Synthesis, Spectroscopy, and Structure of the Mixed-valence Complexes $[Pt^{II}(en)_2][Pt^{IV}(en)_2X_2][Pt^{III}_2(H_2P_2O_5)_4X_2]$ (en = 1,2-Diaminoethane, X = Br or I)

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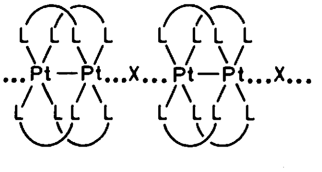
The complexes $[Pt^{II}(en)_2][Pt^{IV}(en)_2X_2][Pt^{III}_2(H_2P_2O_5)_4X_2]$ (en = 1,2-diaminoethane) have been obtained as copper coloured needles (X = Br) or metallic green dichroic microcrystals (X = I) by the reaction of $K_4[Pt^{II}_2(H_2P_2O_5)_4]\cdot 2H_2O$ with $[Pt^{IV}(en)_2X_2]X_2$ in aqueous solution at 100 °C. Spectroscopic evidence favours a formulation for the complexes which involves a halogen-bridged linear-chain Pt^{II}–Pt^{IV} cation in association with a dimeric Pt^{III} anion. The absorption spectra are characterised by three bands, the one of lowest wavenumber being assigned to the $Pt^{II}(d_{z^2}) \longrightarrow Pt^{IV}(d_{z^2})$ intervalence transition of the chain cation and the next to the $d_\sigma \longrightarrow d_{\sigma^*}$ transition of the dimeric anion. The complexes are unusual in that they contain class II (partly-localised valence) cation chains while at the same time the interaction between the cation and anion is of the class I (highly-localised valence) type. The infrared, Raman, and resonance-Raman spectra of the two complexes have been studied in detail, the Raman spectra at *ca.* 80 K being characterised (among other things) by a progression [to $10\nu_1'$ (X = Br) and $5\nu_1'$ (X = I)] in the symmetric X–Pt^{IV}–X mode (ν_1') of the cation chain when the exciting line is at resonance with the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence band, and by a progression (to $9\nu_1$, X = Br or I) in the Pt^{III}–Pt^{III} stretching mode (ν_1) of the anion at resonance with the $\sigma \longrightarrow \sigma^*$ transition. Single-crystal resonance-Raman spectra of the bromide at *ca.* 15 K show progressions in ν_1' and ν_1 as follows: $v_1'\nu_1'$ to $v_1' = 11$, $v_1\nu_1$ to $v_1 = 12$, $v_1\nu_1 + \nu_2$ to $v_1 = 9$, and $v_1\nu_1 + 2\nu_2$ to $v_1 = 8$, where ν_2 is the Pt^{III}–Br symmetric stretching mode of the anion. The formulation for the complexes is unique in that it involves platinum in three different oxidation states.

Complexes containing linear chains of transition-metal atoms have, on account of their highly unusual properties, attracted considerable recent attention.[1–3] The study of those containing the metal in more than one oxidation state has been particularly important in furthering the understanding of electron-transfer processes[4] and in elucidating the mechanisms of electrical conductivity processes.[5] In such complexes, the ligands (L) must be able to adopt a square-planar configuration about the metal atom in order to allow close stacking of ML_4 units.[6] Our main interest in the field has been in the synthesis of new materials and in the correlation of optical properties and crystal structures for a series of halogen-bridged mixed-valence complexes of platinum and palladium,[7,8] for example of the type $[M^{II}L_4][M^{IV}L_4X_2][ClO_4]_4$, where L is an amine and X is Cl, Br, or I. The use of building blocks of discrete $M_2(L\text{–}L)_4$, L–L = $H_2P_2O_5^{2-}$ (diphosphonate) or $CH_3C(S)S^-$ (dithioacetate), has recently been demonstrated to lead to linear-chain complexes of platinum having a formal oxidation state for the metal ions of +2.5 (see below).[9,10] The conductivities of these complexes were found to range between 10^{-3} and 10^{-4} Ω^{-1} cm^{-1}, indicating that they are better semiconductors than those containing $\cdots M^{II}L_4 \cdots X\text{–}M^{IV}L_4\text{–}X \cdots$ chains, for which the conductivities range between 10^{-7} and 10^{-10} Ω^{-1} cm^{-1}.[5,11]



The objective of the present work was to incorporate square-planar ML_4 and blocks of $M_2(L\text{–}L)_4$ into chains by treating (*i*) $[Pt^{IV}(en)_2X_2]X_2$ with $K_4[Pt^{II}_2(H_2P_2O_5)_4]\cdot 2H_2O$ and (*ii*) $[Pt^{II}(en)_2]X_2$ with $K_4[Pt^{III}_2(H_2P_2O_5)_4X_2]$ (en = 1,2-diaminoethane; X = Cl, Br, or I). The first reaction, the results from which are reported here, was found to generate a rather different type of complex from that envisaged, *viz.* one involving a linear-chain mixed-valence (Pt^{II}–Pt^{IV}) cation in association with the $[Pt^{III}_2(H_2P_2O_5)_4X_2]^{4-}$ anion. This report describes the reactions concerned, and the spectroscopic (electronic, infrared, Raman, and resonance-Raman) evidence for the above formulation of these new complexes, which are unique in the sense that they involve the metal ion in three different oxidation states. The second reaction leads to the formation of yellow (X = Cl) and orange (X = Br) complexes of the type $[Pt^{II}(en)_2]_2[Pt^{III}_2(H_2P_2O_5)_4X_2]$ and will be described elsewhere.[12]

Experimental

Synthesis.—$K_4[Pt^{II}_2(H_2P_2O_5)_4]\cdot 2H_2O$ and $[Pt^{II}(en)_2]Cl_2$ were prepared by the methods of Sadler and co-workers[13] and Keller,[14] respectively. $[Pt^{IV}(en)_2X_2]X_2$ were obtained by halogen oxidation of $[Pt^{II}(en)_2]Cl_2$ by the method of Bekaroglu *et al.*[15] The complexes $[Pt^{II}(en)_2][Pt^{IV}(en)_2X_2][Pt^{III}_2(H_2P_2O_5)_4X_2]$ (X = Br or I) were prepared by treatment of an aqueous solution of $[Pt^{IV}(en)_2X_2]X_2$ (0.2 g) with an aqueous solution of $K_4[Pt^{II}_2(H_2P_2O_5)_4]\cdot 2H_2O$ (0.2 g) at 100 °C. The bromide is obtained as copper coloured crystals (Found: C, 5.15; H, 2.05; Br, 17.6; N, 5.95; P, 12.9. $C_8H_{40}Br_4N_8O_{20}P_8Pt_4$ requires C, 5.00; H, 2.10; Br, 16.70; N, 5.85; P, 12.95%) and the iodide as metallic green microcrystals (Found: C, 4.55; H, 1.95; I, 23.7; N, 5.30; P, 12.5. $C_8H_{40}I_4N_8O_{20}P_8Pt_4$ requires C, 4.55; H, 1.90, I, 24.15; N, 5.35; P, 11.80%).

