Electronic and Resonance-Raman Spectra of Mixed-valence Ammine Complexes of Palladium and Platinum

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The resonance-Raman spectra of the mixed-valence complexes $[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$, $[Pd(NH_3)_2Br_2]$-$[Pt(NH_3)_2Br_4]$, $[Pd(NH_3)_2Cl_2][Pt(NH_3)_2Cl_4]$, and $[Pd(NH_3)_2Cl_2][Pd(NH_3)_2Cl_4]$ have been recorded at *ca.* 80 K and with a variety of different exciting lines. Assignments for the observed bands and progressions are given. Studies of the excitation profiles of key Raman bands of these complexes, in particular of the axial ν_{sym}(MX) and the non-axial ν_{sym}(MX) and ν_{sym}(MN) modes, have led to a systematic set of assignments for the lowest mixed-valence transitions of these complexes. These are: $Pt^{IV}\leftarrow Pt^{II}$ at $\leqslant$13 000 cm^{-1} in $[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$; $Pt^{IV}\leftarrow Pd^{II}$ at 16 000 cm^{-1} and $Pd^{IV}\leftarrow Pt^{II}$ at $\leqslant$13 000 cm^{-1} in $[Pd(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$; $Pd^{IV}\leftarrow Pt^{II}$ at *ca.* 18 000 cm^{-1} in $[Pd(NH_3)_2Cl_2][Pt(NH_3)_2Cl_4]$; and $Pd^{IV}\leftarrow Pd^{II}$ at *ca.* 13 000 cm^{-1} in $[Pd(NH_3)_2Cl_2]$-$[Pd(NH_3)_2Cl_4]$.

A RAMAN spectrum recorded using exciting radiation whose frequency coincides with that of an electronic transition of a molecule is known as a resonance-Raman (r.R.) spectrum. Such a spectrum differs from a normal Raman spectrum in that the intensities of certain bands are enhanced in the resonance case, and overtone and combination-tone progressions may be observed. The value of r.R. spectroscopy lies in its close connection with electronic-absorption spectroscopy.[1] Those vibrations which are ' active ' in an electronic transition, *i.e.* provide intensity in an absorption band, are also the ones which give rise to the enhanced bands and progressions in the r.R. spectrum. Therefore, since the widths of Raman bands are normally very much less than those of electronic-absorption bands, it is possible, by monitoring the changes in the Raman spectrum as the frequency of the exciting radiation is changed, to deduce the modes which are active in the resonant electronic transition. This is especially valuable in the case of mixed-valence compounds for which the absorption bands are typically thousands of wavenumbers in width even at low temperatures. A further point of interest concerns the variation in Raman-band intensities as the frequency of the exciting radiation is changed. A plot of such a variation in intensity is known as an excitation profile. This curve not only confirms that a particular Raman band (and thus the corresponding normal mode) is connected with the resonant electronic transition but also can allow separate absorption bands to be resolved in those cases where two or more are severely overlapped. This potentially higher resolving power of excitation profiles is partly due to the fact that only some of the Raman-active vibrations may be active in a particular transition and partly due to the coherent nature of the Raman effect.[1] Excitation profiles have been of considerable use in previous r.R. studies of mixed-valence compounds, in that relatively sharp features have been resolved from very broad absorption bands.

In our earlier papers on one-dimensional mixed-valence complexes we have reported the r.R. spectra of complexes of the types (*a*) $[Pt(NEtH_2)_4]$-$[Pt(NEtH_2)_4X_2]X_4\cdot nH_2O$ [$n = 4$ (X = Cl or Br) or 0 (X = Br or I)],[2-4] (*b*) $[Pt(en)X_2][Pt(en)X_4]$, and (*c*) $[Pt(en)_2][Pt(en)_2X_2][ClO_4]_4$ (en = 1,2-diaminoethane, X = Cl or Br).[5] The resonant electronic transition in these complexes is the axially polarised mixed-valence $5d_{z^2}\leftarrow 5d_{z^2}$ transition and the r.R. spectra are characterised by long progressions based on the axial platinum–halogen breathing mode, ν(X–Pt–X). This paper is concerned with complexes of the general formula [*trans*-$M(NH_3)_2X_2$][*trans*-$M'(NH_3)_2X_4$] (M or M′ = Pt or Pd, X = Cl or Br) and subsequently written as [M,M′]X

