

Palladium(II,IV) Mixed-valence Complexes of 1,2-Diaminoethane, 1,3-Diaminopropane, and Diethylenetriamine: Syntheses, Electronic, Infrared, Raman, and Resonance Raman Spectra and X-Ray Studies

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The syntheses of the neutral, linear-chain mixed-valence complexes $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$, $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$, $[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]$, and a mixed-valence complex of empirical formula $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$, where en = 1,2-diaminoethane and tn = 1,3-diaminopropane, are reported, together with their electronic, infrared, Raman, and resonance Raman spectra. In addition, the synthesis and spectroscopic properties of the first palladium complex of the +1 charge type, $[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2$, where dien = diethylenetriamine, is reported. The electronic spectra of the complexes are characterised by intense, broad intervalence bands which decrease in wavenumber in the order $\text{Cl} > \text{Br}$. The resonance Raman spectra show overtone progressions (ν_1, ν_1) in the axial $\text{X}-\text{Pd}^{\text{IV}}-\text{X}$ symmetric stretching mode (ν_1), which lies at ca. 260 cm^{-1} for $\text{X} = \text{Cl}$ and at ca. 145 cm^{-1} for $\text{X} = \text{Br}$, and combination tones $\nu_1\nu_1 + \nu_n$, where ν_n is the $\nu(\text{Pd}-\text{X})$ equatorial stretching mode, or $\nu_2, \nu_{\text{asym}}(\text{X}-\text{Pd}^{\text{IV}}-\text{X})$, the antisymmetric chain-stretching mode. The excitation profiles of the ν_1 and $2\nu_1$ bands of the neutral chain complexes do not reach maxima even with excitation of the lowest available wavenumber ($12\,510\text{ cm}^{-1}$). These complexes appear to be more delocalised than those of the +2 charge type. Powder diffraction data indicate that $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ and $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$ are isostructural and belong to space group *Ama*2.

During the past few years, the richness of the chemistry and spectroscopy of mixed-valence complexes has been amply demonstrated. One area of particular interest is the study of the electronic, vibrational, and structural properties of a series of halogen-bridged, linear-chain complexes, and of the relationships between these properties and others such as electrical conductivity. Although the initial studies were primarily concerned with platinum(II)-platinum(IV) complexes,^{1,2} these have since been extended to the (more highly conducting) analogous palladium complexes of the +2 charge type³ and to mixed-metal palladium(II)-platinum(IV) complexes.⁴ The present report is concerned with the preparations and spectroscopic properties of linear-chain palladium(II)-palladium(IV) complexes of the neutral and +1 charge types. Four of the new complexes, $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$, $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$, $[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]$, and $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ involve the diamines $\text{L}-\text{L} = 1,2$ -diaminoethane (en) or 1,3-diaminopropane (tn) co-ordinated in the equatorial plane, while the fifth, $[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2$, involves the terdentate ligand $\text{L}-\text{L}-\text{L} =$ diethylenetriamine (dien) co-ordinated in the equatorial plane.

Experimental

Preparations.—(a) $[\text{Pd}(\text{L}-\text{L})\text{Cl}_2]$ ($\text{L}-\text{L} = \text{en}$ or tn). The methods of Drew and Tress⁵ and Basolo *et al.*^{6,7} were modified for the preparation of $[\text{Pt}(\text{en})\text{Cl}_2]$ since that of McCormick *et al.*⁸ gave poor yields and impure products. Aliquots (2 cm^3) of a solution of the amine (0.5 cm^3 in 100 cm^3 water) were added dropwise to a stirred solution of $\text{K}_2[\text{PdCl}_4]$ (0.5 g in 30 cm^3 water). The yellow precipitate of $[\text{Pd}(\text{L}-\text{L})\text{Cl}_2]$ which is formed after several minutes was filtered off immediately, further amine added to the mother-liquor, and the procedure repeated until no more $[\text{Pd}(\text{L}-\text{L})\text{Cl}_2]$ could be precipitated. If the yellow precipitate is not filtered off immediately, reaction with more amine occurs and this leads to the formation of the pink Magnus-type salt, $[\text{Pd}(\text{L}-\text{L})_2][\text{PdCl}_4]$. By keeping a low concentration of amine the yield of the pink salt was kept to a minimum. The yellow $[\text{Pd}(\text{L}-\text{L})\text{Cl}_2]$ was washed with cold

water, absolute alcohol, and diethyl ether, and then dried in air. Typical yields were $> 80\%$.

A second method for preparing $[\text{Pd}(\text{L}-\text{L})\text{Cl}_2]$ in quantitative yield was by adding hydrochloric acid (11 mol dm^{-3}) to a cold aqueous solution of $[\text{Pd}(\text{L}-\text{L})_2]\text{Cl}_2$.