Instrumental.—Electronic spectra were recorded using a Cary 14 spectrometer on Nujol mulls of the complexes at 295 K. Infrared spectra were recorded at 295 and 80 K using a Bruker IFS 113V interferometer. Samples were prepared as discs in alkali-halide matrices for measurements in the range 4 000—400 cm^{-1} and as wax discs for those in the range 600—20 cm^{-1}.

Raman spectra were recorded using a Spex 1401 double monochromator with 1 200 line mm^{-1} Bausch and Lomb gratings and a Spex 14018/R6 double monochromator with 1 800 line mm^{-1} Jobin–Yvon holographic gratings. Coherent Radiation Ltd. model CR3, CR3000 K, and CR12 lasers provided exciting lines of wavelengths between 337.1 and 799.3 nm. Detection was by photon counting using an RCA C31034A photomultiplier. Raman spectra of each complex were recorded as $K_2[SO_4]$ discs at both 295 and *ca.* 80 K. A cylindrical lens was used to line focus the incident beam and thus minimise any possible heating of the sample. Laser power was kept below 50 mW on the sample. Calibration of spectra was effected by reference to the emission spectrum of neon. Intensities were estimated by peak heights multiplied by full widths at half maximum, and corrected for the response of the instrument. The a_1 band of $[SO_4]^{2-}$ was used as an intensity standard.

Polarised resonance-Raman spectra of single crystals of the bromide were obtained at *ca.* 15 K by use of an Air Products Displex cryostat. Laser power at the crystals was kept to less than 10 mW. The crystals (five needles of dimensions *ca.* 2 × 0.05 × 0.05 mm) were aligned, under a microscope, next to one another with their long axes (z) parallel to each other, and then placed on the cryostat with their long axes parallel to the electric vector of the incident beam. An analyser was used to select the $y(zz)x$ and $y(zy)x$ components of the scattered radiation.

Results

Electronic Spectra.—The crystals of the two complexes show remarkable metallic reflection which is lost on being ground to powders. The bromide is copper coloured and the iodide is gold-green; both form as needle-shaped crystals and both are black as powders. The bromide is dichroic, being black with the electric vector of the incident beam parallel to the long axis of the crystals and brown when perpendicular to it. The iodide appears black in both orientations.

The electronic spectrum of each complex between 5 000 and 35 000 cm^{-1} (Figures 1 and 2) consists of three bands, the wavenumbers of which are greater for the bromide than for the iodide. The band maxima are 17 000, 23 300, and 29 700 cm^{-1} for the bromide and 11 000, 18 000, and 27 000 cm^{-1} for the iodide, all the half-band widths being $\sim$5 000 cm^{-1}. The band of lowest wavenumber is assigned in each case to the intervalence transition $Pt^{II}(d_{z^2}) \longrightarrow Pt^{IV}(d_{z^2})$ of the cation and the next to the $d_\sigma \longrightarrow d_{\sigma^*}$ transition of the dimeric platinum(III) anion.

The argument for the assignment of the band of lowest wavenumber to an intervalence band rests on both wavenumber and intensity grounds. Thus, the $[Pt^{II}(en)_2][Pt^{IV}(en)_2Br_2]^{4+}$ cation chain is known to give rise to a $Pt^{II} \longrightarrow Pt^{IV}$ intervalence band at *ca.* 17 000 cm^{-1}; the band maximum is somewhat sensitive to the counter ion, lying at 18 450, 18 000, or 15 870 cm^{-1} when the counter ion is $[ClO_4]^-$, Br^-, or $[CuBr_4]^{3-}$, respectively.[8] The $[Pt^{II}(en)_2][Pt^{IV}(en)_2I_2]^{4+}$ cation chain likewise is known to have its intervalence band at 14 000 cm^{-1} in the case of the perchlorate salt.[8]

The second band in the electronic spectrum of each complex occurs $\geqslant$5 000 cm^{-1} to the red of the $\sigma \longrightarrow \sigma^*$ transition of the $[Pt^{III}_2(H_2P_2O_5)_4X_2]^{4-}$ ions, as established for their potassium salts.[9] Despite this shift, the second band is assigned to the $\sigma \longrightarrow \sigma^*$ transition of the anion on the basis of excitation profile measurements (see later).

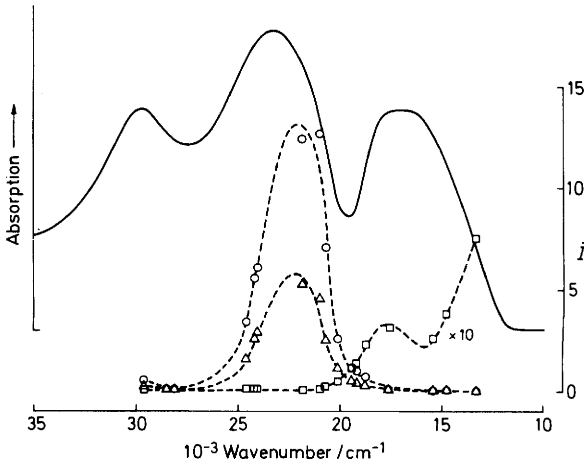


Figure 1. Electronic spectrum (Nujol mull, 295 K) and excitation profiles (*ca.* 80 K) of the $\nu_1'(Br–Pt^{IV}–Br)$ (□) band of the cation and the $\nu_1(Pt^{III}–Pt^{III})$ (○) and $\nu_2(Pt^{III}–Br)$ (△) bands of the anion for $[Pt^{II}(en)_2][Pt^{IV}(en)_2Br_2][Pt^{III}_2(H_2P_2O_5)_4Br_2]$