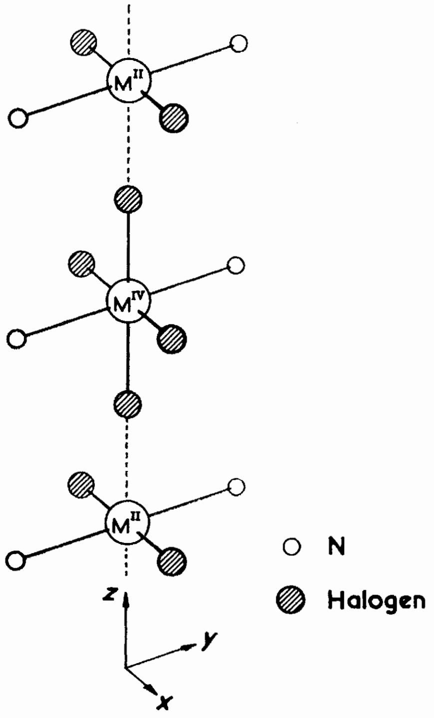

FIGURE 1 Structure of complexes with the general formula $[M^{II}(NH_3)_2X_2][M^{IV}(NH_3)_2X_4]$($M^{II}$ and M^{IV} = Pd or Pt, X = Cl or Br). Hydrogen atoms are not indicated

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[1] A. R. Gregory, W. H. Hennecker, W. C. Siebrand, and M. Zgierski, *J. Chem. Phys.*, 1975, **63**, 5475.

[2] R. J. H. Clark, M. L. Franks, and W. R. Trumble, *Chem. Phys. Letters*, 1976, **41**, 287.

[3] R. J. H. Clark and M. L. Franks, *J.C.S. Dalton*, 1977, 198.

[4] R. J. H. Clark and P. C. Turtle, *Inorg. Chem.*, 1978, in the press.

[5] J. R. Campbell, R. J. H. Clark, and P. C. Turtle, *Inorg. Chem.*, 1978, in the press.

(see Figure 1 for the structure). Clark and Trumble [6] have investigated the room-temperature r.R. spectra of the complexes [Pd,Pd]Cl and [Pd,Pt]Cl and concluded that excitation in the visible region is resonant with a mixed-valence transition only for the latter complex. One notable aspect of this previous work was that the nature of the r.R. spectra of these ammine complexes is very different from that of the complexes given in (*a*)—(*c*) above. In order to try and find the reasons for this difference we have investigated further complexes of this type. This paper is thus primarily concerned with results obtained on the complexes [Pt,Pt]Br and [Pd,Pt]Br at both room and liquid-nitrogen temperatures, but we have also investigated the complexes [Pd,Pt]Cl and [Pd,Pd]Cl at liquid-nitrogen temperatures.

The results, particularly those on Raman-band excitation profiles, have led to a set of assignments for the mixed-valence transitions of these complexes.

EXPERIMENTAL

The complexes [Pd,Pt]Cl and [Pt,Pt]Br were kindly supplied by Dr. W. R. Trumble; [Pd,Pt]Br and [Pd,Pd]Cl were prepared by literature methods.[7–10]

Raman spectra were recorded using a Spex 1401 double monochromator in conjunction with Coherent Radiation model 52 Ar^+ and Kr^+ and CR12 Ar^+ lasers, and a model 490 tunable dye laser employing rhodamine 6G or sodium fluorescein. Detection was by conventional photon-counting techniques using an RCA C31034 photomultiplier tube. Room-temperature Raman spectra were obtained with a rotating sample holder,[11] low-temperature spectra with a sampling arrangement described previously.[4] Intensity measurements were made relative to the band of $K_2[SO_4]$ at 981 cm^{-1} as internal standard. The mol ratio of sulphate : mixed-valence complex was *ca.* 1 500 : 1. Absorption spectra were recorded on a Cary 14 spectrometer.

RESULTS AND DISCUSSION

Before discussing the individual complexes in detail, a general point must be mentioned. Long overtone progressions, such as are observed for these complexes, can only arise from totally symmetric modes [1] (unless we make the assumption that in the excited electronic state the molecule is distorted from the ground-state symmetry). Thus the Raman intensity arises from a Franck–Condon type of mechanism rather than from a Herzberg–Teller coupling mechanism. It is also assumed throughout this paper, as in previous papers, that other strong bands appearing in the r.R. spectra arise from totally symmetric modes.

