Electronic, Infrared, and Resonance-Raman Spectra of Mixed-valence Iodide-bridged Linear-chain Complexes of Platinum

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Electronic, i.r., and resonance-Raman (r.R.) spectra of mixed-valence complexes of platinum, $[Pt(en)I_2][Pt(en)I_4]$, $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$, and *cis*-$[Pt(NH_3)_2(SCN)_2][Pt(NH_3)_2(SCN)_2I_2]$, where en = 1,2-diaminoethane, have been recorded as powders or discs at *ca.* 80 K. In addition, a single-crystal polarized r.R. spectrum of $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$ at room temperature has been obtained. Under r.R. conditions, progressions in ν_1 (120—123 cm^{-1}), the symmetric X–Pt^{IV}–X stretching mode of the quadrivalent constituent, reach to 7, 9, and 8 members, respectively. The results confirm in the first two cases, and demonstrate in the last case, that the complexes are linear-chain iodide-bridged species. Brief results are also given on $K_4[PtI_4][PtI_6]$. The excitation profiles of ν_1 and $2\nu_1$ of $[Pt(en)I_2][Pt(en)I_4]$ and $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$ all maximize near to, but on the low-wavenumber side of, the intervalence band maximum. Those of ν_1 and $2\nu_1$ of the thiocyanate complex display a double maximum for which no explanation can be advanced.

THERE is considerable interest [1-6] in the mixed-valence platinum and palladium complexes of the types $[M^{II}L_4][M^{IV}L_4X_2]Y_4$, where M = Pt or Pd, L = ethylamine, $\frac{1}{2}$ 1,2-diaminoethane (en), $\frac{1}{2}$ 1,2- or 1,3-diaminopropane, X = Cl, Br, or I, and Y = Cl, Br, I, BF_4, or ClO_4, and $[M'^{II}L_2X_2][M^{IV}L_2X_4]$ where L = NH_3 or $\frac{1}{2}$ en, M = M′ = Pt or Pd, and X = Cl, Br, or I. The interest stems primarily from their highly anisotropic spectral and electrical conductance properties, which typify those of class II mixed-valence complexes.[2] In particular, the polarization of the $Pt^{II}\rightarrow Pt^{IV}$ mixed-valence band, and of the resonance-Raman (r.R.)-excited progressions in the ν_1, $\nu_{sym}(X–Pt^{IV}–X)$ band associated with the Cl or Br atoms which bridge the Pt^{II} and Pt^{IV} atoms along the chain, have been extensively explored.[7-14] By contrast, related information on analogous iodo-complexes is sparse,[12] a surprising situation in view of the fact that iodo-complexes have higher electrical conductances than chloro- or bromo-complexes [15-17] and that their conductances can increase by a factor of as much as 10^9 on their being compressed at 140 kbar.[15,†] Moreover both *X*-ray photoelectron as well as crystallographic data suggest [18] that in linear-chain iodo-complexes the platinum atoms much more nearly approach the Pt^{III} state than is the case for the analogous chloro- or bromo-complexes.

The present investigation is concerned therefore with the complexes $[Pt(en)I_2][Pt(en)I_4]$, $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$, and *cis*-$[Pt(NH_3)_2(SCN)_2][Pt(NH_3)_2(SCN)_2I_2]$. The structures of the first two complexes are known [19-21] to consist of parallel infinite chains of $\cdots I–Pt^{IV}–I\cdots Pt^{II}\cdots$ units. The neutral square-planar $[Pt(en)I_2]$ and tetragonal-bipyramidal $[Pt(en)I_4]$ entities form mixed parallel stacks in the first complex, whereas in the second a similar situation prevails with respect to the square-planar cations $[Pt(en)_2]^{2+}$ and tetragonal-bipyramidal cations $[Pt(en)_2I_2]^{2+}$ [Figure 1(*a*) and (*b*)]. The ClO_4^- ions in the latter case also line up parallel to the chain axis, being hydrogen-bonded to the amine nitrogen atoms. The structure of the thiocyanate complex has not yet been deduced crystallographically, but from the results reported herein [22] it is clear that it must likewise be an iodine-bridged linear-chain complex as shown in Figure 1(*c*). Some results are also included on the related chain complex $K_4[PtI_4][PtI_6]$.