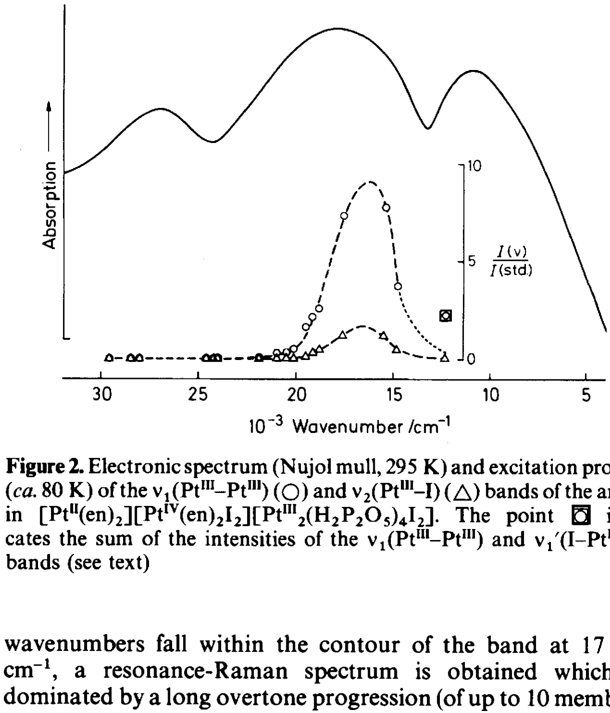


Figure 2. Electronic spectrum (Nujol mull, 295 K) and excitation profiles (*ca.* 80 K) of the $\nu_1(Pt^{III}–Pt^{III})$ (○) and $\nu_2(Pt^{III}–I)$ (△) bands of the anion in $[Pt^{II}(en)_2][Pt^{IV}(en)_2I_2][Pt^{III}_2(H_2P_2O_5)_4I_2]$. The point ▣ indicates the sum of the intensities of the $\nu_1(Pt^{III}–Pt^{III})$ and $\nu_1'(I–Pt^{IV}–I)$ bands (see text)

Raman Spectra.—(*a*) *Bromo-complex.* Raman spectra of the complexes were recorded with a variety of exciting lines (337.1—752.5 nm). The bromo-complex gives distinctly different spectra on being irradiated within the contours of each of the three absorption bands. With exciting lines whose wavenumbers fall within the contour of the band at 17 000 cm^{-1}, a resonance-Raman spectrum is obtained which is dominated by a long overtone progression (of up to 10 members at *ca.* 80 K) in a mode designated ν_1' (175 cm^{-1}) (Figure 3, Table 1). This is characteristic of the behaviour of linear-chain halogen-bridged Pt^{II}–Pt^{IV} species on irradiation within the contour of their $Pt^{II} \longrightarrow Pt^{IV}$ intervalence band.[7,8] With exciting lines whose wavenumbers fall within the contour of the band at 23 300 cm^{-1}, the spectrum at *ca.* 80 K is dominated by different overtone progressions, one of up to nine members in a mode designated ν_1 (138 cm^{-1}), together with a weaker one of up to two members in a mode designated ν_2 (229 cm^{-1}); combination bands $v_1\nu_1 + \nu_2$ as far as $v_1 = 7$ and $v_1\nu_1 + 2\nu_2$ as far as $v_1 = 5$ are also evident in this spectrum (Figure 4, Table 1). Excitation within the contour of the highest energy band at 29 700 cm^{-1} gives rise to a normal Raman spectrum, which consists of only two bands at 138 and 229 cm^{-1} (see later). It is critically important to note that for none of the available exciting lines could combination bands be observed between the band at 175 cm^{-1} and either the 138 or the 229

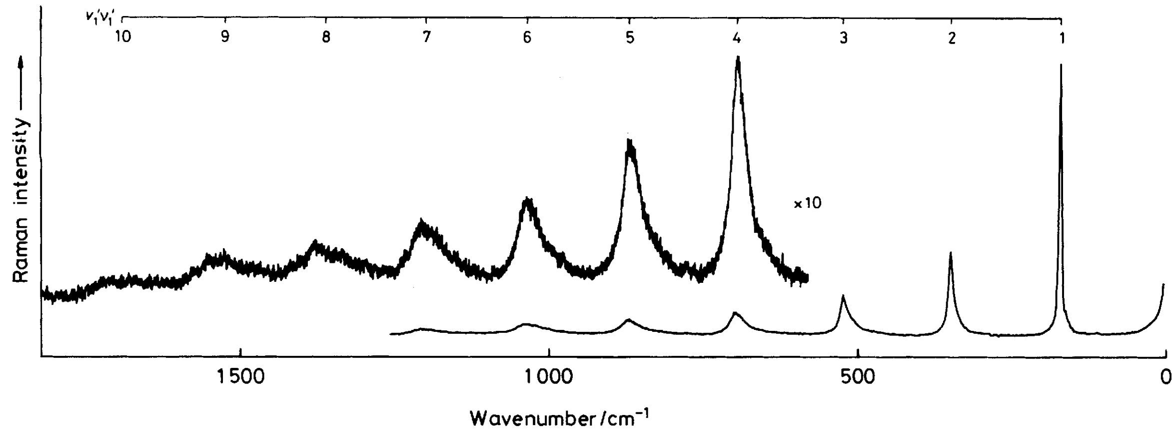


Figure 3. Raman spectrum of $[Pt^{II}(en)_2][Pt^{IV}(en)_2Br_2][Pt^{III}{}_2(H_2P_2O_5)_4Br_2]$ at resonance with the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence band of the cation chain ($K_2[SO_4]$ disc at *ca.* 80 K, λ_0 = 676.4 nm, spectral slit width $\sim$2 cm^{-1})

