(16)
Pt(2)	6 198(1)	2 314(1)	7 430(1)
I(12)	6 286(1)	4 716(2)	6 418(1)
I(22)	6 334(1)	6 136(2)	9 922(1)
N(12)	6 898(9)	3 250(23)	8 601(10)
N(22)	6 147(9)	368(19)	8 222(10)
N(32)	5 552(8)	921(19)	6 362(11)
C(12)	7 045(12)	2 026(26)	9 346(13)
C(22)	6 852(11)	350(24)	8 974(15)
C(32)	5 610(12)	583(31)	8 642(17)
C(42)	6 011(12)	−1 066(27)	7 618(14)
C(52)	5 411(12)	−690(25)	6 739(15)
Complex (**3**)			
Pt	−1 672(1)	2 500	242(1)
I(1)	670(2)	2 500	−1 315(2)
I(2)	−2 904(1)	699(1)	−1 986(1)
I(3)	2 750(2)	2 500	4 851(2)
N(1)	−718(15)	1 115(12)	2 093(17)
N(2)	−3 421(21)	2 500	1 718(24)
C(1)	−1 532(19)	982(15)	3 546(22)
C(2)	−3 210(20)	1 302(16)	2 839(22)
C(3)	−5 062(31)	2 500	719(36)

factor calculation with isotropic thermal parameters. The SHELX system of computer programs was used.[8] Atomic scattering factors, corrected for the anomalous dispersion of platinum and iodine, were taken from ref. 9. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2.

All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

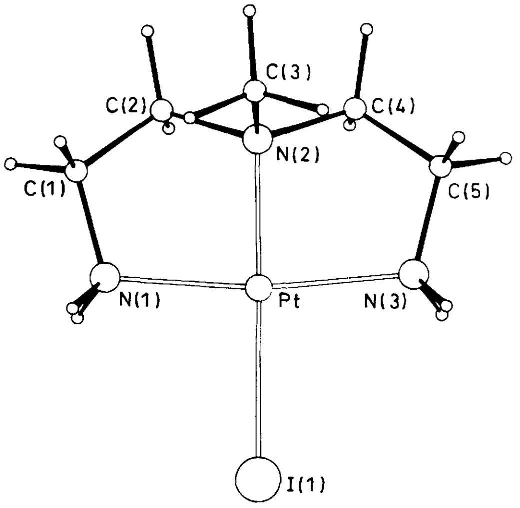

Figure 2. View of the structure of the cation [Pt(4Me-dien)I]$^+$ in (**2**) with the atomic numbering scheme

Table 3. Selected bond distances (Å) and angles (°) in the complex cations

	(**1**)	(**2a**)	(**2b**)	(**3**)
Pt–I(1)	2.574(2)	2.577(2)	2.581(2)	2.637(2)
Pt–N(1)	2.04(1)	2.05(2)	2.03(1)	2.08(1)
Pt–N(2)	2.03(2)	2.00(2)	2.05(2)	2.13(2)
Pt–N(3)	2.02(1)	2.06(2)	2.07(1)	
N(1)–C(1)	1.51(3)	1.49(3)	1.49(3)	1.47(2)
C(1)–C(2)	1.60(3)	1.49(6)	1.50(3)	1.52(2)
C(2)–N(2)	1.49(2)	1.47(4)	1.50(2)	1.52(2)
N(2)–C(3)	1.55(2)	1.51(3)	1.47(4)	1.50(3)
N(2)–C(4)	1.44(2)	1.50(6)	1.48(3)	
C(4)–C(5)	1.60(3)	1.47(5)	1.51(3)	
N(3)–C(5)	1.54(3)	1.50(4)	1.52(3)	
Pt–I(2)[a]				2.625(1)
I(1)–Pt–N(1)	94.9(4)	93.6(6)	94.4(5)	93.5(4)
I(1)–Pt–N(3)	93.9(5)	95.4(5)	95.7(4)	
N(1)–Pt–N(2)	85.6(6)	85.7(7)	85.9(7)	82.9(4)
N(1)–Pt–N(3)[b]	168.4(7)	170.0(7)	168.6(7)	89.4(5)
N(2)–Pt–N(3)	85.4(6)	85.4(7)	83.9(6)	
Pt–N(1)–C(1)	109(1)	108(2)	109(1)	113(1)
Pt–N(2)–C(2)	108(1)	107(2)	104(1)	107(1)
Pt–N(2)–C(3)	115(1)	113(2)	112(1)	119(1)
Pt–N(2)–C(4)	109(1)	107(2)	107(1)	
Pt–N(3)–C(5)	110(1)	109(1)	109(1)	
N(1)–C(1)–C(2)	111(2)	112(2)	112(2)	109(1)
C(1)–C(2)–N(2)	104(2)	111(2)	110(2)	112(1)
C(2)–N(2)–C(3)	112(1)	104(2)	108(2)	106(1)
C(2)–N(2)–C(4)[c]	108(1)	120(3)	114(2)	113(1)
C(3)–N(2)–C(4)	105(2)	106(3)	112(2)	
N(2)–C(4)–C(5)	107(2)	112(3)	109(2)	
C(4)–C(5)–N(3)	108(2)	110(3)	109(2)	
I(1)–Pt–I(2)[a]				88.12(5)
I(2)–Pt–N(1)[a]				88.9(4)
I(2)–Pt–I(2′)[a,d]				92.88(4)
I(2)–Pt–N(2)[a]				95.3(1)

