Neutral Chain Bromide- and Iodide-bridged Platinum(II,IV) Complexes of 1,2-Diaminoethane and Thiocyanate: Synthesis, Electronic, Infrared, Raman, and Resonance-Raman Studies

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The complexes $Pt(en)(SCN)_2X$, en = 1,2-diaminoethane, X = Br or I, have been synthesised and, on the basis of a study of their electronic, i.r., and resonance-Raman spectra, established to be linear-chain, halogen-bridged complexes, $[Pt(en)(SCN)_2][Pt(en)(SCN)_2X_2]$. The electronic spectra are characterised by broad, intense bands (maxima at *ca.* 17 800 cm^{-1} for X = Br and at <13 000 cm^{-1} for X = I). The i.r. spectra are near superpositions of those of the constituent complexes, the band shifts on complex formation being greater for the iodide-bridged complex. The resonance-Raman spectra are dominated by long overtone progressions in ν_1, the Raman-active, symmetric (X–Pt^{IV}–X) stretch, reaching $7\nu_1$ for X = Br or I. Subsidiary progressions $v_1\nu_1 + \nu_n$ are observed for X = Br, where ν_n is identified as $\nu(Pt\text{–}S)_{eq}$. The form of the resonance-Raman spectra, ν_1 excitation profiles, and ν_1 wavenumber dependence on the wavenumber of the exciting line, ν_0, are discussed in terms of unresolved components of ν_1 and of their relative intensity dependence on temperature and ν_0.

The relationship between the optical and electrical properties of mixed-valence linear-chain, halogen-bridged complexes of platinum and palladium, which are highly anisotropic semiconductors, is of considerable interest.[1,2] The vibrational and electronic properties of neutral chain complexes with N donor or halogen off-axis ligands have been well documented.[3,4] The present work establishes the properties of two further neutral-chain, mixed-valence complexes containing S donor off-axis ligands, namely thiocyanate, in addition to the usual off-axis amines.

Although many complexes have been synthesised in the course of this work, with the bridging ligands chloride, bromide, or iodide and with various 1,2-diaminoalkanes co-ordinated in equatorial positions, only two, $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$ and $[Pt(en)(SCN)_2][Pt(en)(SCN)_2I_2]$, where en = 1,2-diaminoethane, have been established to be analytically pure; the spectroscopic work has thus been confined to these complexes.

Experimental

Preparations.—The complexes $[Pt(L\text{–}L)(SCN)_2]$, where L–L = 1,2-diaminoethane or a substituted 1,2-diaminoalkane, were prepared by the method of Mureinik and Robb,[5] but starting with $K_2[PtCl_4]$ rather than $H_2[PtCl_6]$.

The complex $Pt(en)(SCN)_2I$ was prepared by partial oxidation of $[Pt(en)(SCN)_2]$ with iodine in ethanol.[6]

The complex $Pt(en)(SCN)_2Br$, which is new, was prepared by dissolving $[Pt(en)(SCN)_2]$ in the minimum volume of dimethylformamide, adding sufficient bromine to oxidise half of the $[Pt(en)(SCN)_2]$, and then precipitating the resulting mixed-valence complex by the careful addition of ice-cold water to the reaction mixture.

$Pt(en)(SCN)_2I$. Found: C, 9.90; H, 1.75; I, 25.5; N, 11.3; S, 12.7. Calc. for $C_4H_8IN_4S_2Pt$: C, 9.65; H, 1.60; I, 25.5; N, 11.25; S, 12.85%.

$Pt(en)(SCN)_2Br$. Found: C, 10.8; H, 1.75; Br, 17.8; N, 12.4; S, 14.1. Calc. for $C_4H_8BrN_4S_2Pt$: C, 10.65; H, 1.80; Br, 17.7; N, 12.4; S, 14.2%.