[Pt,Pt]Br.—This complex exhibits two kinds of resonance behaviour. Excitation in the red region produces a r.R. spectrum which is dominated by progressions in both axial and off-axis Pt^{IV}–Br stretching modes, while for excitation in the blue region a progression in the Pt^{IV}–N stretching mode begins to dominate (Figure 2, Table 1). In this respect, the spectrum of [Pt,Pt]Br resembles that of [Pd,Pd]Cl.[6]

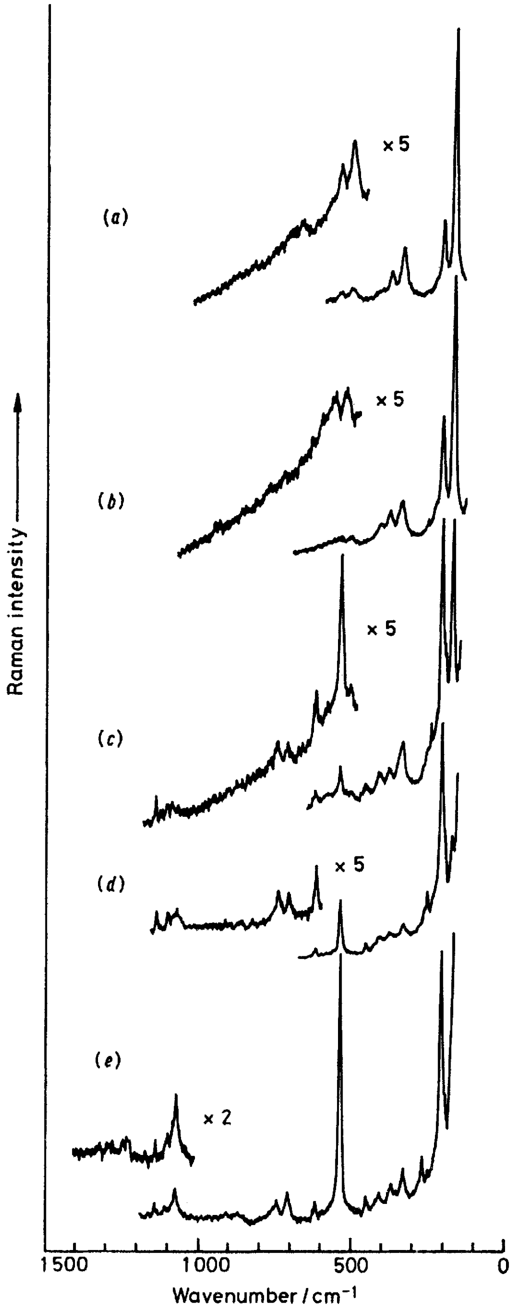

FIGURE 2 Resonance-Raman spectra of the complex [Pt,Pt]Br, recorded with (*a*) 647.1; (*b*) 568.2; (*c*) 514.5; (*d*) 488.0; and (*e*) 457.9-nm excitation at 293 K. Spectral slit width *ca.* 2 cm^{-1}. Scale-expansion factors are indicated in the body of the diagram

The two resonance conditions are clearly demonstrated by the excitation profiles for the bands attributable to

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[6] R. J. H. Clark and W. R. Trumble, *Inorg. Chem.*, 1976, **15**, 1030.

[7] J. Wallén, C. Brosset, and N.-G. Vannerberg, *Arkiv Kemi*, 1961, **18**, 541.

[8] A. J. Cohen and N. Davidson, *J. Amer. Chem. Soc.*, 1951, **73**, 1955.

[9] L. V. Interrante, K. W. Browall, and F. P. Bundy, *Inorg. Chem.*, 1974, **13**, 1158.

[10] D. Hall and P. P. Williams, *Acta Cryst.*, 1958, **11**, 624.

[11] R. J. H. Clark, in ' Advances in Infrared and Raman Spectroscopy,' eds. R. J. H. Clark and R. E. Hester, Heyden, London, 1975, vol. 1, p. 143.

platinum–bromine and platinum–nitrogen stretching modes (Figure 3).

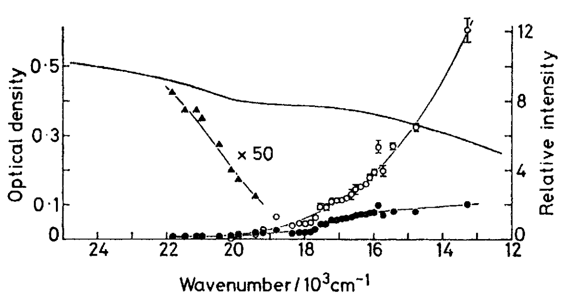

FIGURE 3 Excitation profiles for the Raman bands arising from the axial (ν_1, ○) and non-axial (ν_2, ●) platinum–bromine stretching modes of the complex [Pt,Pt]Br, and of the non-axial platinum–nitrogen stretching mode (▲), measured relative to the band of the $[SO_4]^{2-}$ ion at 981 cm^{-1} as internal standard. The electronic (diffuse-reflectance) spectrum of the complex in the visible region is also given (—)

An important point about the r.R. spectrum of [Pt,Pt]Br is that the wavenumber of the axial Pt–Br stretching fundamental (165.4 cm^{-1}) is lower than that of the corresponding off-axis one (206.3 cm^{-1}). This result can be attributed to the effects of halide bridging, and it is consistent with Hall and William's values (Table 2) [10] for the Pt–Br bond lengths since $r(\text{Pt–Br})_{\text{eq}} < r(\text{Pt–Br})_{\text{ax}}$. The earlier bond-length data [7] on this complex, and also on [Pd,Pt]Cl and [Pd,Pd]Cl, are almost certainly in error on this point, since these workers reported that the axial metal–halogen bond length was shorter than the off-axis one (Table 2).