[a] Only for compound (**3**). [b] N(1)–Pt–N(1′) in compound (**3**). [c] C(2)–N(2)–C(2′) in compound (**3**). [d] Primed atoms are related to unprimed ones by the transformation $x, \frac{1}{2} - y, z$.

Raman and Resonance Raman Spectroscopy.—The Raman and resonance Raman spectra of the complexes were recorded on a Spex 14018 (R6) spectrometer containing Jobin-Yvon holographic gratings with 1 800 lines mm^{-1}. Coherent Radiation Kr$^+$ (models 52 and CR3000K) and Ar$^+$ (Innova 70) lasers were used. Photon counting was effected by use of a cooled RCA C31034 photomultiplier. All complexes were analysed in the

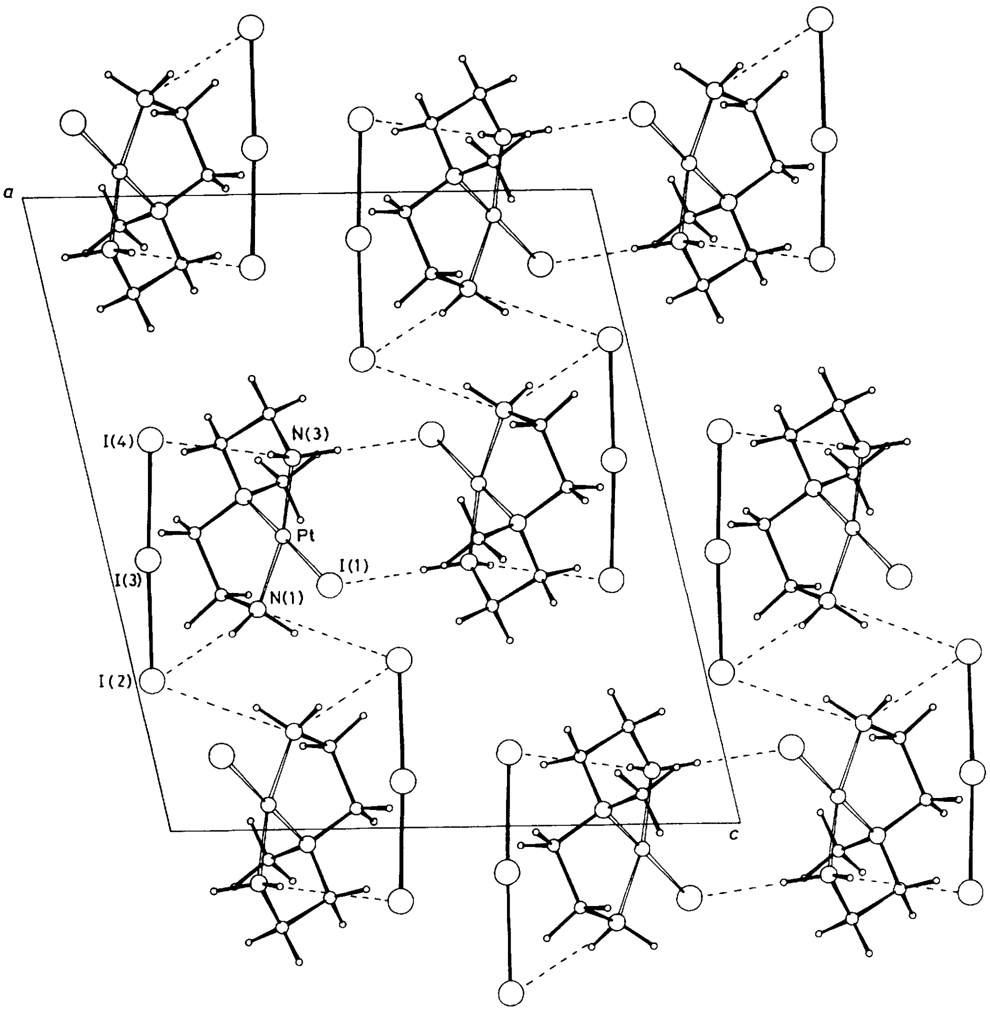

Figure 3. Projection of the structure of complex (**1**) along the [010] plane

form of pressed discs cooled to approximately 80 K. In the case of the mixed-valence complex, the sample was dispersed in K_2SO_4; the symmetric stretch of the anion, at approximately 986 cm^{-1}, was used as the internal intensity standard.