(b) $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$. Chlorine was bubbled through a suspension of $[\text{Pd}(\text{en})\text{Cl}_2]$ in water until a red precipitate in an orange-brown solution was formed (ca. 5 min). The mixture was then warmed on a water-bath until metallic green-gold plates were formed; these were filtered off, washed with cold water, ethanol, and ether, and then dried in air (Found: C, 8.95; H, 3.05; Cl, 39.6; N, 10.1. Calc. for $\text{C}_2\text{H}_8\text{Cl}_3\text{N}_2\text{Pd}$: C, 8.80; H, 2.95; Cl, 39.0; N, 10.25%).

(c) $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$. Bromine in a saturated aqueous solution of KBr was added to an aqueous suspension of $[\text{Pd}(\text{en})\text{Cl}_2]$ and the mixture warmed and allowed to stand for 1 h. The gold-brown microcrystals formed were washed with cold water, ethanol, and ether, and dried in air (Found: C, 5.95; H, 1.75; Br, 60.0; N, 6.85. Calc. for $\text{C}_2\text{H}_8\text{Br}_3\text{N}_2\text{Pd}$: C, 5.90; H, 2.0; Br, 59.0; N, 6.90%).

(d) $[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]$. This complex was obtained as gold-brown crystals by method (c), the starting material being $[\text{Pd}(\text{tn})\text{Cl}_2]$ (Found: C, 9.25; H, 2.50; Br, 57.0; N, 6.85. Calc. for $\text{C}_3\text{H}_{10}\text{Br}_3\text{N}_2\text{Pd}$: C, 8.55; H, 2.40; Br, 57.0; N, 6.65%).

(e) $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$. By treatment of an aqueous suspension of $[\text{Pd}(\text{en})\text{Cl}_2]$ with bromine in dilute HBr, gold-brown microcrystals of the complex $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ were obtained (Found: C, 7.25; H, 2.25; Br, 34.7; Cl, 14.5; N, 8.35. Calc. for $\text{C}_4\text{H}_{16}\text{Br}_3\text{Cl}_3\text{N}_4\text{Pd}_2$: C, 7.05; H, 2.35; Br, 35.3; Cl, 15.6; N, 8.25%). The bromine and chlorine contents appear to vary slightly with each preparation.

(f) $[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2$. This complex was obtained as gold platelets by method (c). The crystals were found to occlude bromine, as deduced by elemental analyses. This could be removed by grinding the crystals into a powder and pumping on them for a few hours (Found: C, 10.05; H, 2.70; Br, 53.9; N, 8.75. Calc. for $\text{C}_4\text{H}_{13}\text{Br}_3\text{N}_3\text{Pd}$: C, 10.7; H, 2.90; Br, 53.3; N, 9.35%).

Attempts to prepare analogous 1,2-diaminopropane com-

Table 1. Summary of data on complexes studied

Complex	Crystal colour	Powder colour	Intervalence band max. ^a / cm ⁻¹	ω_1 /cm ⁻¹	x_{11} /cm ⁻¹	$I(2\nu_1)/I(\nu_1)$ (λ_0 /nm)	Progn. ν_1
[Pd(en)Cl ₂][Pd(en)Cl ₄]	Gold-green	Purple	17 000	261.0 ± 0.3	-0.77 ± 0.09	0.57 (676.4)	8 ν_1
[Pd(en)Br ₂][Pd(en)Br ₄]	Gold	Blue	12 800	148.6 ± 0.3	-0.06 ± 0.1	0.53 (752.5)	6 ν_1
[Pd(tn)Br ₂][Pd(tn)Br ₄]	Gold	Blue	13 800	147.2 ^b	ca. 0	0.45 (752.5)	5 ν_1
Pd ₂ (en) ₂ Br ₃ Cl ₃	Gold	Blue	12 800	148.6		(752.5)	6 ν_1
[Pd(dien)Br][Pd(dien)-Br ₃]Br ₂	Gold	Blue	9 900	147.2 ^b		(799.3)	3 ν_1

^a The ν_1 band excitation profiles all maximise at less than 12 500 cm⁻¹. ^b ν_1 Value.