TABLE 1

Wavenumbers of the Raman bands of the complex $[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$ [a]

$\tilde{\nu}$/cm^{-1}			$\tilde{\nu}$/cm^{-1}		
R.t.[b]	L.t.[b]	Assignment	R.t.	L.t.	Assignment
83.9			540.9		$\nu(\text{Pt}^{\text{IV}}\text{–N})$
87.3	85.5			542.6	$2\nu_1 + \nu_2$
	112.4		584	583	$\nu_1 + 2\nu_2$
169.9	165.4	$\nu(\text{Pt}^{\text{IV}}\text{–Br})$, ν_1	621		
	176 (sh)		626		
196.0				644	$4\nu_1$
204.9	206.3	$\nu(\text{Pt}^{\text{IV}}\text{–Br})$, ν_2	671		
	212.9			708	$3\nu_1 + \nu_2$
237.9			711		
	268.2		746		
333.5				751	$2\nu_1 + 2\nu_2$
338.8	330.8	$2\nu_1$		827	$5\nu_1$
377.7	378.6	$\nu_1 + \nu_2$		872	$4\nu_1 + \nu_2$
410.0	417.5	$2\nu_2$		918	$3\nu_1 + 2\nu_2$
454.3			1 080		$2\nu(\text{Pt}^{\text{IV}}\text{–N})$
506.2	496.5	$3\nu_1$	1 146		

[a] $[Pt(NH_3)_2Br_2]$ bands at 206 and 535 cm^{-1} (P. J. Hendra, *Spectrochim. Acta*, 1967, **A23**, 1275); $[Pt(NH_3)_2Br_4]$ bands at 110, 207, and 538 cm^{-1} (D. W. James and M. J. Nolan, *J. Raman Spectroscopy*, 1973, **1**, 271). [b] R.t. = Room temperature, L.t. = liquid-nitrogen temperature.

[Pd,Pt]Br.—Although this complex also shows two resonance conditions they are not the same as for [Pt,Pt]Br. Excitation in the red region gives rise to a Raman spectrum which is dominated by progressions in axial and off-axis metal–bromine stretching modes (Figure 4). Use of exciting radiation in the yellow region produces a similar spectrum to that in the red region, except that the band assigned to the axial metal–bromine stretching fundamental has shifted to a slightly higher wavenumber, as have overtones based thereon. Clearly there are two axial fundamentals, and the two bands to which they give rise are apparent in Figure 4; these bands occur at 179 and 190 cm^{-1} (Table 3). The excitation profile of the composite axial metal–bromine band shows two resonance conditions (Figure 5), one at *ca.* 16 000 and the other at <13 000 cm^{-1}. This clearly demonstrates the ability of excitation