Instrumentation.—Electronic spectra (295 K) were recorded on a Cary 14 spectrometer as Nujol mulls of the samples between quartz plates. Infrared spectra were recorded in the region 650—20 cm^{-1} as wax discs of the complexes, with a Bruker IFS 113V interferometer. An RIIC liquid-nitrogen cryostat was used to obtain spectra at *ca.* 80 K.

Table 1. Summary of properties of complexes

Complex	$[Pt(en)(SCN)_2]$- $[Pt(en)(SCN)_2Br_2]$	$[Pt(en)(SCN)_2]$- $[Pt(en)(SCN)_2I_2]$
Colour	Green metallic crystals Blue powder	Gold metallic crystals Blue powder
Intervalence max./cm^{-1}	17 800	
E.p. max./cm^{-1}	$\leqslant$15 500	
$\omega_1{}^a$/cm^{-1}	180.8 ± 0.1^b	122.5 ± 0.1^c
$x_{11}{}^a$/cm^{-1}	-0.22 ± 0.02^b	-0.51 ± 0.02^c
$I(2\nu_1)/I(\nu_1)$	0.54^b	0.51^c
Progression length	$6\nu_1{}^b$ $7\nu_1{}^d$	$6\nu_1{}^c$
Dispersion of ν_1/cm^{-1}	11.2 (676.4—406.7 nm)	10.4 (676.4—482.5 nm)

[a] See text. [b] λ_0 = 514.5 nm. [c] λ_0 = 676.4 nm. [d] λ_0 = 647.1 nm.

Raman spectra were recorded on a Spex 14018/R6 spectrometer. Exciting radiation was provided by Coherent Radiation model CR 12 (Ar^+) and CR 3000 K (Kr^+) lasers. Samples were held in the form of pressed $K[ClO_4]$ discs at *ca.* 80 K, using a liquid nitrogen and Dewar assembly. Spectra were calibrated by reference to the Rayleigh line, it having been separately established from the pure rotational spectrum of oxygen gas that the dispersion of the spectrometer is linear to within ±0.3 cm^{-1}.

All Raman band intensities were corrected for the spectral response of the instruments.

Results and Discussion

Electronic Spectra.—Crystals of the complexes are dichroic. The colours of the crystals and powders, together with related spectroscopic data for the complexes, are listed in Table 1.

The spectrum of $Pt(en)(SCN)_2Br$ (Figure 1) is dominated by a strong, broad, featureless band with the maximum at *ca.*

17 800 cm^{-1}. Such a spectrum is characteristic of halogen-bridged, mixed-valence complexes of platinum and hence this band is assigned to the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence transition by analogy with corresponding assignments for related complexes.[7] The transition is lower in wavenumber than that for the related $Pt(dach)Br_3$[8] (dach = 1,2-diaminocyclohexane) and $Pt(en)Br_3$ complexes.[7] The weaker peak at *ca.* 26 000 cm^{-1} is assigned to a *d–d* transition of the Pt^{IV} unit.

Infrared Spectra.—The i.r. spectra of $Pt(en)(SCN)_2Br$, $Pt(en)(SCN)_2I$, as well as that of the $[Pt(en)(SCN)_2]$ monomer, have

Table 2. Wavenumbers (cm^{-1}) and assignments of bands observed in the i.r. spectra of $[Pt(en)(SCN)_2]$, $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$, and $[Pt(en)(SCN)_2][Pt(en)(SCN)_2I_2]$[a]

$[Pt(en)(SCN)_2]$[b]	$[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$[c]	$[Pt(en)(SCN)_2][Pt(en)(SCN)_2I_2]$[d]	Assignment
	614w		
582s	574 (sh)		$\nu(Pt-N)$
	566m	564m	
550s	553m		
	546m	544m	
475s	472w		Ring mode
462m			$\delta(SCN)$
459m	456s	458w	
		452m	
		446w	
430m	434w		$\delta(SCN)$
427m	424m		
	420m	418m	
	405m		
	339m		$\nu(Pt-S)$
	334m		
327m	322w		
319m	312m	319w	
304m	306m	309w	
	297m	302w	
284m	275m	266s	$\delta(N-Pt-N)$
	239vs		ν_2, $\nu_{asym}(Br-Pt^{IV}-Br)$
224vs		234s	
	213m,br		
		191m	ν_2, $\nu_{asym}(I-Pt^{IV}-I)$?
189w	185m,br		
170w	165w		$\delta(N-Pt-N)$
		152w,br	