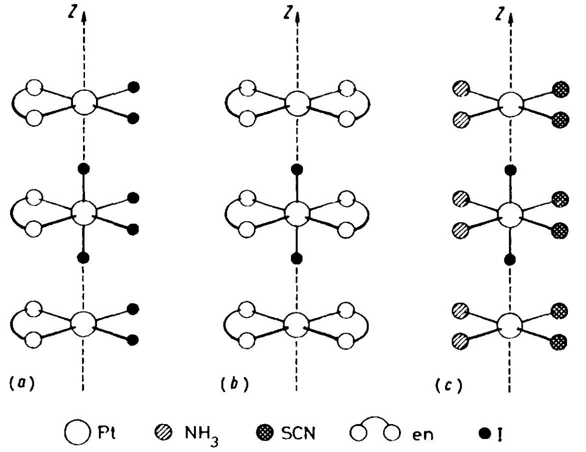

FIGURE 1 Structures of the complexes: (*a*) $[Pt(en)I_2][Pt(en)I_4]$; (*b*) $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$ excluding the ClO_4^- ion; and (*c*) that proposed for *cis*-$[Pt(NH_3)_2(SCN)_2][Pt(NH_3)_2(SCN)_2I_2]$

EXPERIMENTAL

The complex $[Pt(en)I_2][Pt(en)I_4]$ was obtained as bronze platelets by the method of Watt and McCarley [23] and $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$ as gold needles by the method of Bekaroglu *et al.*; [24] single crystals of the perchlorate salt were grown by slow cooling of saturated aqueous solutions of the constituents. Both complexes analyzed satisfactorily for the correct empirical formulae. The complex *cis*-$[Pt(NH_3)_2(SCN)_2][Pt(NH_3)_2(SCN)_2I_2]$ was provided by Professor H. J. Keller,[22,25] and $K_4[PtI_4][PtI_6]$ was obtained by the method of Thiele *et al.*[26]

Electronic spectra were obtained on a Cary 14 spectrometer by transmission through pressed discs of the complexes dispersed in CsI or $K[ClO_4]$. Infrared spectra of CsI pellets were recorded on a Perkin-Elmer 225 spectro-

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† Throughout this paper: 1 bar = 10^5 Pa.

meter (200—4 000 cm^{-1}) and of Polythene pellets on a Beckmann IR 720M spectrometer (50—400 cm^{-1}).

Raman spectra were recorded using Spex 1401 and 14018 (R6) double monochromators equipped with 1 200 line mm^{-1} Bausch and Lomb gratings and 1 800 line mm^{-1} Jobin–Yvon holographic gratings, respectively. Exciting radiation was provided by Coherent Radiation models 52 Ar^+ and 52 Kr^+ lasers. Detection was by standard photon-counting techniques employing cooled RCA C31034 photomultiplier tubes. Room-temperature spectra were obtained by the rotating-sample technique [27] and at *ca.* 80 K from pressed discs of the sample in $K_2[SO_4]$ in conjunction with a cylindrical lens; the latter focused the beam as a line on the surface of the sample in order to minimize local heating and decomposition.

The spectra were calibrated with neon emission lines and all band intensities were corrected for the spectral response of the instruments. Excitation profiles were recorded at *ca.* 80 K with respect to the band of $K_2[SO_4]$ at 981 cm^{-1}, as internal standard.

RESULTS AND DISCUSSION

The complexes studied are typical examples of Class II mixed-valence complexes, *i.e.* they are complexes in which distinct valence sites are expected crystallographically but in which there is some interaction between the metal atoms at these sites. Most physical properties (*e.g.* i.r. spectra) of such complexes are simple superpositions of those of the constituent complexes. However, the electronic and resonance Raman (r.R.) spectra are not and accordingly these spectra are discussed in detail, the key properties of the complexes being summarized in Table 1.