Results and Discussion

A common procedure for the preparation of mixed-valence chain complexes of platinum is to treat an aqueous solution of a platinum(II) species with half the amount of an oxidising agent required to oxidise this species to platinum(IV). Chain complexes, stacked alternately platinum(II)/platinum(IV), crystallise from such solutions, typically as long, deeply coloured needles. Thus treatment of (**2**) in water with I_2–HI led to the formation of the mixed-valence complex (**4**) in quantitative yield. However, all attempts to crystallise it in order to obtain good single crystals for an *X*-ray structural study resulted in the formation of separate crystals of the four- and six-co-ordinate species [Pt(4Me-dien)I]X [X = I_3^- (**1**) or I^- (**2**)] and [Pt(4Me-dien)I_3]I (**3**).

In order to understand the reason for this behaviour we undertook an *X*-ray structural investigation of the three mononuclear species involved.

Crystal Structures of the Complexes [Pt(4Me-dien)I]I_3 (**1**), [Pt(4Me-dien)I]I (**2**), *and* [Pt(4Me-dien)I_3]I (**3**).—Complexes (**1**) and (**2**) contain the same complex cation, $[Pt(4Me\text{-}dien)I]^+$, and different anions (I_3^- and I^-, respectively); two crystallographically independent molecules are present in (**2**), (**2a**) and (**2b**), but these are not significantly different from one another. In both (**1**) and (**2**) the complex cation approximates to C_s point-group symmetry, the mirror plane passing through the C(3), N(2), Pt, and I(1) atoms (Figures 1 and 2 respectively).

One iodine and three nitrogen atoms are bound to each platinum atom. A slight strain within the terdentate ligand is responsible for the observed deviations from the ideal square-planar co-ordination. These are: displacement on one side of the co-ordination plane [best weighted plane through Pt, I(1), N(1), N(2), and N(3)] of the terminal nitrogen atoms of the triamine [*ca.* 0.10 Å for N(1) and N(3)]; smaller values for N–Pt–N angles with respect to N–Pt–I (*ca.* 85 compared to 95°); folding of the Pt, N(1), N(2) and Pt, N(2), N(3) planes [7.2(6) and 4.8(6)° in (**1**) and (**2**), respectively].

The differences in bond lengths and angles between (**1**) and (**2**) (Table 3) are not significant and are probably determined by intermolecular interactions.

Figures 3 and 4 illustrate the crystal packing of complexes (**1**) and (**2**), respectively. Complex (**1**) consists of zigzagged layers of $[Pt(4Me\text{-}dien)I]^+$ cations and I_3^- anions parallel to the $(-1, 0, 1)$ plane. All four N-hydrogen atoms of each complex are involved in hydrogen bonds. One hydrogen atom interacts with the co-ordinated iodine atom of another complex and *vice versa* so that two complexes are linked together to form a duplex. Two more hydrogen atoms, one from each terminal nitrogen atom of the triamine, interact with an I_3^- anion which