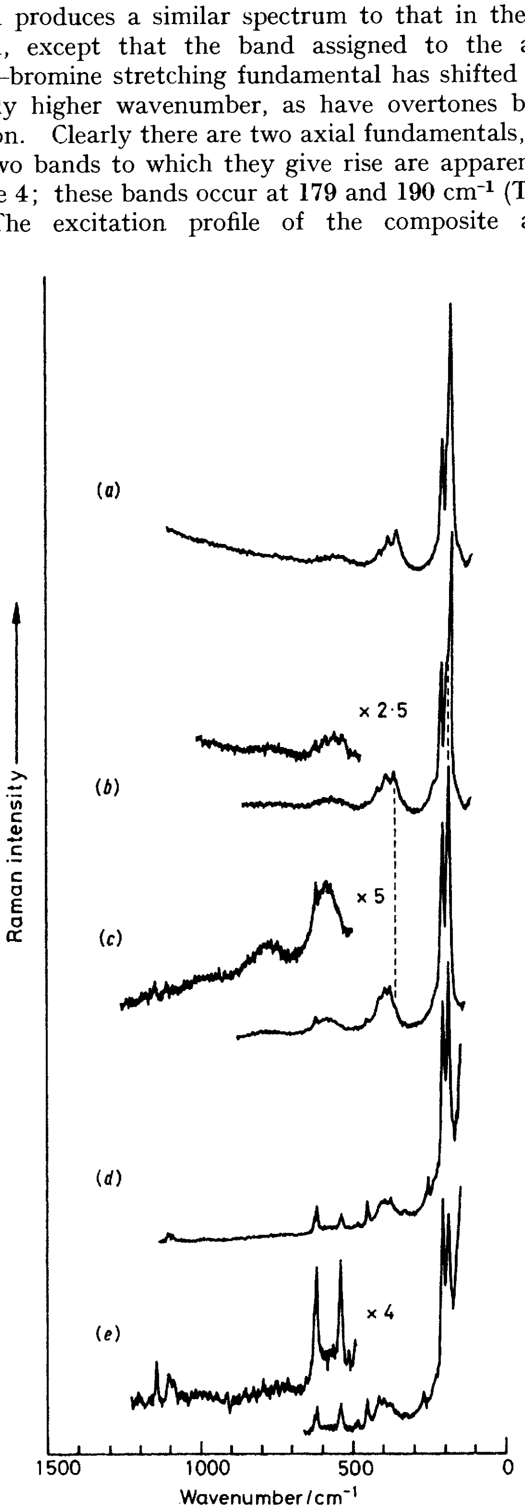

FIGURE 4 Resonance-Raman spectrum of the complex [Pd,Pt]-Br recorded with (*a*) 676.4, (*b*) 647.1, (*c*) 568.2, (*d*) 488.0, and (*e*) 457.9-nm excitation at 293 K. Spectral slit width *ca.* 3 cm^{-1}. Scale-expansion factors are indicated in the body of the diagram

profiles to separate an electronic band from an extremely broad, almost featureless, absorption-band contour.

TABLE 2

Crystallographic data on the mixed-valence complexes

Complex	Crystal form[a]	r(MN)	$r(MX)_{ax}$	$r(MX)_{eq}$	Ref.
		Å			
[Pt,Pt]Br	Bronze needles	1.9	2.50 3.03	2.45	10
[Pd,Pt]Br	Green-black needles				
[Pd,Pt]Cl[b]	Dark red needles	1.95 (Pt) 1.90 (Pd)	2.03 3.30	2.28 ±0.08	7
[Pd,Pd]Cl[b]	Black-gold needles	1.90	1.99 3.22	2.29 ±0.05	7

[a] The colours of the four complexes in finely powdered form are dark grey, orange-brown, orange, and black respectively. [b] The errors in the bond lengths given in ref. 7 appear to be substantial (±0.05 — ±0.10 Å). In the case of r(MX), the values given in ref. 7 are almost certainly incorrect. See ref. 10.

TABLE 3

Wavenumbers of the Raman bands of the complex $[Pd(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$ *

$\tilde{\nu}/cm^{-1}$			$\tilde{\nu}/cm^{-1}$		
R.t.	L.t.	Assignment	R.t.	L.t.	Assignment
	170.1 (sh)		412.1	417.4	$2\nu_3$
179.3	181.8	ν(M–Br), ν_1		420.5	
190.0	189.2	ν(M-Br), ν_2	447.2	448.7	$\nu_3 + 236.9$?
207.9	209.4	ν(M-Br), ν_3	454.6		
	211.3			485.3w	$\nu(Pd^{II}–N)$
234.5	236.9			514	
249.9			539	540	$3\nu_1$
269.8			565	569	$3\nu_2, 2\nu_1 + \nu_3$
	342.8	2 × 170.1?		597	
357.7	357.8	$2\nu_1$		600	$2\nu_1 + 2\nu_3$
	361.0		617		
379.1	382.8	$2\nu_2$	620		
384.7	389.6	$\nu_1 + \nu_3$	778		
396.9	397.8	$\nu_2 + \nu_3$			

* $[Pd(NH_3)_2Br_2]$ bands at 93.4, 183.9, 202.6, and 486.6 cm^{-1} (this work); $[Pt(NH_3)_2Br_4]$ bands at 110, 207, and 538 cm^{-1} (D. W. James and M. J. Nolan, *J. Raman Spectroscopy*, 1973, **1**, 271).

If this complex were either [Pd,Pt]Br or [Pt,Pd]Br, *i.e.* $[Pd^{II}(NH_3)_2Br_2][Pt^{IV}(NH_3)_2Br_4]$ or $[Pt^{II}(NH_3)_2Br_2]$-$[Pd^{IV}(NH_3)_2Br_4]$, then only a single axial M–Br stretching band would be expected (Pt^{IV}–Br or Pd^{IV}–Br). The fact that two axial modes are clearly present in the r.R. spectrum of the complex suggests that it is in fact a mixture of the two possible mixed-valence complexes, as suggested by Wallén *et al.*,[7] rather than either [Pd,Pt]Br or [Pt,Pd]Br alone.