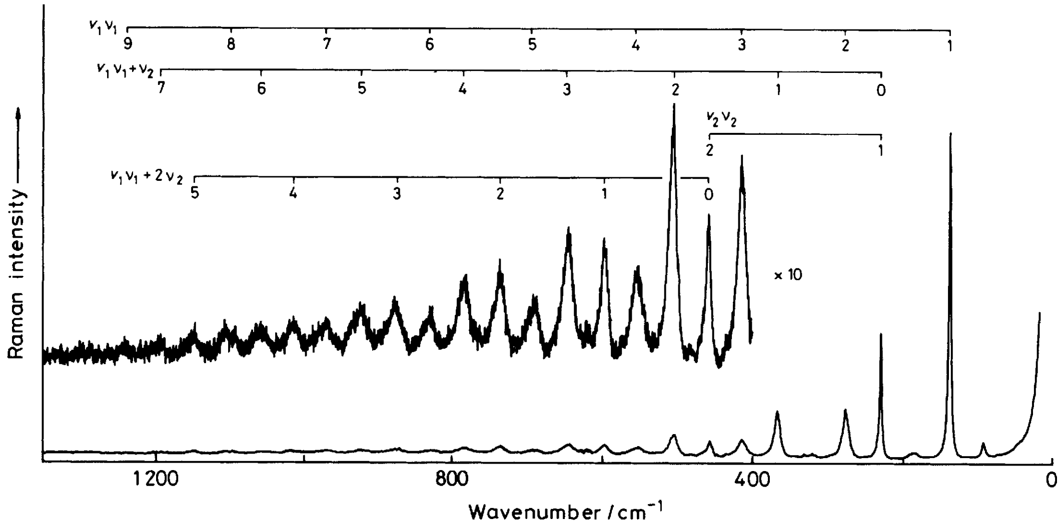


Figure 4. Raman spectrum of $[Pt^{II}(en)_2][Pt^{IV}(en)_2Br_2][Pt^{III}{}_2(H_2P_2O_5)_4Br_2]$ at resonance with the $d_\sigma \longrightarrow d_{\sigma^*}$ band of the anion ($K_2[SO_4]$ disc at *ca.* 80 K, λ_0 = 457.9 nm, spectral slit width $\sim$2 cm^{-1})

cm^{-1} band; this suggests that the band at 175 cm^{-1} is associated with a different species (*i.e.* the cation) from that to which the other two bands belong (*i.e.* the anion). The bands at 138 and 229 cm^{-1} are assigned to the $\nu(Pt^{III}-Pt^{III})$ and $\nu(Pt^{III}-Br)$ modes of the $[Pt_2(H_2P_2O_5)_4Br_2]^{4-}$ anion (*cf.* the potassium salt of this ion is known to give rise to analogous bands at 134 and 222 cm^{-1}, respectively).

The polarised single-crystal spectrum of the bromide at *ca.* 15 K (Figure 5) shows clearly that the ν_1', ν_1, and ν_2 bands, as well as their associated overtone and combination bands, are strongly *z*-polarised. Under these conditions, the observed progressions are as follows: $v_1'\nu_1'$ to $v_1' = 11$, $v_1\nu_1$ to $v_1 = 12$, $v_1\nu_1 + \nu_2$ to $v_1 = 9$, and $v_1\nu_1 + 2\nu_2$ to $v_1 = 8$. The vibrational frequencies are very slightly temperature dependent, ν_1' falling from 175.0 to 174.1 cm^{-1} (676.4 nm excitation) and ν_1 and ν_2 increasing from 137.6 and 228.6 cm^{-1} respectively, to 139.3 and 230.4 cm^{-1} respectively (457.9 nm excitation), on decreasing the temperature from *ca.* 80 to *ca.* 15 K. These results also suggest that ν_1' on the one hand and ν_1 and ν_2 on the other hand are associated with different species. Also noteworthy is the intense fluorescence (Figure 6) with 457.9 nm excitation, this reaching a maximum at *ca.* 13 300 cm^{-1}.

A further important observation is that ν_1' depends on the wavelength of the exciting line used to gather the data, increasing from 175.0 cm^{-1} with 676.4 nm excitation to 182.4 cm^{-1} with 457.9 nm excitation. Such a shift is characteristic of the symmetric chain-stretching mode of linear-chain complexes,[16] and confirms the nature of the cation. The anion modes are, as expected, unshifted with change of wavelength of the exciting line.

(b) *Iodo-complex.* The Raman spectrum of the iodo-complex (Table 2) is entirely analogous to that described above for the bromide. Excitation with 752.5 nm radiation (2 300 cm^{-1} from the maximum of the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence band of this complex) leads to the development of a five-membered progression in ν_1', the symmetric chain-stretching mode $\nu_{sym}(I-Pt^{IV}-I)$ being at 117.2 cm^{-1} (Table 2). On the other hand, excitation with the 647.1 nm line (within the contour of the $\sigma \longrightarrow \sigma^*$ transition of the anion) leads to the development of the following progressions which can readily be attributed to modes of the $[Pt^{III}{}_2(H_2P_2O_5)_4I_2]^{4-}$ anion: $v_1\nu_1$ to $v_1 = 9$, $v_1\nu_1 + \nu_2$ to $v_1 = 7$, $v_1\nu_1 + 2\nu_2$ to $v_1 = 2$, and $v_2\nu_2$ to $v_2 = 2$, where ν_1 = 121.6 cm^{-1}, the $Pt^{III}-Pt^{III}$ stretching mode and ν_2 = 199.6 cm^{-1}, the $Pt^{III}-I$ stretching mode (Figure 7). A summary of the spectroscopic properties of the complexes is given in Table 3 which includes details on harmonic wavenumbers (ω_1,ω_1') and anharmonicity constants (x_{11},x_{11}') derived by standard procedures from the observed overtone progressions.