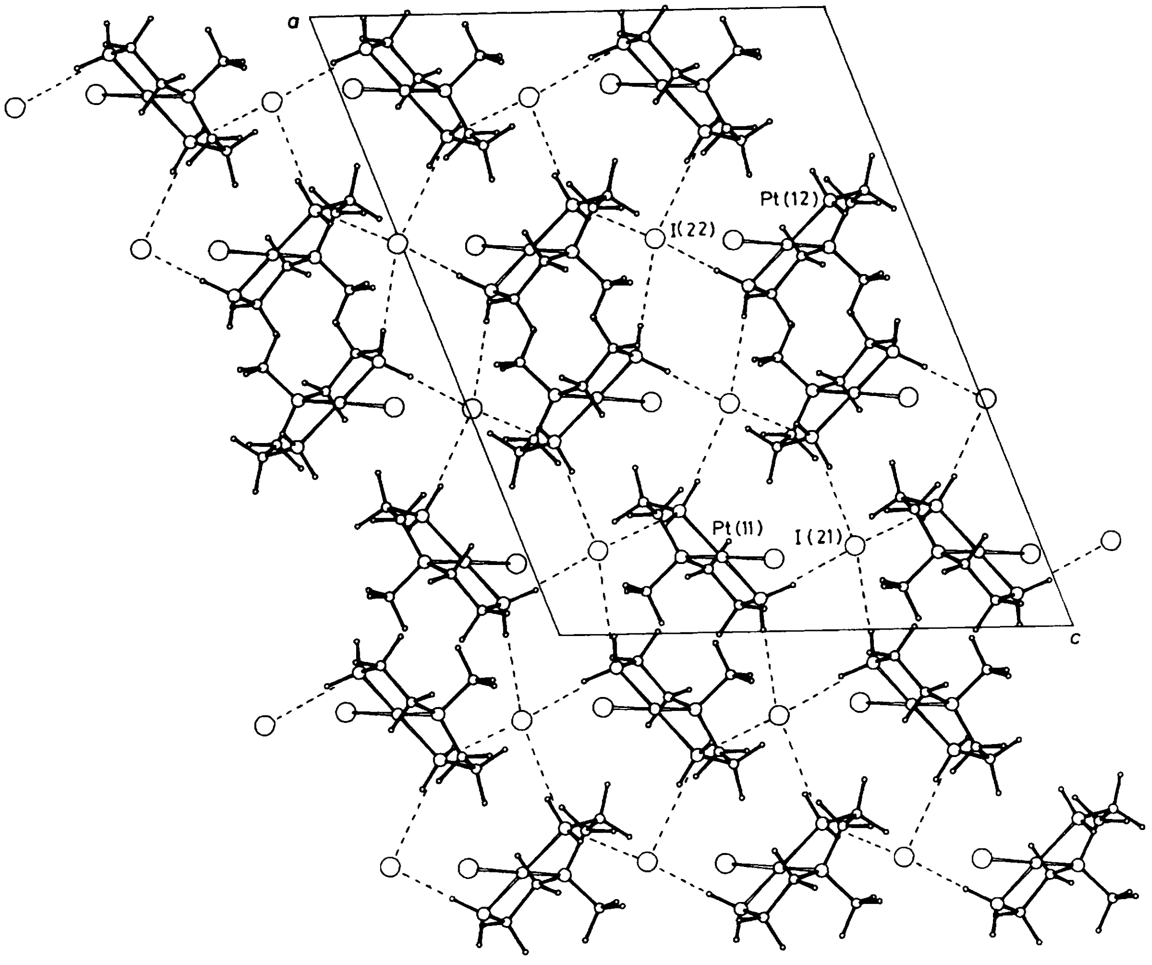

Figure 4. Projection of the structure of complex (**2**) along the [010] plane

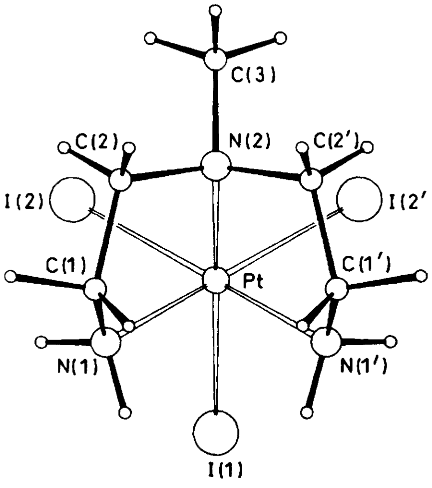

Figure 5. View of the structure of the cation [Pt(4Me-dien)I_3]$^+$ in complex (**3**) with the atomic numbering scheme

spans the complex cation from the other side. The fourth N-hydrogen atom interacts with the I_3^- of another duplex.

The I_3^- ion is slightly asymmetric [I(2)–I(3) 2.924(2), I(3)–I(4) 2.886(2) Å] and nearly linear [I(2)–I(3)–I(4) 177.11(7)°]. The small bending could be caused by a repulsion between the platinum atom and the central iodine atom [Pt $\cdots$ I(3) 3.830(2) Å] while the terminal iodine atoms are anchored to the terminal nitrogen atoms of the terdentate ligand.

In complex (**2**) (Figure 4) the crystal packing consists of alternate double layers of crystallographically independent complex cations parallel to the (100) plane. Also in this case all four N-hydrogen atoms of each complex are involved in hydrogen bonds. Two hydrogen atoms, one from each terminal nitrogen atom, bind two I^- anions which also interact, in a similar way, with other molecules of the complex to form a chain. The other two N-hydrogen atoms interact, one with an I^- anion of a second chain of the same layer and the other with an I^- anion of another layer.