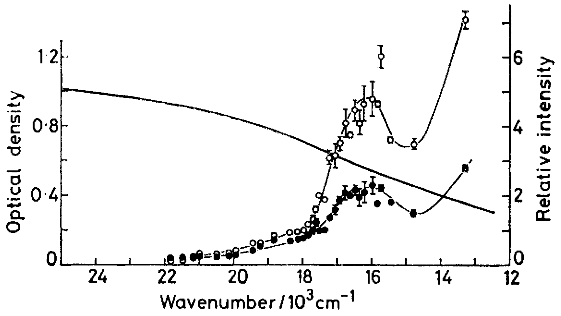

FIGURE 5 Excitation profiles for the bands arising from the axial (○) and non-axial (●) metal–bromine stretching modes of the complex [Pd,Pt]Br, measured relative to the band of the $[SO_4]^{2-}$ ion at 981 cm^{-1} as internal standard. The electronic (transmission) spectrum of the complex in the visible region is also given (——)

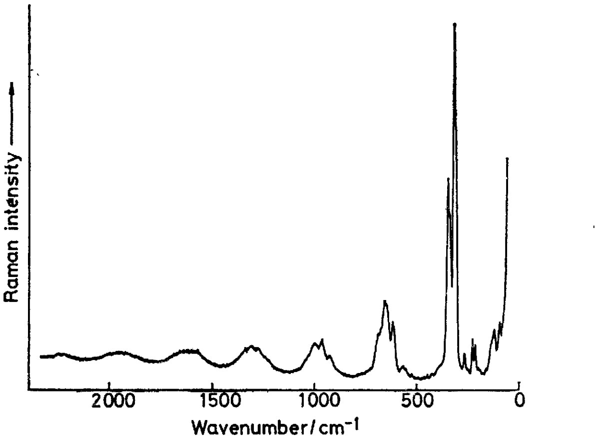

FIGURE 6 Resonance-Raman spectrum of the complex [Pd,Pt]-Cl recorded at *ca.* 80 K with 514.5-nm excitation

[Pd,Pt]Cl.—The room-temperature r.R. spectrum of [Pd,Pt]Cl has been reported to show various progressions in the off-axis and axial metal–chlorine stretching modes, based on (apparently) three fundamentals. We have now recorded the r.R. spectrum of this complex at liquid-nitrogen temperature in an attempt to resolve the complex overtone bands present in the spectra at room temperature. The low-temperature spectrum is shown in Figure 6, and band assignments are given in Table 4.

TABLE 4

Wavenumbers (cm^{-1}) of the Raman bands of the complex $[Pd(NH_3)_2Cl_2][Pt(NH_3)_2Cl_4]$

R.t.[a]	L.t.[b]	Assignment
174	183	
	213	
220	227	
	265	$\nu(Pd^{IV}–Cl), \nu_{ax}$
309	311	$\nu(Pd^{IV}–Cl), \nu_1$ (eq)
323	322	$\nu(Pt^{IV}–Cl)_1\ \nu_2$ (ax)
	339	$\nu(Pt^{IV}–Cl), \nu_3$ (eq)
343	349	$\nu(Pt^{IV}–Cl), \nu_4$ (eq)
	423	
490		
	524	$2\nu_{ax}$?
541, 552	553	
(614)	618	$2\nu_1$
648	648	$\nu_1 + \nu_3, 2\nu_2$
	659	$\nu_2 + \nu_3, \nu_1 + \nu_4$
	687	$\nu_3 + \nu_4$
	924	$3\nu_1$
(953)	962	$3\nu_2, 2\nu_1 + \nu_3$
981	1 001	$2\nu_3 + \nu_2, 2\nu_2 + \nu_4$
	1 035	$\nu_3 + 2\nu_4$
1 283	1 277	$3\nu_2 + \nu_1, 3\nu_1 + \nu_3$
(1 307)	1 307	$2\nu_1 + 2\nu_3, 3\nu_2 + \nu_3$
	1 341	$3\nu_3 + \nu_2$
	1 570	$4\nu_1 + \nu_2$
1 623	1 607	$4\nu_2 + \nu_1$
(1 629)	1 648	
1 965	1 932	5th overtone

[a] Taken from ref. 5. Values in parentheses refer to 568.2-nm excitation, others to 488.0-nm excitation. [b] Wavenumbers of a KCl disc of the complex, measured at *ca.* 80 K with 514.5-nm excitation. Other bands at 97, 112, 124, 138, and 162 cm^{-1}.