[a] Recorded in the range 660—20 cm^{-1}, as a wax disc at *ca.* 80 K. [b] Also bands at 142s, 109m, and 100m. [c] Also bands at 147m, 118vs, and 92m. [d] Also bands at 112s and 69m.

Table 3. Wavenumbers, relative intensities, full widths at half-maximum, and assignments of bands observed in the resonance-Raman spectrum of $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$*

$\tilde{\nu}$/cm^{-1}	$I(\nu_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	Assignment
90			
109			
180.2	1.0	5.1	ν_1, $\nu_{sym}(Br-Pt^{IV}-Br)$
206.6			$\delta(N-Pt-N)$ or $\nu(Pt-S)$
215			$\delta(N-Pt-N)$?
239.1			ν_2, $\nu_{asym}(Br-Pt^{IV}-Br)$?
272.4			$\nu(Pt-S)$
298.3			$\nu(Pt-S)$
360.8	0.54	9.2	$2\nu_1$
387.2			$\nu_1 + 206$
419			$\nu_1 + 215$ or $\delta(SCN)$
448			$\nu_1 + 272$ or $\delta(SCN)$
477.4			$\nu_1 + 298$
540.0	0.23	11.8	$3\nu_1$
570			$2\nu_1 + 206$ or $\nu(Pt-N)$
658			$2\nu_1 + 298$
718.9	0.13	17.2	$4\nu_1$
832			$3\nu_1 + 298$
897.4	0.07	25	$5\nu_1$
925			
975			
1 076	<0.07	>30	$6\nu_1$
1 124			

* Recorded as a $K[ClO_4]$ disc at *ca.* 80 K, slit widths of 200, 250, and 200 μm, using 514.5-nm excitation.

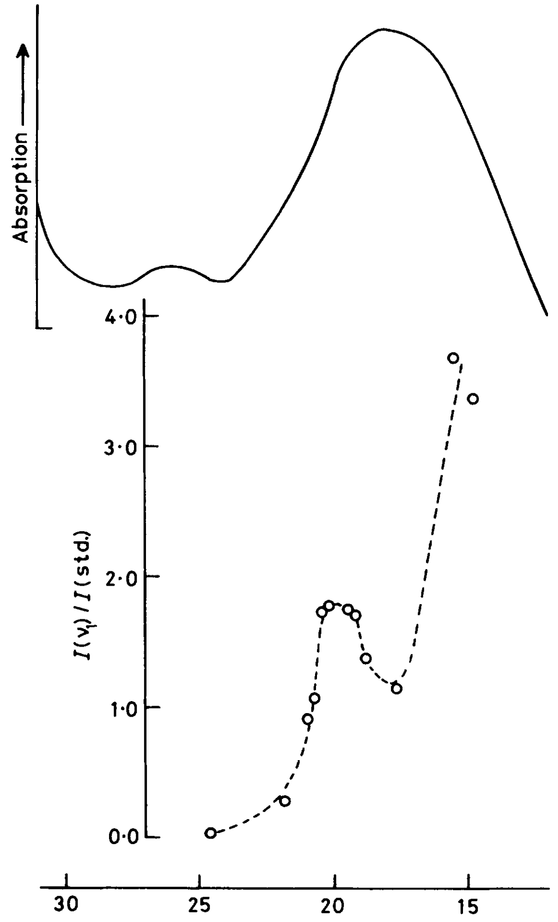

Figure 1. Electronic spectrum (295 K) and excitation profile (at *ca.* 40 K) of the ν_1 band of $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$