On comparison of the structures of (**1**) and (**2**) with that of [Pt(dien)X]X (X = Cl, Br, or NO_3)[10,11] it does not appear that the introduction of a methyl group on the central nitrogen atom of dien has caused significant changes to the structure of the cation.

The structure of the complex cation of (**3**) is depicted in Figure 5. This cation has a distorted octahedral geometry with crystallographically imposed C_s symmetry, the mirror plane passing through the C(3), N(2), Pt, and I(1) atoms. The two terminal nitrogen atoms of the triamine ligand are co-ordinated *cis* to each other and the two condensed rings have an imposed δλ conformation.

The Pt–N distances do not differ significantly from one another and agree well with usual values for Pt^{IV}–N(amine) bonds.[12] The same applies to the Pt–I bond lengths.[1] It is noteworthy, however, that these values are slightly bigger (by *ca.* 0.05 Å) than those found for complexes (**1**) and (**2**), and the

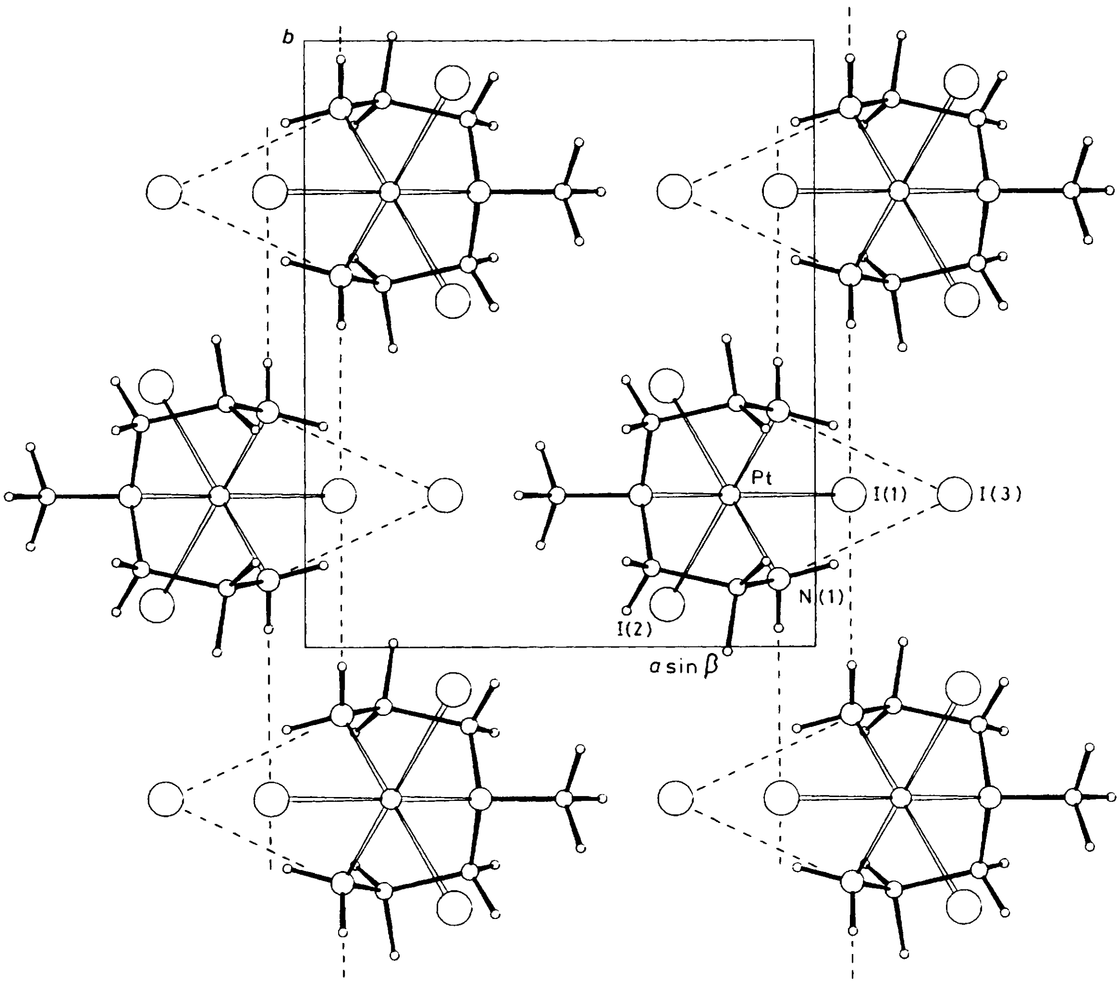

Figure 6. Projection of the structure of complex (**3**) along the [001] plane

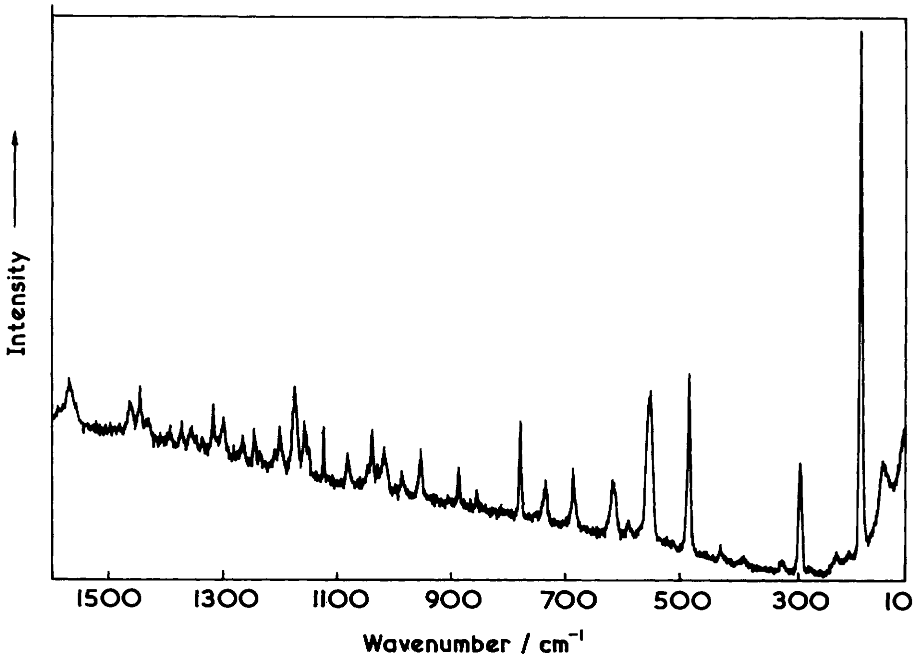

Figure 7. Raman spectrum (λ_0 = 514.5 nm) of [Pt(4Me-dien)I]I, (**2**), as a K_2SO_4 disc at *ca.* 80 K

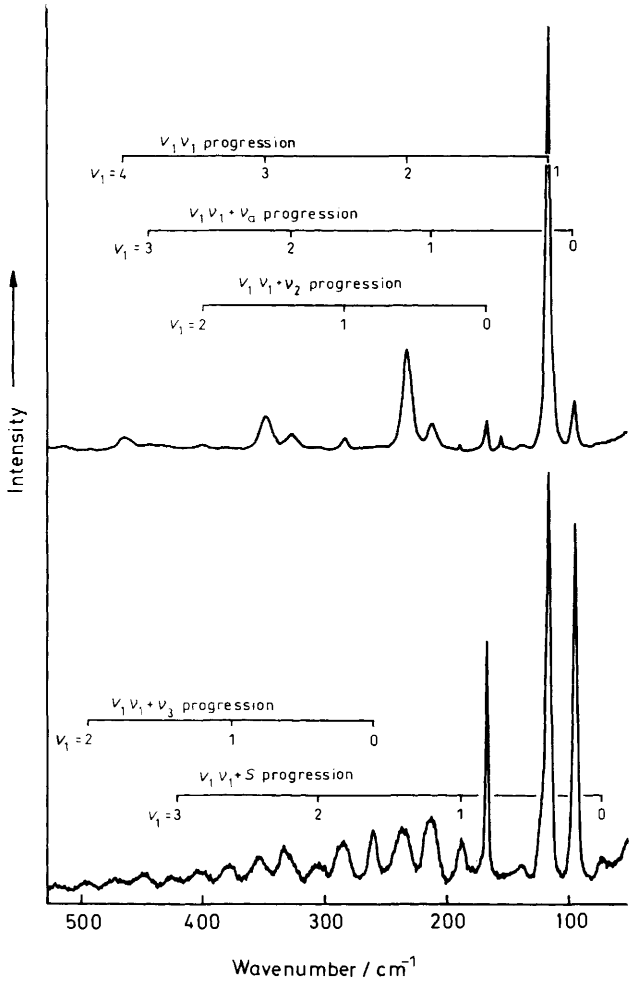

Figure 8. Raman (λ_0 = 647.1 nm, lower) and resonance Raman (λ_0 = 799.3 nm, upper) spectra of $[Pt(4Me\text{-}dien)I][Pt(4Me\text{-}dien)I_3]I_2$, (**4**), as a K_2SO_4 disc at *ca.* 80 K