The assignments remain tentative because the resolution of the overtone bands higher than the second was not improved very much at low temperatures. However, it is clear from the spectra that there are four bands in the region expected for metal–chlorine stretching fundamentals. The band assignments in Table 4 have been made on the basis that, for isolated complexes of the same stereochemistry and metal-atom oxidation state, ν(Pt–X) > ν(Pd–X) and ν(M–X)(bridging) < ν(M–X)(terminal); thus $\nu(\mathrm{Pd^{IV}–Cl})_{\mathrm{ax}}$ is at 265 $\mathrm{cm^{-1}}$ and $\nu(\mathrm{Pt^{IV}–Cl})_{\mathrm{ax}}$ at 311 $\mathrm{cm^{-1}}$. Since the bands at 265 and 311 $\mathrm{cm^{-1}}$ are strongest using excitation in the 17 000—18 000 $\mathrm{cm^{-1}}$ region, the electronic band in this region is assigned to the $\mathrm{Pd^{IV}{\leftarrow}Pt^{II}}$ mixed-valence transition. Excitation profiles for the different ν(M–Cl) bands of this complex would be difficult to determine owing to the degree to which the various bands overlap one another.

TABLE 5

Excitation profiles (e.p.) and electronic-spectral data on the mixed-valence complexes studied

	Mixed-valence band maxima ($\mathrm{cm^{-1}}$)			
Complex	ν(MN)-sensitive	longest progression	ν(MX)-sensitive	longest progression
[Pt,Pt]Br	>22 000 ($\mathrm{Pt^{IV}{\leftarrow}Pt^{II}}$)	$2\nu(\mathrm{Pt^{IV}–N})$	<13 000 ($\mathrm{Pt^{IV}{\leftarrow}Pt^{II}}$)	$5\nu_1$, $\nu(\mathrm{Pt^{IV}–Br})$
[Pd,Pt]Br	u.v.		16 000 ($\mathrm{Pt^{IV}{\leftarrow}Pd^{II}}$)	$3\nu_1$, $\nu(\mathrm{Pd^{IV}–Br})$
			<13 000 ($\mathrm{Pd^{IV}{\leftarrow}Pt^{II}}$)	$3\nu_2$, $\nu(\mathrm{Pt^{IV}–Br})$
[Pd,Pt]Cl	≈ 26 000?		18 900 ≈ 18 500 (e.p.) ($\mathrm{Pd^{IV}{\leftarrow}Pt^{II}}$)	$6\nu_1$, $\nu(\mathrm{M^{IV}–Cl})$
[Pd,Pd]Cl	19 000 ($\perp$) * ≈ 20 000 (e.p.) ($\mathrm{Pd^{IV}{\leftarrow}Pd^{II}}$)	4ν(Pd–N)	13 000 ($\parallel$) * ($\mathrm{Pd^{IV}{\leftarrow}Pd^{II}}$)	$2\nu_1$, ν(Pd–Cl)

* Ref. 12.

On the same basis, we can then also assign the electronic band of [Pd,Pt]Br at *ca.* 16 000 $\mathrm{cm^{-1}}$ to $\mathrm{Pt^{IV}{\leftarrow}Pd^{II}}$ and that at $\leqslant$13 000 $\mathrm{cm^{-1}}$ to $\mathrm{Pd^{IV}{\leftarrow}Pt^{II}}$.

[Pd,Pd]Cl.—The low-temperature r.R. spectrum of [Pd,Pd]Cl is very similar to that of the previously published [6] room-temperature spectrum and is therefore not reproduced here. The principal differences are in the relative intensities of bands and some slight changes in band wavenumbers. The off-axis $\nu(\mathrm{Pd^{IV}–Cl})$ band is undoubtedly that at 315 ± 5 $\mathrm{cm^{-1}}$. The position of the corresponding axial stretch is uncertain. There are two bands in the room-temperature spectrum at 243 and 256 $\mathrm{cm^{-1}}$ which are shifted by *ca.* 10 $\mathrm{cm^{-1}}$ to lower frequency at *ca.* 80 K. Presumably, one of these arises from the axial mode but it would require a r.R. spectrum obtained with far-red excitation (*ca.* 13 000 $\mathrm{cm^{-1}}$, the estimated [6,12] position of the mixed-valence transition) to determine which one it is.