Table 4. Wavenumbers and assignments of bands observed in the resonance-Raman spectrum of $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$*

$\tilde{\nu}$/cm^{-1}	Assignment	$\tilde{\nu}$/cm^{-1}	Assignment
91		703	$4\nu_1$
177	ν_1, $\nu_{sym}(Br-Pt^{IV}-Br)$	877	$5\nu_1$
205br	$\delta(N-Pt-N)$	944	$[ClO_4]^-$
299w	$\nu(Pt-S)$	1 048	$6\nu_1$
355	$2\nu_1$	1 229	$7\nu_1$
385	$\nu_1 + 205$	1 350	
416	$\delta(SCN)$	1 400	
528	$3\nu_1$		

* Recorded as a $K[ClO_4]$ disc at *ca.* 80 K, slit widths of 200, 250, and 200 μm, using 647.1-nm excitation.

been recorded at *ca.* 80 K in the region 650—20 cm^{-1} (Figure 2). The wavenumbers and assignments of the bands are listed in Table 2, the assignments being based on those for previously reported complexes.[5,9—11]

The wavenumbers of the bands observed in the spectra of the Pt(en)(SCN)$_2$Br and Pt(en)(SCN)$_2$I complexes, with the exception of the metal–halogen stretch, are close to those for the monomer although greater band shifts and relative intensity changes on complex formation are detected for the iodide-bridged complex. The [SCN]$^-$ ligand, which is S bonded in the monomer,[6] clearly remains so on formation of the halogenated species because bands readily assignable to ν(Pt–S) are evident in the i.r. spectra. The band at 239 cm^{-1} for X = Br and at 191 cm^{-1} for X = I in the spectra of the bromo and iodo complexes, respectively, is tentatively assigned to the ν_2, ν_{asym}(X–Pt^{IV}–X), stretching mode, on the assumption (established in the next

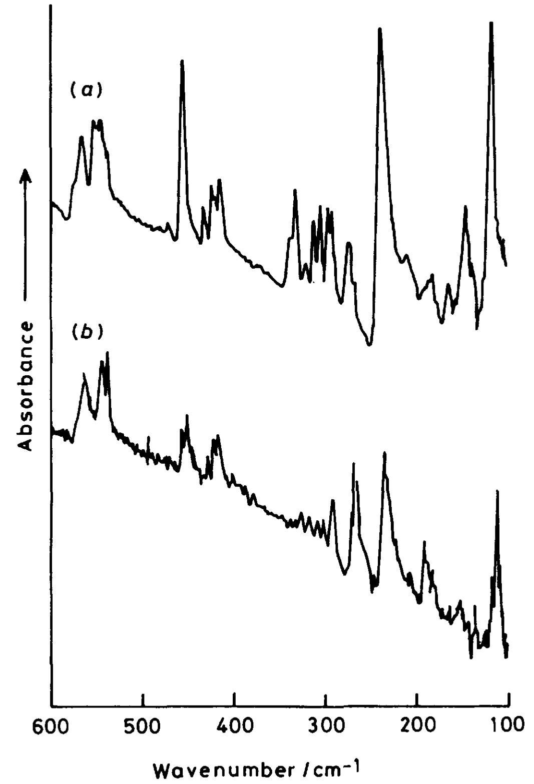

Figure 2. Fourier-transform i.r. spectra (as wax discs at 80 K) of (*a*) [Pt(en)(SCN)$_2$][Pt(en)(SCN)$_2$Br$_2$] and (*b*) [Pt(en)(SCN)$_2$][Pt(en)(SCN)$_2$I$_2$]