differences appear to have real significance. The I–Pt–I, I–Pt–N, and N–Pt–N angles lie in the range previously reported; however those inside the chelate ring are even smaller (by *ca.* 3°) than those deduced for complexes (**1**) and (**2**), probably as a consequence of the lengthening of the Pt–N bonds. The packing within the crystal is shown in Figure 6. The cations are arranged in chains parallel to the (010) plane. Of the four amine hydrogen atoms of the co-ordinated ligand, two (one from each terminal nitrogen atom) interact with the I^- counter ion and each of the other two with the co-ordinated I(1) atoms of adjacent cations.

Structures of several complexes of the type $[M(dien)X_3]^{n+}$ and $[M(dien)_2]^{n+}$ (n = 0—3) have been determined in which the dien ligand can have either a planar (*mer*) or a bent (*fac*) conformation.[12,13] In the case of platinum(IV) complexes the *mer* conformation has been found only for mixed-valence chain complexes in which the octahedral entity is inserted between two planar platinum(II) entities. By contrast all monomeric platinum(IV) complexes adopt the *fac* conformation.[1] This could indicate that, starting with a platinum(II) species in which the dien ligand is expected to be planar, the first oxidation product has a *mer* conformation; this product would then either crystallise with residual platinum(II) species to give a mixed-valence chain complex or isomerise to the *fac* complex.

Table 4. Wavenumbers, intensities, and assignments of bands observed in the Raman spectrum of $[Pt(4Me\text{-}dien)I][Pt(4Me\text{-}dien)I_3]I_2$, (**4**), λ_0 = 647.1 nm *

Wavenumber/cm^{-1}	Intensity	Assignment
72.5	vw	Skeletal (*s*) or $\nu_2 - \nu_a$
94.5	s	ν_a
116.5	vs	$\nu_1(I\text{-}Pt^{IV}\text{-}I)$
139.0	vw	
167.0	s	ν_2, $\nu(Pt\text{-}I)_{eq}$
188.0	w	$\nu_1 + s$
213.5	m	$\nu_1 + \nu_a$
235.5	m	$2\nu_1$
260.5	m	ν_3
285.5	mw	$\nu_1 + \nu_2$
305.5	w	$2\nu_1 + s$
333.0	w	$2\nu_1 + \nu_a$
353.5	w	$3\nu_1$
378	w	$\nu_1 + \nu_3$
402	w	$2\nu_1 + \nu_2$
425	w	$3\nu_1 + s$
448	w	$3\nu_1 + \nu_a$
472	vw	$4\nu_1$
495	vw	$2\nu_1 + \nu_3$
521	vw	$3\nu_1 + \nu_2$
529	vw	

* The members of the $v_1\nu_1$ progression have, with 799.3-nm excitation, slightly lower wavenumbers (with the exception of ν_1) than with 647.1-nm excitation as frequently observed for chain complexes (R. J. H. Clark and M. Kurmoo, *J. Chem. Soc., Faraday Trans. 2*, 1983, 519; R. J. H. Clark and D. J. Michael, *J. Mol. Struct.*, 1988, **189**, 173); *viz.* ν_1, 117.0; $2\nu_1$, 233.0; $3\nu_1$, 348.0; $4\nu_1$, 463; $5\nu_1$, 578; $6\nu_1$, 693 cm^{-1}.

The oxidation reaction, carried out on the platinum substrate in which the dien ligand has a methyl substituent on the central nitrogen atom, led initially to the formation of the mixed-valence chain complex; however all attempts to recrystallise this resulted in the formation of separate crystals of (**3**) (which cannot give the mixed-valence complex) and (**2**).

The *X*-ray investigations have shown that, in cases in which a conformation of the ligand is planar [complexes (**1**) and (**2**)], the methyl substituent on the central nitrogen atom extends out of the meridional plane where it would interact strongly with any group in the axial position; for this reason the mixed-valence chain complex is not stable to recrystallisation.

On the other hand for the octahedral species, the isomerisation of the ligand from the *mer* to the *fac* conformation [*cf.* (**3**)] has moved the methyl substituent from a position in which it was interacting strongly with an axial iodine atom [C(Me)–N–Pt–I torsion angle of 0° and C(methyl)–I distance of *ca.* 3 Å] to a less-hindered situation [C(Me)–N–Pt–I 45° and C(methyl)–I 3.7 Å]. Therefore the presence of a methyl substituent on the central nitrogen atom of dien has two effects: to destabilise the mixed-valence chain complex and to increase the tendency of the terdentate ligand to assume a bent (*fac*) conformation in the octahedral complex.