Electronic Spectra.—The complex $[Pt(en)I_2][Pt(en)I_4]$ is formed as bronze platelets which can be ground to a black powder, whereas the constituents $[Pt(en)I_2]$ and $[Pt(en)I_4]$ are pale yellow and brown, respectively. The spectrum of the mixed-valence complex shows a broad featureless band, maximizing at 14 400 cm^{-1} (Figure 2).

TABLE 1

Summary of data on complexes studied

Complex	$[Pt(en)I_2][Pt(en)I_4]$	$[Pt(en)_2][Pt(en)_2I_2]$-$[ClO_4]_4$	$[Pt(NH_3)_2(SCN)_2]$-$[Pt(NH_3)_2(SCN)_2I_2]$	$K_4[PtI_4][PtI_6]$
Crystal colour [a]	Bronze plates	Gold needles	Dark green	Bronze
Powder colour	Black	Blue	Mauve	Black
Mixed-valence band max.[b]/cm^{-1}	14 400	14 000	18 200	$<$12 500
F.w.h.m./cm^{-1}	5 000	6 000	2 500	$>$6 000
Excitation profile max (ν_1)/cm^{-1}	13 000	13 800	17 600, 14 300	$<$12 500
ω_1/cm^{-1}	121.2 ± 0.3	122.6 ± 0.5	120.4 ± 0.2	*ca.* 113
x_{11}/cm^{-1}	−0.33 ± 0.07	−0.61 ± 0.09	−0.15 ± 0.03	*ca.* 0
Progression [c] (ν_1) at *ca.* 80 K	$7\nu_1$	$9\nu_1$	$8\nu_1$	$3\nu_1$
$I(2\nu_1)/I(\nu_1)$ [d]	0.51	0.55	0.45	0.24
Pt^{IV}–I/Å	Pt^{II}–Pt^{IV} 5.682 Å	2.791,[e] 2.704,[f] 2.726 [f]		2.70
Pt^{II}–I/Å		3.036,[e] 3.115,[f] 3.029 [f]		3.20

[a] By reflected light. [b] By transmission. [c] ν_1 is the $\nu_{sym}(I-Pt^{IV}-I)$ fundamental. [d] On resonance. [e] Ref. 20. [f] Ref. 21.

The complex $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$ is obtained as gold needles, which appear blue on being ground. The crystals are very dichroic when seen under a microscope, being blue with the electric vector of the incident radiation parallel to the chain axis and almost colourless when it is perpendicular to this axis. Its electronic spectrum in a $K[ClO_4]$ disc consists of a broad band in the visible region, maximizing at 14 000 cm^{-1} (Figure 3).

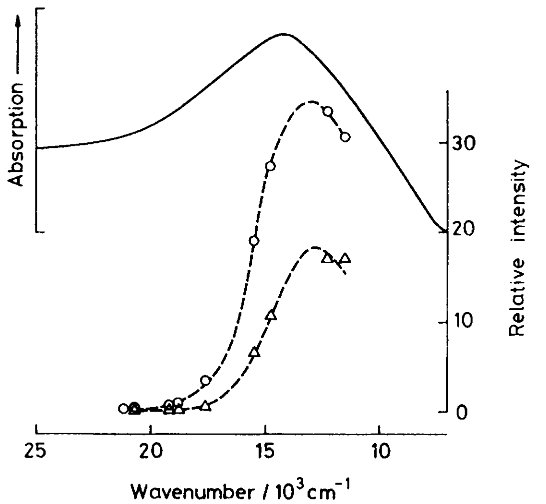

FIGURE 2 Electronic spectrum of $[Pt(en)I_2][Pt(en)I_4]$ as a CsI disc and excitation profiles of the Stokes ν_1 (○) and $2\nu_1$ (△) bands

These colour changes from the bulk material to the powder form have been attributed to particle-size effects.[14]

The complex *cis*-$[Pt(NH_3)_2(SCN)_2][Pt(NH_3)_2(SCN)_2I_2]$ is formed as dark green lustrous crystals [25] which appear mauve on being ground into powder. The electronic spectrum of this complex in a CsI disc shows a strong band at 18 200 cm^{-1} (Figure 4) and a full width at half-maximum of only 2 500 cm^{-1}, which is the smallest observed for this type of complex (a more typical value is 5 000—6 000 cm^{-1}).