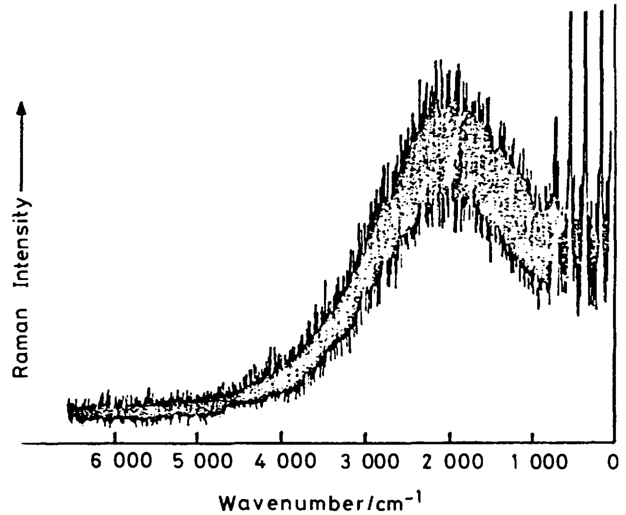

Figure 4. Resonance-Raman spectrum of [Pt(en)(SCN)$_2$][Pt(en)(SCN)$_2$Br$_2$] recorded as a K[ClO$_4$] disc at *ca.* 80 K, λ_0 = 514.5 nm, showing vibrational Raman spectrum together with luminescence band B

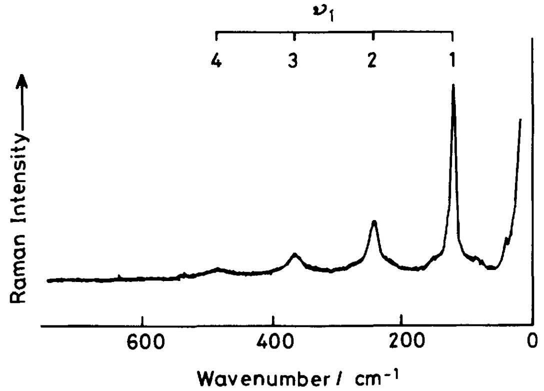

Figure 5. Resonance-Raman spectrum of [Pt(en)(SCN)$_2$][Pt(en)(SCN)$_2$I$_2$] recorded as a K[ClO$_4$] disc at *ca.* 80 K, λ_0 = 676.4 nm, showing vibrational Raman spectrum only

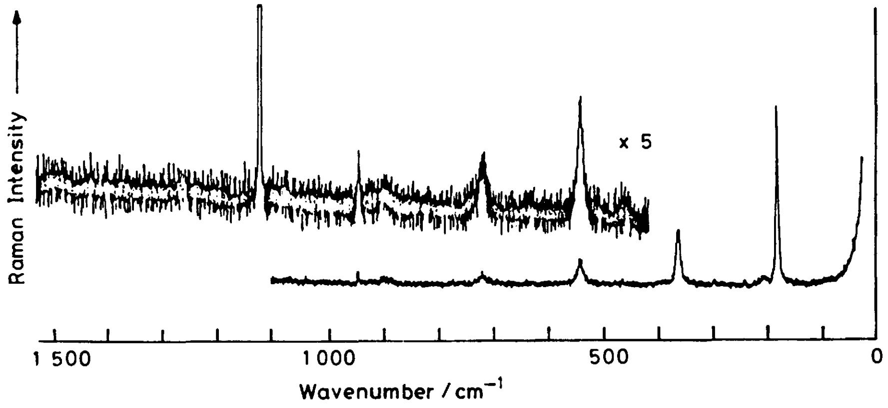

Figure 3. Resonance-Raman spectrum of [Pt(en)(SCN)$_2$][Pt(en)(SCN)$_2$Br$_2$] recorded as a K[ClO$_4$] disc at *ca.* 80 K, λ_0 = 514.5 nm, showing vibrational Raman spectrum only

Table 5. Wavenumbers, relative intensities, full widths at half-maximum, and assignments of bands observed in the resonance-Raman spectrum of $[Pt(en)(SCN)_2][Pt(en)(SCN)_2I_2]$*