Table 1. Wavenumbers, full widths at half maximum (f.w.h.m.), and relative intensities of bands observed in the resonance-Raman spectra * of $[Pt^{II}(en)_2][Pt^{IV}(en)_2Br_2][Pt^{III}_2(H_2P_2O_5)_4Br_2]$

$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	$I(\nu)/I(\nu_1')$	Assignment
(*a*) 676.4 nm excitation			
175.0	8.4	1.00	$\nu_1',\nu_{sym}(Br-Pt^{IV}-Br)$
215			$\delta(N-Pt-N)$
349.1	20	0.58	$2\nu_1'$
522.2	31	0.36	$3\nu_1'$
695	38	0.22	$4\nu_1'$
866	50	0.13	$5\nu_1'$
1 040	65	0.07	$6\nu_1'$
1 210	75	0.04	$7\nu_1'$
1 375	>75	<0.04	$8\nu_1'$
1 535	>75	<0.04	$9\nu_1'$
1 700	>75	<0.04	$10\nu_1'$
(*b*) 457.9 nm excitation			
91.2	4.8	0.07	$\delta(Pt^{III}-Pt^{III}-Br)$
137.6	3.4	1.00	$\nu_1,\nu(Pt^{III}-Pt^{III})$
143.5			
182.4	12	0.05	$\nu_1',\nu_{sym}(Br-Pt^{IV}-Br)$
228.6	4.2	0.45	$\nu_2,\nu(Pt^{III}-Br)$
275.6	7.8	0.33	$2\nu_1$
319.3			Ring bending
329.7			$\nu(Pt^{III}-P)$
341.3			Ring bending
366.3	8.4	0.33	$\nu_1 + \nu_2$
413.1	12.4	0.21	$3\nu_1$
456.9	11.6	0.15	$2\nu_2$
504.2	12	0.23	$2\nu_1 + \nu_2$
550.8	18	0.12	$4\nu_1$
595.0	12	0.10	$\nu_1 + 2\nu_2$
641.9	15	0.13	$3\nu_1 + \nu_2$
688.4	18	0.08	$5\nu_1$
732.8	18	0.11	$2\nu_1 + 2\nu_2$
780.4	21	0.11	$4\nu_1 + \nu_2$
824.8	20	0.06	$6\nu_1$
872.5	27	0.10	$3\nu_1 + 2\nu_2$
917.4	28	0.08	$5\nu_1 + \nu_2$
961.7	24	0.05	$7\nu_1$
1 010			$4\nu_1 + 2\nu_2$
1 055			$6\nu_1 + \nu_2$
1 100			$8\nu_1$
1 145			$5\nu_1 + 2\nu_2$
1 190			$7\nu_1 + \nu_2$
1 235			$9\nu_1$

* Obtained as a $K_2[SO_4]$ disc at *ca.* 80 K.

Infrared Spectra.—The infrared spectra of the complexes are simply superpositions of those of the constituent ions. Band assignments, based in part of those of Stein *et al.*,[17] are given in Table 4.

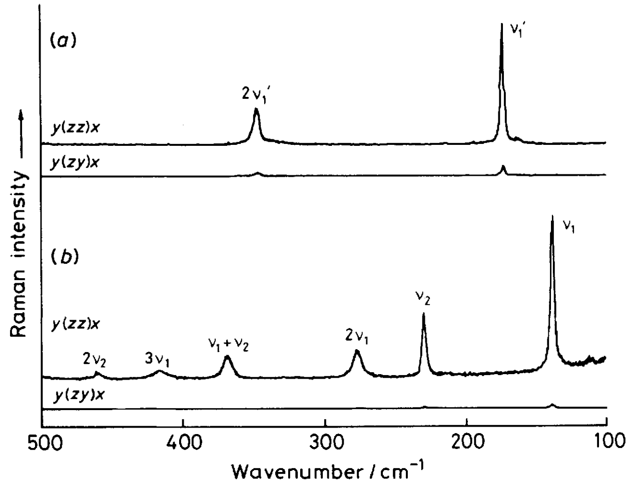


Figure 5. Polarised Raman spectra of a single crystal of $[Pt^{II}(en)_2][Pt^{IV}(en)_2Br_2][Pt^{III}_2(H_2P_2O_5)_4Br_2]$ at resonance with (*a*) the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence band (λ_0 = 676.4 nm) and (*b*) the $d_\sigma \longrightarrow d_{\sigma^*}$ band (λ_0 = 457.9 nm). Temperature = *ca.* 15 K, slit widths 180—250—180 µm (*ca.* 1 cm^{-1} at 676.4 nm and *ca.* 2.5 cm^{-1} at 457.9 nm)

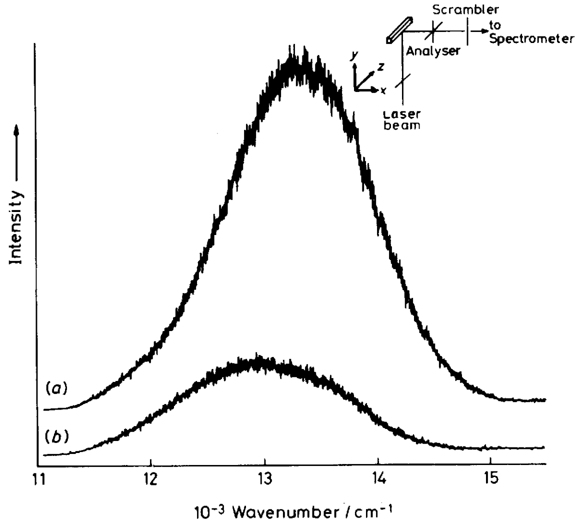
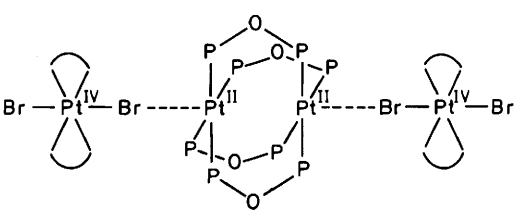


Figure 6. Luminescence spectra of a single crystal of $[Pt^{II}(en)_2]$-$[Pt^{IV}(en)_2Br_2][Pt^{III}_2(H_2P_2O_5)_4Br_2]$ at *ca.* 15 K; λ_0 = 457.9 nm, (*a*) *y*(*zz*)*x*, (*b*) *y*(*zy*)*x*