Raman Spectroscopy.—The Raman spectrum of the platinum(II) complex (**2**) is shown in Figure 7. The corresponding platinum(IV) complex (**3**) absorbed more of the incident radiation than did (**2**) and consequently its Raman spectrum does not show the large number of bands (associated primarily with the 4Me-dien ligand) at higher Raman shift seen in Figure 7. However, the Raman spectrum of (**3**) did show a band at 172 cm^{-1}, which is assigned to the Pt^{IV}–I symmetric stretch.

The Raman spectrum (λ_0 = 647.1 nm) of the mixed-valence complex (**4**) is shown in Figure 8. This figure also indicates the resonance enhancement of several progressions in the spectrum, features which are clearly observed on changing the wavelength of the exciting line towards the deep red, *i.e.* within the contour of the intervalence band. Enhancement occurs for the $v_1\nu_1$

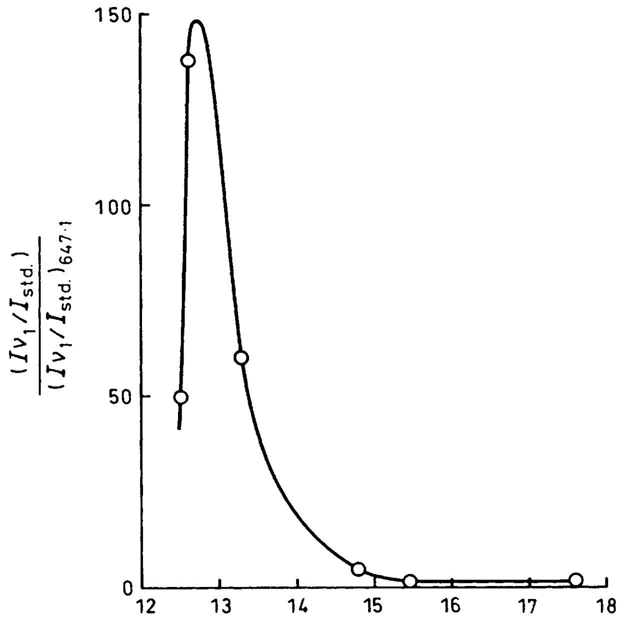

Figure 9. Normalised excitation profile of the ν_1 band of $[Pt(4Me\text{-}dien)I][Pt(4Me\text{-}dien)I_3]I_2$, (4)

progression (up to $v_1 = 6$ is observed) and weaker enhancement occurs for the $v_1\nu_1 + \nu_a$ progression up to $v_1 = 5$ (where ν_a is an unassigned enabling mode, *cf.* a similar band reported in ref. 14), and $v_1\nu_1 + \nu_2$ up to $v_1 = 3$ [where ν_2 is $\nu(Pt\text{–}I)_{eq}$]. Other progressions detected in the 647.1-nm spectrum include $v_1\nu_1 + \nu_3$ up to $v_1 = 2$ and $v_1\nu_1 + s$ up to $v_1 = 3$, where neither of the enabling modes ν_3 or s could be assigned (although s could be the difference mode $\nu_2 - \nu_a$). Peak assignments for the spectrum ($\lambda_0 = 647.1$ nm) in Figure 8 are given in Table 4.

The excitation profile (e.p.), which allows for variation in spectral response and intensity dependence on wavenumber and which is normalised (at $\lambda_0 = 647.1$ nm, enhancement factor = 1), is shown in Figure 9. The e.p. reaches a maximum at *ca.* 13 000 cm^{-1}, indicating that ν_1 is coupled strongly with the intervalence transition.

Conclusions

This investigation has revealed that a methyl substituent on the dien ligand has a significant effect on the formation and stability of mixed-valence chain complexes. This effect, probably of steric origin, is connected with the capability of the dien ligand to keep a *mer* conformation without interacting strongly with the apical ligands in an octahedral geometry. In the case of 4Me-dien the interaction between the methyl substituent and an apical iodine atom is estimated to be very strong [C(Me) • • • I *ca.* 3.0 Å]; thus on recrystallisation the chain is destroyed and *mer*-to-*fac* isomerisation occurs with consequent relief of the steric hindrance [C(Me) • • • I 3.7 Å]. The *mer*-to-*fac* isomerisation of the dien ligands apparently occurs in all discrete platinum(IV) species; only in the chain complexes is the *mer* conformation retained around platinum(IV), because in this case it is 'sandwiched' between platinum(II) species.

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