These strong, axially polarized, bands are assigned to the intervalence charge transfer ($Pt^{II} \longrightarrow Pt^{IV}$) along the chain.[2,6]

Infrared Spectra.—The i.r. spectra of the three complexes show mainly a superposition of the spectra of the constituent complexes. The spectra have been assigned (Table 2) by analogy to previously reported assignments.[28-31]

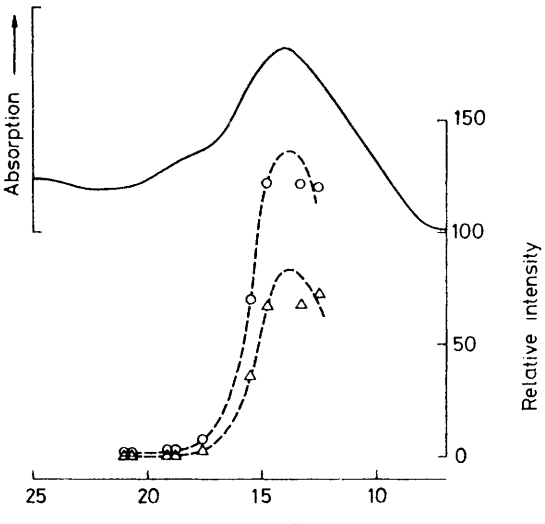

FIGURE 3 Electronic spectrum of $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$ as a $K[ClO_4]$ disc and excitation profiles as in Figure 2

Resonance-Raman Spectra.—The resonance-Raman (r.R.) spectra of the complexes $[Pt(en)I_2][Pt(en)I_4]$, $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$, and *cis*-$[Pt(NH_3)_2(SCN)_2]$-$[Pt(NH_3)_2(SCN)_2I_2]$ at *ca.* 80 K are shown in Figures 5—7, respectively, and the wavenumbers and assignments of the observed bands are listed in Tables 3—5.

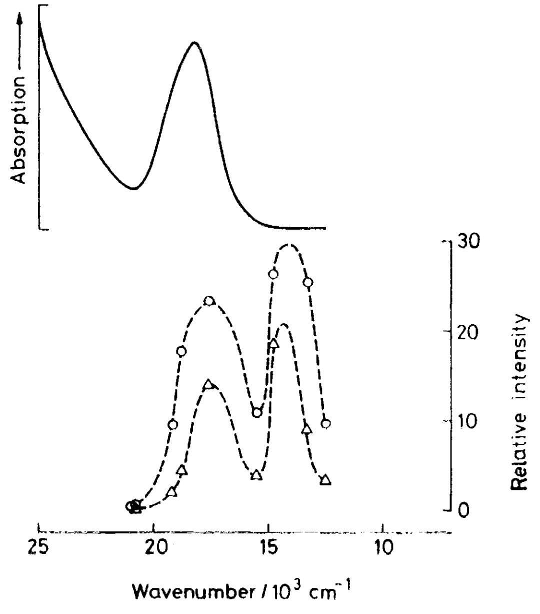

FIGURE 4 Electronic spectrum of *cis*-$[Pt(NH_3)_2(SCN)_2][Pt(NH_3)_2(SCN)_2I_2]$ as a CsI disc and excitation profiles as in Figure 2