Discussion

Since the microanalytical data for the bromo-complex indicate an empirical formula of $C_8H_{40}Br_4N_8O_{20}P_8Pt_4$, or two units of $[Pt(en)_2Br_2]^{2+}$ to one of $[Pt_2(H_2P_2O_5)_4]^{4-}$, possible structures for the complex could be (*a*) Pt^{IV} cations and a Pt^{II}_2 anion with no interaction between the metal centres and thus no intervalence transition (class I, or localised-valence complex).[18,19] This formulation might be expected since the metal centres have quite different ligand fields (N_4Br_2 and P_4Pt chromophores, respectively). (*b*) A linear tetranuclear species, as shown below, with significant interaction between the metal centres, *via* the p_z(Br) and the $d_{z^2}(Pt^{II})$ orbitals; such a species would be expected to give rise to intervalence transitions of the sort $d_{\sigma^*}(Pt^{II}_2) \longrightarrow d_{z^2}(Pt^{IV})$ (class II, or partly localised-valence complex). (*c*) Linear-chain polymeric halogen-bridged cation chains $[Pt^{II}(en)_2][Pt^{IV}(en)_2Br_2]^{4+}$ in association with $[Pt^{III}_2(H_2P_2O_5)_4Br_2]^{4-}$ anions; such a complex would have an intervalence transition of the sort $Pt^{II}(d_{z^2}) \longrightarrow Pt^{IV}(d_{z^2})$[7,8] (class II cation chain) and no interaction between Pt^{III} and either the Pt^{II} or Pt^{IV} of the chain (class I type interaction).



P–O–P = HO–P(O)–O–P(O)–OH

The first possibility would be a yellow complex with

Table 2. Wavenumbers, f.w.h.m. and relative intensities of bands observed in the resonance-Raman spectra* of $[Pt^{II}(en)_2][Pt^{IV}(en)_2I_2]$-$[Pt^{III}{}_2(H_2P_2O_5)_4I_2]$

$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	$I(\nu)/I(\nu_1')$	Assignment
(*a*) 752.5 nm excitation			
117.2	14.2	1.00	$\nu_1'{}_{sym}(I-Pt^{IV}-I)$
199.6			$\nu_2,\nu(Pt^{III}-I)$
231	24	0.50	$2\nu_1'$
344	33	0.24	$3\nu_1'$
457	40	0.16	$4\nu_1'$
570	50	0.10	$5\nu_1'$
(*b*) 647.1 nm excitation			
43.2			
78.4			$\delta(Pt^{III}-Pt^{III}-I)$
121.6	5.5	1.00	$\nu_1,\nu(Pt^{III}-Pt^{III})$
199.6	5.0	0.15	$\nu_2,\nu(Pt^{III}-I)$
242.0	15	0.82	$2\nu_1$
320.7	13	0.21	$\nu_1 + \nu_2$
363.9	21	0.55	$3\nu_1$
398.8			$2\nu_2$
441.3	21	0.21	$2\nu_1 + \nu_2$
484.9	26	0.38	$4\nu_1$
520			$\nu_1 + 2\nu_2$
563.9	32	0.24	$3\nu_1 + \nu_2$
606.7	36	0.32	$5\nu_1$
640			$2\nu_1 + 2\nu_2$
684	40	0.20	$4\nu_1 + \nu_2$
727	~45	~0.20	$6\nu_1$
805			$5\nu_1 + \nu_2$
850			$7\nu_1$
925			$6\nu_1 + \nu_2$
970			$8\nu_1$
1 040			$7\nu_1 + \nu_2$
1 090			$9\nu_1$

* Obtained as a $K_2[SO_4]$ disc at *ca.* 80 K.

Table 3. Summary of data for the complexes $[Pt^{II}(en)_2][Pt^{IV}(en)_2X_2]$-$[Pt^{III}{}_2(H_2P_2O_5)_4X_2]$*

	X = Br	X = I
Crystals	Copper needles	Gold-green needles
Powder	Black	Black
$\tilde{\nu}(Pt^{II} \longrightarrow Pt^{IV})$/cm^{-1}	17 000	11 000
$\tilde{\nu}(d_\sigma \longrightarrow d_{\sigma^*})$/cm^{-1}	23 300	18 000
$\omega_1'(X-Pt^{IV}-X)$/cm^{-1}	175.7 ± 0.3	~116
x_{11}'/cm^{-1}	−0.39 ± 0.03	
$\omega_1(Pt^{III}-Pt^{III})$/cm^{-1}	138.8 ± 0.3	121.6 ± 0.3
x_{11}/cm^{-1}	−0.04 ± 0.03	−0.04 ± 0.03
$\tilde{\nu}_2(Pt^{III}-X)$/cm^{-1}	228.6	199.6
x_{12}/cm^{-1}	−0.1 ± 0.05	+0.35 ± 0.05
$v_1\nu_1$ progression	$v_1 = 9(12)$	$v_1 = 9$
$v_1\nu_1 + \nu_2$	$v_1 = 7(9)$	$v_1 = 7$
$v_1\nu_1 + 2\nu_2$	$v_1 = 5(8)$	$v_1 = 2$
$v_2\nu_2$	$v_2 = 2(2)$	$v_2 = 2$
$v_1'\nu_1'$	$v_1' = 10(11)$	$v_1' = 5$

* Raman data relate to measurements taken on samples at *ca.* 80 K; those in parentheses relate to measurements on single crystals at *ca.* 15 K.