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	Assignment
37			Plasma
73			
83			$\delta(I-Pt^{IV}-I)$
121.6	1.0	9.9	ν_1, $\nu_{sym}(I-Pt^{IV}-I)$
146.7			
191			ν_2, $\nu_{asym}(I-Pt^{IV}-I)$?
205			$\delta(N-Pt-N)$
241.8	0.51	19.1	$2\nu_1$
269.7			$\nu(Pt-S)$
361.4	0.3	31	$3\nu_1$
479.9	0.16	39	$4\nu_1$
545			$\nu(Pt-N)$
597	<0.16	>40	$5\nu_1$
717	<0.16	>40	$6\nu_1$

* Recorded as a $K[ClO_4]$ disc at *ca.* 80 K, slit widths of 150, 200, and 150 μm, using 676.4-nm excitation.

Table 6. Wavenumbers of (*i*) the ν_1 band of $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$ and (*ii*) the ν_1 and δ(I-Pt-I) bands of $[Pt(en)(SCN)_2][Pt(en)(SCN)_2I_2]$ measured at the peak maximum with different exciting lines[a]

(*i*)

λ_0/nm	ν_1/cm^{-1}	λ_0/nm	ν_1/cm^{-1}
406.7	187.7 ± 0.1	514.5	180.2 ± 0.1
457.9	182.6 ± 0.3	530.9	179.5 ± 0.1
476.5	181.6 ± 0.1	568.2	179.4 ± 0.2
487.9	181.5 ± 0.2	647.1	177.0 ± 0.1
501.7	180.4 ± 0.2	676.4	176.5 ± 0.1

(*ii*)

λ_0/nm	ν_1/cm^{-1}	δ(I-Pt-I)/cm^{-1}
676.4	119.2 ± 0.4	82.7 ± 0.3
647.1	120.0 ± 0.1	82.4 ± 0.4
568.2	121.9 ± 0.3	82.2 ± 0.4
520.8	126.6 ± 0.5[b]	88.0 ± 1.0
482.5	129.6 ± 1.0	91.2 ± 2.0

[a] Recorded at *ca.* 80 K as a $K[ClO_4]$ disc. [b] Additional peak at *ca.* 120.6 ± 0.4 cm^{-1}.

section) that these are linear-chain, halogen-bridged complexes. Moreover, there is a sloping background in the i.r. spectrum of each complex, a feature not present in the spectra of the monomers, but often observed in the i.r. spectra of mixed-valence complexes.[4]

Raman and Resonance-Raman Spectra.—The Raman and resonance-Raman spectra of the $Pt(en)(SCN)_2X$ complexes were recorded as $K[ClO_4]$ discs at *ca.* 80 K. The spectra are dominated by long overtone progressions in a band assignable to ν_1, the totally symmetric $(X-Pt^{IV}-X)$ stretching vibration, the wavenumber of which is characteristic of that of a halogen-bridge mode. Thus the $Pt(en)(SCN)_2X$ complexes are indeed mixed valence and halogen bridged and should be formulated as $[Pt(en)(SCN)_2][Pt(en)(SCN)_2X_2]$. The spectra are shown in Figures 3—5 and the band wavenumbers and assignments are given in Tables 3—5. Harmonic wavenumbers (ω_1) and anharmonicity constants (x_{11}) are given (on the basis of the usual approximations)[12] in Table 1. These are calculated on the assumption that the most intense component of the ν_1 fundamental[13] gives rise to the most intense component of each overtone.

For the bromide-bridged complex (Figure 3) the overtone progression reaches $6\nu_1$ (ν_1 = 180.2 cm^{-1}) for λ_0 = 514.5 nm and $7\nu_1$ (ν_1 = 177 cm^{-1}), for λ_0 = 647.1 nm. All the members of the progression are asymmetric to the low wavenumber side; this implies that there is more than one component to the ν_1 and $n\nu_1$ bands. It was not, however, possible to resolve any of the components under the experimental conditions used. There are several subsidiary progressions $v_1\nu_1 + \nu_n$ apparent, the longest reaching to $3\nu_1 + \nu_n$, where ν_n is assigned to a ν(Pt–S) mode. The subsidiary progressions are less intense for λ_0 = 647.1 nm than for λ_0 = 514.5 nm, this possibly being a function of incident laser power and hence temperature, which may alter the relative intensities of component bands to ν_1.[13] The appearance of the subsidiary progressions involving ν(Pt–S) implies that this mode is intimately connected with the structural changes consequent upon the intervalence transition.