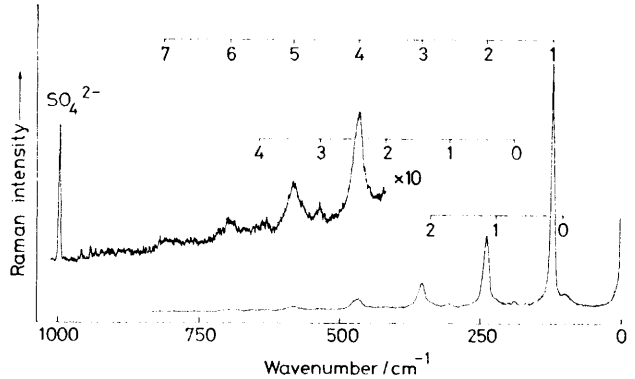

FIGURE 5 Resonance-Raman spectrum of $[Pt(en)I_2][Pt(en)I_4]$ as a $K_2[SO_4]$ disc recorded with 752.5 nm excitation at *ca.* 80 K. Slit width *ca.* 1.5 cm^{-1}

As noted in previous studies of this sort, excitation of a complex with radiation whose wavenumber falls within the contour of the axially polarized intervalence transition gives rise to a r.R. spectrum which is dominated by a long progression in the symmetric (X–Pt^{IV}–X) stretching mode (ν_1). The progression reaches to $7\nu_1$, $9\nu_1$, and $8\nu_1$, for the three complexes, respectively. Also observed are secondary progressions, based on the band at *ca.* 180 cm^{-1}, which possibly arises from the asymmetric stretch, ν_{asym}(IPt–I), in the chain. These progressions are very weak and the progression-forming mode is again ν_1.

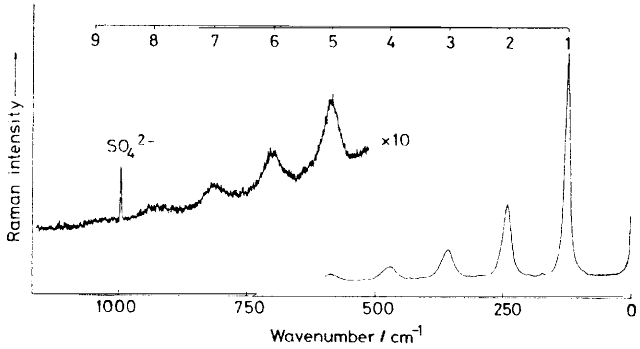

FIGURE 6 Resonance-Raman spectrum of $[Pt(en)_2][Pt(en)_2I_2]$-$[ClO_4]_4$ as a $K_2[SO_4]$ disc recorded as in Figure 5

Observation of a large number of overtones of a totally symmetric fundamental makes it possible, by standard procedures, to determine the harmonic frequency (ω_1)

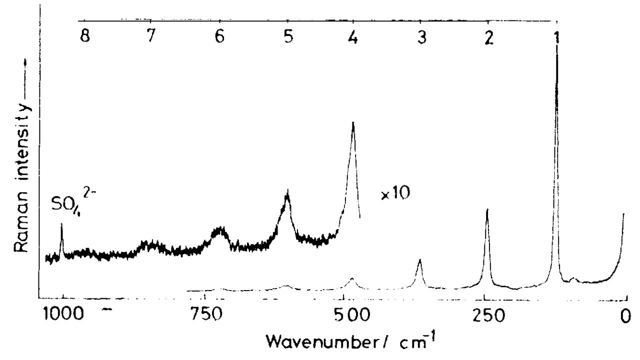

FIGURE 7 Resonance-Raman spectrum of *cis*-$[Pt(NH_3)_2(SCN)_2]$-$[Pt(NH_3)_2(SCN)_2I_2]$ as a $K_2[SO_4]$ disc recorded with 568.2 nm excitation at *ca.* 80 K. Slit width *ca.* 1.5 cm^{-1}

and anharmonicity constant (x_{11}). The results of such analyses on the present data are given in Table 1.