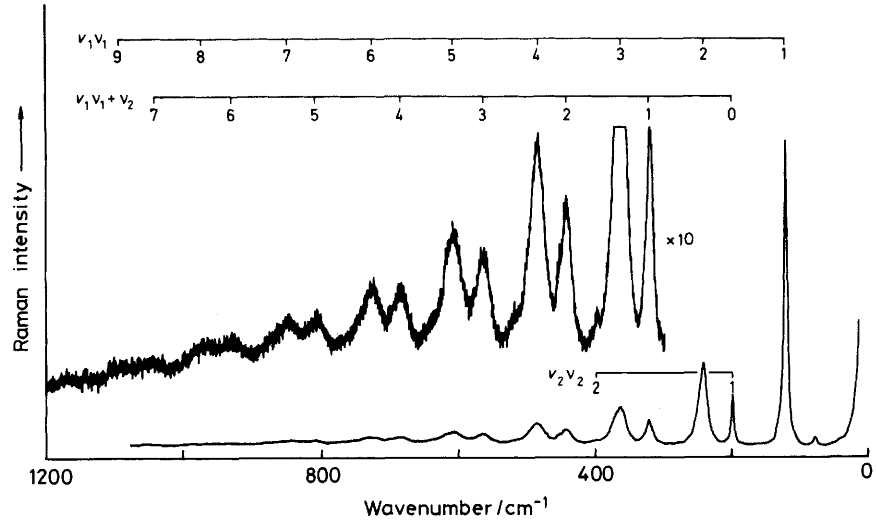


Figure 7. Raman spectrum of $[Pt^{II}(en)_2][Pt^{IV}(en)_2I_2][Pt^{III}{}_2(H_2P_2O_5)_4I_2]$ at resonance with the $d_\sigma \longrightarrow d_{\sigma^*}$ band of the anion ($K_2[SO_4]$ disc at *ca.* 80 K, λ_0 = 647.1 nm, spectral slit width ~1.5 cm^{-1})

absorption in the ultraviolet due to the $d_{\sigma^*} \longrightarrow p_z$ transition in the dimeric anion[20,21] and the $Br \longrightarrow Pt^{IV}$ charge-transfer transition of the cation; both constituents are yellow as simple salts or in solution. The Raman spectrum of such a salt would be the superposition of those of *trans*-$[Pt^{IV}(en)_2Br_2]^{2+}$ and $[Pt^{II}{}_2(H_2P_2O_5)_4]^{4-}$ and would thus be characterised by having its strongest bands at 212 cm^{-1} [$\nu(Pt^{IV}-Br)$[22]] and 116 cm^{-1} [$\nu(Pt^{II}-Pt^{II})$[17]], respectively. These expectations differ substantially from those found for the title bromo-complex, both in respect to its electronic as well as its Raman spectrum.

The second possibility is more feasible, since such a complex would show an intervalence band in addition to bands characteristic of the anion and cation. It would thus be expected to be strongly coloured, as are most mixed-valence complexes belonging to class II.[18,19] The resonance-Raman spectrum of such a complex would be expected to show bands due to $\nu(Pt^{II}-Pt^{II})$, $\nu(Pt^{IV}-Br)_{bridge}$, and $\nu(Pt^{IV}-Br)_{terminal}$ and combination bands involving all three modes. The Raman band wavenumbers would depend markedly on the magnitude of the interaction between the metal centres. However, since there is no evidence for any combination bands between either $\nu(Pt-Pt)$ at 138 cm^{-1} or the $\nu(Pt-Br)_{terminal}$ at 229 cm^{-1} with $\nu(Pt-Br)_{bridge}$ at 175 cm^{-1}, this formulation is considered to be improbable.

A complex possessing the third possible structure would also possess an intervalence transition such as that known for many

Table 4. Wavenumbers (cm^{-1}) of the bands observed in the infrared spectra of $[\mathrm{Pt^{II}(en)_2}][\mathrm{Pt^{IV}(en)_2X_2}][\mathrm{Pt^{III}{}_2(H_2P_2O_5)_4X_2}]$

X = Br	X = I	Assignment *	X = Br	X = I	Assignment *
3 430m br	3 400w br	ν(OH)	930m	920m	$\nu(\mathrm{PO})_{\mathrm{terminal}}$
3 310m	3 285m		890 (sh)	890m	$\delta(\mathrm{CH_2})_{\mathrm{rock}}$
3 280m	3 265w		812mw	825m	$\delta(\mathrm{NH_2})_{\mathrm{rock}}$
3 225m	3 235m		785w (sh)	800m (sh)	
3 200 (sh)	3 215m	ν(NH)	753w (sh)	760w	
3 100m	3 160w		743w (sh)		
3 060w	3 125w		723s	722s	ν(POP)
3 000w	3 060m		620w		
2 960w (sh)	2 995m		595w	590w	
2 890w	2 970m		588w		ν(Pt–N)
2 670vw	2 670vw	ν(CH)		553w	
2 640vw			545w	542w	
2 600vw	2 600vw		525m	523m	$\delta(\mathrm{PO_2})$
1 700w br	1 720m br	δ(OH)	472vw	472w	δ(N–C–C–N)
1 600s	1 602s			465m	$\delta(\mathrm{PO_2})$
1 590s (sh)	1 580s (sh)	$\delta(\mathrm{NH_2})_{\mathrm{sym}}$	455m	455m	
1 570m (sh)			434vw	430w	δ(N–C–C–N)
	1 460w	$\delta(\mathrm{CH_2})_{\mathrm{sym}}$	378vw	390vw	
1 457m	1 452m		363w	359vw	
	1 410w		351m	351m	
1 385w	1 380w	$\delta(\mathrm{CH_2})_{\mathrm{wag}}$	344m	341m	ν(Pt–P)
1 340m	1 340m		313m	312m	
1 325m	1 330m		287w	287w	δ(N–Pt–N)
1 310m	1 315m	$\delta(\mathrm{NH_2})_{\mathrm{wag}}$	252w	254w	
1 300m	1 302m		239w	240w	Ring bending
1 275m	1 290m		206w		$\nu(\mathrm{Pt^{III}}$–Br)
1 235m	1 260m		186w	186w	
	1 187w	$\delta(\mathrm{NH_2})_{\mathrm{wag}}$	154w	152w	
1 165vw	1 178w		149w		
1 095vs	1 085vs		131w		
1 057s	1 057s	$\nu(\mathrm{PO})_{\mathrm{terminal}}$	110w		
1 020m (sh)	1 030m (sh)				

* Assignments are based on those of Stein *et al.*, [17] D. B. Powell and N. Sheppard, *Spectrochim. Acta*, 1960, **17**, 68; G. W. Watt and D. S. Klett, *Inorg. Chem.*, 1966, **5**, 1278; Y. Omura, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta, Ser. A*, 1971, **27**, 1153.

halogen-bridged complexes and found at *ca.* 17 000 cm^{-1} (see above)[23] for $[\mathrm{Pt^{II}(en)_2}][\mathrm{Pt^{IV}(en)_2Br_2}]\mathrm{Y_4}$ (Y = $[\mathrm{ClO_4}]^-$, $\mathrm{Br^-}$, or $[\mathrm{CuBr_4}]^{3-}$). Excitation within the contour of this band would be expected to lead to a resonance-Raman spectrum dominated by a long overtone progression based on the totally symmetric chain-stretching mode, $\nu_{\mathrm{sym}}(\mathrm{Br{-}Pt^{IV}{-}Br})$, which is known to occur in the region of *ca.* 175 cm^{-1}.[23] This is consistent with the observed result on the title bromo-complex (Table 1).