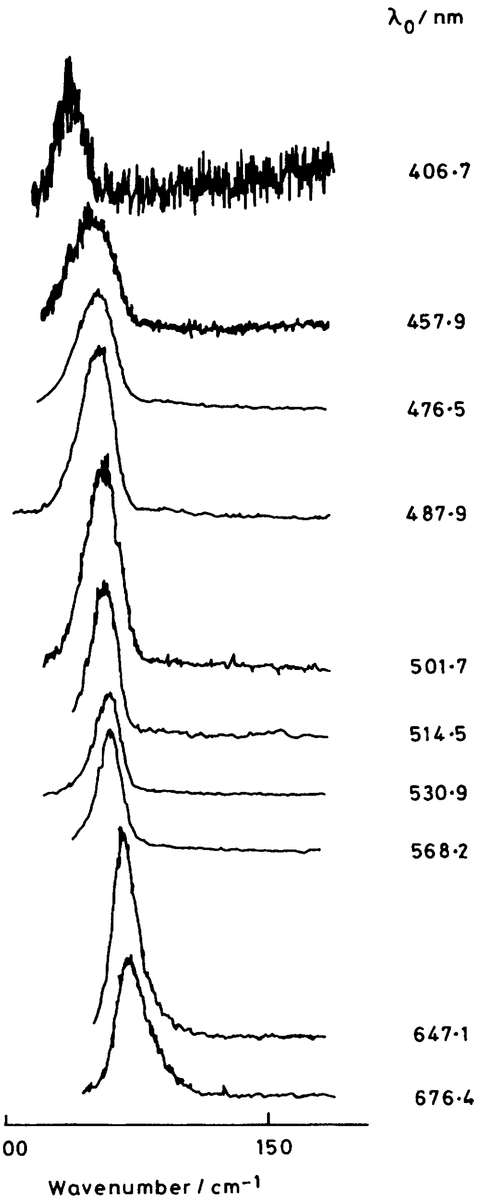

Figure 6. The ν_1 peak of $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$ recorded as a $K[ClO_4]$ disc at *ca.* 80 K, for exciting lines in the range 406.7—676.4 nm

Although luminescence band B[14,15] is apparent (Figure 4) in the resonance-Raman spectrum, luminescence band L[14,15]

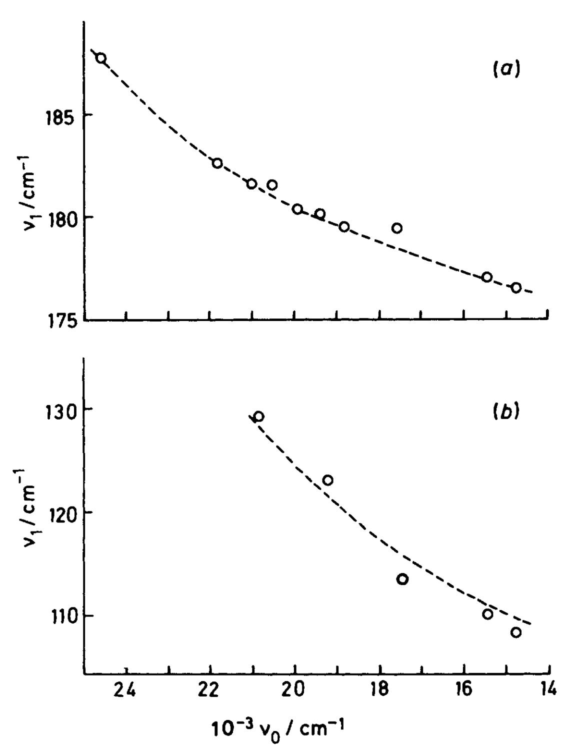

Figure 7. Plot of the wavenumber of the ν_1 band maximum of (*a*) $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$ and (*b*) $[Pt(en)(SCN)_2][Pt(en)(SCN)_2I_2]$ *versus* the exciting line wavenumber, recorded in each case as a $K[ClO_4]$ disc at *ca.* 80 K