In each case, the full-width at half-maximum (f.w.h.m.) of the members of the progression in ν_1 increases with increase in the vibrational quantum number, v_1, and the band intensities show a continuous decrease with increase in v_1; both of these features are typical of r.R. progressions. Moreover, the f.w.h.m. of the members of the ν_1 progression increases faster the larger is the anharmonicity constant x_{11}; this feature is understandable in terms of hot-band contributions to Raman band intensities.[32]

TABLE 2

Wavenumbers (cm^{-1}) and assignments of bands observed in the i.r. spectra

$[Pt(en)I_2]$-$[Pt(en)I_4]$	$[Pt(en)_2]$-$[Pt(en)_2I_2][ClO_4]_4$	*cis*-$[Pt(NH_3)_2(SCN)_2]$-$[Pt(NH_3)_2(SCN)_2I_2]$
95m	117m,br	98w
109vs	172s 183s $\}$ ν(Pt–I)	124m
142m	261s	144m
179vs 186vs $\}$ ν(Pt–I)	273w	158m
193 (sh)	295m δ(N–Pt–N)	184(sh) 198s $\}$ ν(Pt–I)
224s	352s	232vs? δ(S–Pt–S)
284m δ(N–Pt–N)	362m	287vs δ(N–Pt–N)
425m	480m,br ClO_4^-	320vs ν(Pt–S)
435m		704vw 776vw $\}$ ν(CS)
515m ν(Pt–N)		856w $\delta(NH_3)$
		1 310s
		1 328m
		2 115s 2 120(sh) $\}$ ν(CN)
		3 150s 3 270s $\}$ $\nu(NH_2)$

The fact that the r.R. spectra of all three complexes are closely similar establishes that *cis*-$[Pt(NH_3)_2(SCN)_2]$-$[Pt(NH_3)_2(SCN)_2I_2]$, like the other two (for which *X*-ray data are available), is an iodine-bridged linear-chain mixed-valence complex. The possibility that the I_3^- ion could be present in the thiocyanate complex is ruled out since (*a*) ν_1 occurs at 120.1 cm^{-1}, whereas the symmetric stretch (ν_1) of the I_3^- ion is at 111 cm^{-1}, and (*b*) CsI_3 shows no resonance enhancement of its ν_1 band nor any overtone progressions with exciting lines in the 13 000—18 000 cm^{-1} region ($\lambda_{max.}$ for I_3^- is at 355 nm).

TABLE 3

Wavenumbers (cm^{-1}), relative intensities, f.w.h.m. (cm^{-1}), and assignments of bands observed in the r.R. spectrum of $[Pt(en)I_2][Pt(en)I_4]$ at *ca.* 80 K

ν *	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\nu_{1/2}$	Assignment
95.9			ν_a
120.1	1.00	7.5	ν_1, $\nu(I-Pt^{IV}-I)$
181.7			ν_2
215.1			$\nu_1 + \nu_a$
240.5	0.51	13.9	$2\nu_1$
301.6			$\nu_1 + \nu_2$
334.1			$2\nu_1 + \nu_a$
360.2	0.33	19	$3\nu_1$
423.2			$2\nu_1 + \nu_2$
455.7			$3\nu_1 + \nu_a$
479.5	0.20	25	$4\nu_1$
524.5			$3\nu_1 + \nu_2$
596.1	0.11	33	$5\nu_1$
644.0			$4\nu_1 + \nu_2$
714.8	0.07	40	$6\nu_1$
827	0.04	*ca.* 50	$7\nu_1$

* Obtained as a $K_2[SO_4]$ disc with 676.4 nm excitation.

TABLE 4

Wavenumbers (cm^{-1}), relative intensities, f.w.h.m. (cm^{-1}), and assignments of bands observed in the r.R. spectrum of $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$ at *ca.* 80 K

ν *	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\nu_{1/2}$	Assignment
121.5	1.00	10.2	ν_1, $\nu(I-Pt^{IV}-I)$
162.0			ν_2
184.9			ν_3
243.1	0.55	19	$2\nu_1$
277.5			$\nu_1 + \nu_2$
292.2			$\nu_1 + \nu_3$
360.9	0.34	27	$3\nu_1$
402.4			$2\nu_1 + \nu_2$
475.9	0.21	33	$4\nu_1$
521.7			$3\nu_1 + \nu_2$
591.3	0.13	39	$5\nu_1$
631.5			$4\nu_1 + \nu_2$
703.1	0.08	43	$6\nu_1$
822.7	0.05	47	$7\nu_1$
942.9	0.03	*ca.* 55	$8\nu_1$
1 053	0.01		$9\nu_1$

* Obtained as a $K_2[SO_4]$ disc with 676.4 nm excitation.