The anion $[\mathrm{Pt^{III}{}_2(H_2P_2O_5)_4Br_2}]^{4-}$ is known to show two bands in its electronic spectrum at 29 400 and 32 800 cm^{-1} (in aqueous solution), that of higher energy being the more intense and assigned to the $d_\sigma \longrightarrow d_{\sigma^*}$ transition.[20] The Raman spectrum of its potassium salt in aqueous solution has been found to give rise to two bands at 134 and 224 cm^{-1} which are assigned to the $\nu(\mathrm{Pt^{III}{-}Pt^{III}})$ and $\nu(\mathrm{Pt^{III}{-}Br})$ modes respectively.[17] Both the electronic as well as the Raman spectra (Table 1) of the complex are thus consistent with the presence of the $[\mathrm{Pt^{III}{}_2(H_2P_2O_5)_4Br_2}]^{4-}$ ion.

The results indicate that the structure of the bromo-complex is $[\mathrm{Pt^{II}(en)_2}][\mathrm{Pt^{IV}(en)_2Br_2}][\mathrm{Pt^{III}{}_2(H_2P_2O_5)_4Br_2}]$. This is confirmed by the lack of the combination bands between bands attributed to the cation and those attributed to the anion. The assignment of the electronic bands and the proposed structure for the complex are strengthened by consideration of the plots of the excitation profiles of the $\nu_1'\{\nu_{\mathrm{sym}}(\mathrm{Br{-}Pt^{IV}{-}Br})\}$, $\nu_1\{\nu(\mathrm{Pt^{III}{-}Pt^{III}})\}$, and $\nu_2\{\nu(\mathrm{Pt^{III}{-}Br})\}$ modes. While the excitation profile of the chain symmetric-stretching mode, ν_1' maximises to the red of the band of lowest energy (17 000 cm^{-1}), a well established feature of halogen-bridged mixed-valence complexes,[8] those of ν_1 and ν_2 of the anion maximise within the contour of the $d_\sigma \longrightarrow d_{\sigma^*}$ band of the anion at 23 300 cm^{-1} (Figure 1). The result clearly demonstrates which Raman-active modes are coupled with which electronic transitions.

The polarised Raman spectra indicate that α_{zz} is the largest element in the scattering tensor for the ν_1' mode of the cation and for the ν_1 and ν_2 modes of the anion, and that the two electronic transitions of lowest energy are *z*-polarised. The result for the cation is in agreement with results on previously studied complexes of a halogen-bridged nature, *i.e.* that the $\mathrm{Pt^{II}} \longrightarrow \mathrm{Pt^{IV}}$ intervalence band is *z*-polarised.[7,8] Since the $d_\sigma \longrightarrow d_{\sigma^*}$ band is also polarised in the same direction, it is concluded that the $\mathrm{Br{-}Pt^{III}{-}Pt^{III}{-}Br}$ backbone of the anion is aligned parallel to the chain axis of the cation.

The spectroscopy of the iodo-complex is entirely analogous to that of the bromo-complex. Irradiation within the contour of the $\mathrm{Pt^{II}} \longrightarrow \mathrm{Pt^{IV}}$ intervalence band[24] leads to the development of a long progression in ν_1', the symmetric chain-stretching mode, whereas irradiation within the contour of the $d_\sigma \longrightarrow d_{\sigma^*}$ transition of the anion leads to the development of various progressions involving ν_1 and ν_2, the $\mathrm{Pt^{III}{-}Pt^{III}}$ and $\mathrm{Pt^{III}{-}I}$ stretching modes, respectively. The excitation profiles of each of these bands (Figure 2) maximise within the contour of the appropriate electronic band.

Conclusions

The structure of the product of the reaction of $[\mathrm{Pt^{IV}(en)_2X_2}]\mathrm{X_2}$ (X = Br or I) and $\mathrm{K_4}[\mathrm{Pt^{II}{}_2(H_2P_2O_5)_4}]\cdot 2\mathrm{H_2O}$ has been shown by use of electronic, infrared, Raman, and resonance-Raman spectroscopy to be $[Pt^{II}(en)_2][Pt^{IV}(en)_2X_2][Pt^{III}_2(H_2P_2O_5)_4X_2]$, *i.e.* a mixed-valence linear-chain cation in association with a dimeric anion. Single-crystal measurements suggest that both the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence and the $d_\sigma \longrightarrow d_{\sigma^*}$ transitions are polarised along the long (*z*) axis of the crystals and that the $Br{-}Pt^{III}{-}Pt^{III}{-}Br$ backbone of the anion is parallel to the $Pt^{II} \cdots Br{-}Pt^{IV}{-}Br \cdots$ cation-chain axis. These complexes are the first known solids established to contain an element in three different oxidation states and also the first to be formulated as involving both class I and class II mixed-valence interactions.

To obtain such complexes by the reaction of $[Pt^{IV}(en)_2X_2]X_2$ (X = Br or I) with $K_4[Pt^{II}_2(H_2P_2O_5)_4]\cdot 2H_2O$, the following mechanism is proposed: oxidation–reduction reaction between cation and anion, equation (i), and formation of the chain mixed-valence complex, equation (ii).

$$[Pt^{IV}(en)_2X_2]^{2+} + [Pt^{II}_2(H_2P_2O_5)_4]^{4-} \longrightarrow [Pt^{II}(en)_2]^{2+} + [Pt^{III}_2(H_2P_2O_5)_4X_2]^{4-} \quad \text{(i)}$$

$$n[Pt^{II}(en)_2]^{2+} + n[Pt^{IV}(en)_2X_2]^{2+} \longrightarrow \{[Pt^{II}(en)_2][Pt^{IV}(en)_2X_2]^{4+}\}_n \quad \text{(ii)}$$

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