General Discussion.—As mentioned above, the main difference between the r.R. spectra of the mixed-valence complexes of general formulae $[\mathrm{M(NH_3)_2X_2}][\mathrm{M'(NH_3)_2X_4}]$ and $[\mathrm{M(NEtH_2)_4}][\mathrm{M(NEtH_2)_4X_2}]\mathrm{X_4{\cdot}4H_2O}$ (X = Cl or Br) is that in the former case bands are obtained arising from both axial and off-axis metal–ligand stretches, but in the latter case the principal bands are those arising from axial metal–halogen stretches only.[2-4] It was proposed in the earlier paper [6] that in both cases the mixed-valence transition was of the type $d_{z^2}{\leftarrow}d_{z^2}$. Bearing in mind the form of the d_{z^2} orbital it is clear that the major consequence of irradiating within the contour of the $d_{z^2}{\leftarrow}d_{z^2}$ band is likely to be felt by the axial modes of the complex with the off-axis modes being much less affected. How then is it possible for off-axis modes to appear in the r.R. spectrum; in particular, progressions in a metal–nitrogen stretching mode? In an earlier paper tentative proposals were made [6] to account for this. First, the local symmetry of the mixed-valence chain is D_{2h} (ignoring the hydrogen atoms) and the electronic states to which the molecule is transferred by the transitions $d_{z^2}{\leftarrow}d_{z^2}$ and $d_{x^2-y^2}{\leftarrow}d_{z^2}$ would therefore have the same symmetry. This means that the two states would mix to some extent, so that the $d_{z^2}{\leftarrow}d_{z^2}$ transition would tend to affect off-axis as well as axial bond lengths. Secondly, it was proposed that the metal–nitrogen progressions might arise because the exciting radiation could be in resonance with a $\mathrm{M^{IV}{\leftarrow}N}$ charge-transfer transition in the blue region. We believe that both proposals can be rejected: the first because the off-axis metal–halogen and metal–nitrogen bands are not affected in the same way by change in the frequency of the exciting radiation (when the metal–halogen band is strongest the metal–nitrogen band is absent and *vice versa*); the second because no such charge-transfer transition would be expected at such a low energy in these complexes and because the isolated platinum(IV) complex, $[\mathrm{Pt(NH_3)_2Br_4}]$, does not give such a progression when irradiated with a blue line. The alternative proposal that we now present is based simply on the assumption that the *d*-orbital energy levels of the isolated metal-(II) and -(IV) complexes remain largely unchanged in the mixed-valence complex.

In the isolated metal(II) complex the ordering of *d*-orbital energy levels should be $z^2 < zx < yz < xy < x^2 - y^2$. In the mixed-valence transition it is generally assumed that an electron is transferred from the d_{z^2}

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[12] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1956, **29**, 421.

orbital of the M^{II} and the r.R. spectra tend to confirm this assumption since bands arising from off-axis vibrations of the metal(II) complex are virtually absent. For the isolated metal(IV) complex there is a slight labelling problem since the principal symmetry axis (normally labelled z) lies along the N–M–N direction, which is the y axis in the mixed-valence complex {*cf.* the situation in the case of the complex $[Pt(NEtH_2)_4][Pt(NEtH_2)_4X_2]X_4 \cdot 4H_2O$ where the principal symmetry axis of the isolated platinum(IV) complex coincides with the chain axis [3]}. We have chosen the N–M–N direction to be the y axis in the isolated metal(IV) complex as well as in the mixed-valence complexes and this leads to a probable d-orbital energy-level ordering of $xz < yz$, $xy < x^2 - z^2 < y^2$ with the $d_{x^2-z^2}$ and d_{y^2} orbitals empty. Hence mixed-valence transitions can occur to the $d_{x^2-z^2}$ or d_{y^2} orbitals of M^{IV}. This model therefore predicts that the lowest mixed-valence transition should be $d_{x^2-z^2}$ $M^{IV} \leftarrow d_{z^2}$ M^{II} which would affect (principally) all the M^{IV}–halogen bond lengths, both axial and off-axis, and that there should be a higher-energy transition of the type d_{y^2} $M^{IV} \leftarrow d_{z^2}$ M^{II} which would affect (principally) the metal–nitrogen bond lengths. The fact that these are the two types of behaviour observed by r.R. spectroscopy for these ammine complexes lends strong support to our model, although of course it is still a crude one. It does not, for instance, take into account the fact that the axial and off-axis metal(IV)–halogen bond lengths are not the same as one another, which will lead to some perturbation of the energy levels. There is also the possibility that the electronic states arising from the two transitions could mix, but any mixing would appear to be small given the differing r.R. behaviour of the Raman bands attributed to the metal–halogen and metal–nitrogen stretching modes.

In the cases of the [Pd,Pt]Cl and [Pd,Pt]Br complexes the second mixed-valence transition must be in the u.v. region and it would require the development of a u.v. laser tunable in the 350—450 nm region to locate it by r.R. spectroscopy. A summary of our electronic spectral results and of the excitation-profile studies is given in Table 5.

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