Figure 8 shows the spectrum of a single crystal (2 × 0.2 × 0.2 mm) of $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$ at room temperature when irradiated with *ca.* 10 mW of the 676.4 nm line of a Kr$^+$ laser. The crystal was oriented so that the chain axis was parallel to the electric vector of the laser beam, and with the polarizer parallel or perpendicular to this axis. Six overtones of ν_1 were observed in the former orientation and almost no

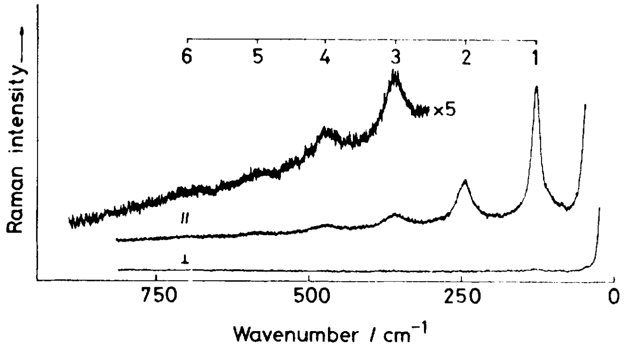

FIGURE 8 Resonance-Raman spectra of a $[Pt(en)_2][Pt(en)_2I_2]$-$[ClO_4]_4$ single crystal recorded with 676.4 nm (*ca.* 10 mW) excitation at *ca.* 295 K, with the electric vector of the incident beam parallel to the chain axis, and the polarizer parallel (‖) and perpendicular (⊥) to this direction. Slit width *ca.* 4 cm^{-1}

TABLE 5

Wavenumbers (cm^{-1}), relative intensities, f.w.h.m. (cm^{-1}), and assignments of bands observed in the r.R. spectrum of *cis*-$[Pt(NH_3)_2(SCN)_2][Pt(NH_3)_2(SCN)_2I_2]$ at *ca.* 80 K

ν *	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\nu_{1/2}$	Assignment
88			
120.1	1.00	5.9	ν_1, $\nu(I-Pt^{IV}-I)$
240.5	0.45	7.9	$2\nu_1$
358.9	0.24	10.2	$3\nu_1$
477.7	0.16	16.5	$4\nu_1$
598.0	0.12	22	$5\nu_1$
716.3	0.06	28	$6\nu_1$
834.2	0.04	39	$7\nu_1$
953.0	0.03	47	$8\nu_1$

* Obtained as a $K_2[SO_4]$ disc with 568.2 nm excitation.

scattering in the latter orientation. This shows the one-dimensionality of these complexes, and that the progression-forming mode is totally symmetric.

A brief study has also been made on the related mixed-valence complex $K_4[PtI_4][PtI_6]$, whose intervalence transition occurs in the i.r. region (Table 1). The r.R. spectrum of this complex is not well developed using the lowest-wavenumber exciting line at our disposal (799.3 nm), and a progression in ν_1 (*ca.* 113 cm^{-1}) was observed to reach only as far as $3\nu_1$ together with combination bands $\nu_1 + 134$ and $\nu_1 + 149$ cm^{-1}. Presumably both the large f.w.h.m. of the intervalence band as well as the inability to reach proper resonance therewith is responsible for the relatively poor r.R. spectrum in this case.

A comparison of the ν_1 values for the four salts studied (Table 1) suggests that the value falls from a cationic to a neutral and from a neutral to an anionic complex in agreement with previously noted trends in metal–halogen stretching frequencies. The excitation profiles of the ν_1 and $2\nu_1$ bands of $[Pt(en)I_2][Pt(en)I_4]$ and $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$ maximize near to, but on the low-wavenumber side of, the electronic band maximum, as observed in studies of this sort on related chloro- and bromo-complexes,[11] but no explanation can be advanced for the double maximum observed in the case of the thiocyanate complex.

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