could not be detected, this being predicted to lie at < 12 000 cm^{-1}, *i.e.* beyond the range of the spectrometer. The excitation profile (e.p.) of the ν_1 band (at *ca.* 40 K) of the bromide is a maximum at $\leqslant$ 15 500 cm^{-1} (Figure 1). There is a second weaker maximum in the e.p. at 19 800 cm^{-1}. This is due to different unresolved components to ν_1 coming onto resonance with different exciting lines.[13] The higher the wavenumber of the component the further to the blue is its resonance position but the lower is its relative degree of intensification compared with those of the lower wavenumber components. This gives rise to characteristic e.p.s, asymmetric to the blue side, and sometimes with resolved shoulders.

The resonance-Raman spectrum of the iodide-bridged complex (Figure 5, Table 5) is similarly dominated by a progression in ν_1, ν_{sym}(I–Pt^{IV}–I), up to $6\nu_1$. Bands due to off-axis vibrations, namely δ(N–Pt–N), ν(Pt–S), and ν(Pt–N) are observed but no subsidiary progressions, $v_1\nu_1 + \nu_n$, were detected (λ_0 = 676.4 nm). No luminescence band, L,[14,15] was observed, this being predicted to occur well beyond the spectrometer detection limit.

The apparent dispersion of ν_1 with change in ν_0 for both the bromide- and iodide-bridged complexes is listed in Table 6 and shown in Figures 6 and 7. As can be seen, the dispersion curve for the bromide-bridged complex (Figure 7) agrees well with that previously proposed,[16] with no dispersion being observed until ν_0 is greater than the band gap (E_g). The fact that the dispersion is observed for $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$ with a ν_0 lower in wavenumber than that for the related complex $[Pt(dach)Br_2][Pt(dach)Br_4]$[8] implies that the band gap in the former is less than that of the latter. This is in agreement with the relative values for the wavenumbers of the intervalence transition as determined by electronic spectroscopy {17 800 cm^{-1} for $[Pt(en)(SCN)_2][Pt(en)(SCN)_2Br_2]$ and 18 200 cm^{-1} for $[Pt(dach)Br_2][Pt(dach)Br_4]$[8]}.

The dispersion curve for the iodide-bridged complex (Figure 7) is virtually linear as expected for $\nu_0 \gg E_g$, the band gap for an iodide-bridged complex of platinum being < 12 000 cm^{-1}. The ν_1 peak is not always symmetrical with differing ν_0 due to the presence of more than one unresolved component to ν_1. Indeed, the apparent dispersion of ν_1 with changing ν_0 has been shown to be due mainly to changes in the relative intensities of these unresolved components with ν_0, the higher wavenumber components gaining intensity relative to those of lower wavenumber as ν_0 moves towards the blue. The band at *ca.* 83 cm^{-1} (λ_0 = 676.4 nm), assigned to δ(I–Pt^{IV}–I) also shows dispersion (*ca.* 8 cm^{-1} for ν_0 from 676.4 to 482.5 nm) implying that this band, too, consists of more than one component.

Conclusions

The two thiocyanate complexes studied display all the spectroscopic behaviour previously established for linear-chain halogen-bridged complexes, and hence they are so formulated. They are thus entirely analogous to the ammonia complex[17] $[Pt(NH_3)_2(SCN)_2][Pt(NH_3)_2(SCN)_2I_2]$, with sulphur-bonded thiocyanate.

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