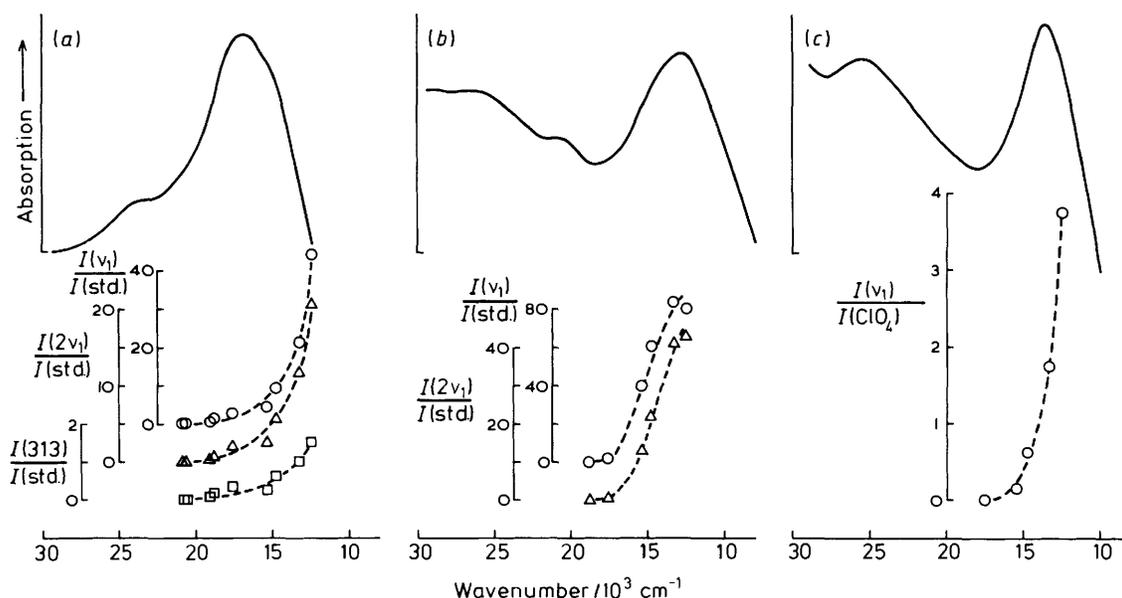


Figure 1. (a) Electronic spectrum (KCl disc at ca. 14 K) and excitation profiles (ca. 80 K) of the ν_1 (○), $2\nu_1$ (△), and 313 cm⁻¹ (□) bands of [Pd(en)Cl₂][Pd(en)Cl₄]. (b) Electronic spectrum (KBr disc at ca. 14 K) and excitation profiles (ca. 80 K) of the ν_1 (○) and $2\nu_1$ (△) bands of [Pd(en)Br₂][Pd(en)Br₄]. (c) Electronic spectrum (KBr disc at 295 K) and excitation profile (ca. 80 K) of the ν_1 (○) band of [Pd(tn)Br₂][Pd(tn)Br₄].

plexes and the 1,3-diaminopropane complex with chlorine bridges were unsuccessful.

The preparation of [Pd(en)I₂][Pd(en)I₄] was attempted by treating [Pd(en)Cl₂] with a solution of iodine in aqueous KI and also by treating [Pd(en)₂][Pd(en)₂Cl₂][ClO₄]₄ with KI in ethanol. Both methods resulted in the formation of a black powder which could not be formulated unambiguously.

Instrumental.—Electronic spectra of the complexes were recorded on a Cary 14 spectrometer at room temperature using pressed discs in an alkali-metal halide matrix. Spectra at 80 and 20 K were obtained by cooling the disc on an Air Products Displex system in conjunction with a Leybold-Heraeus turbomolecular pump, type TM120.

Infrared spectra of the complexes were recorded at ca. 80 K on a Bruker IFS 113V interferometer using wax discs. The Raman spectra were recorded with Spex 1401 and 14018/R6 spectrometers. Exciting radiation was provided by Coherent Radiation models CR3, CR500K, and CR300K lasers. Resonance Raman spectra were obtained at ca. 80 K using a Dewar assembly and pressed discs of the complexes dispersed in K₂[SO₄] or in the appropriate alkali-metal halide. For Pd₂(en)₂Br₃Cl₃, only K₂[SO₄] could be used as disc material, since halogen exchange occurs readily between the complex and

an alkali-metal halide. Excitation-profile measurements were made on samples held at ca. 80 K, band intensities being measured with respect to that of the a_1 band of [SO₄]²⁻ ([ClO₄]⁻ for the tn complex) and corrected for the spectral response of the instrument. Band wavenumbers were calibrated by reference to the emission spectrum of neon where possible, or from the Rayleigh line. X-Ray powder diffraction patterns were recorded on a Philips 1050 diffractometer over the range $2\theta = 6$ –120°.

Results and Discussion

Crystals of the complexes are dichroic. The chloride is blue with the electric vector of the transmitted light parallel to the chain (z) axis and orange-brown when perpendicular to it. The bromides are likewise dark blue and red-brown, respectively. The crystals have a strong metallic sheen which is lost when they are ground to powders. The colours of the crystals and powders are given in Table 1.

The transmission spectra (Figure 1) show a strong broad band [full width at half maximum (f.w.h.m.) ca. 5 000 cm⁻¹] in the visible–near-i.r. region assigned to the Pd^{II}→Pd^{IV} intervalence charge-transfer transition, as for analogous platinum complexes.^{1,2} It occurs (by disc transmission

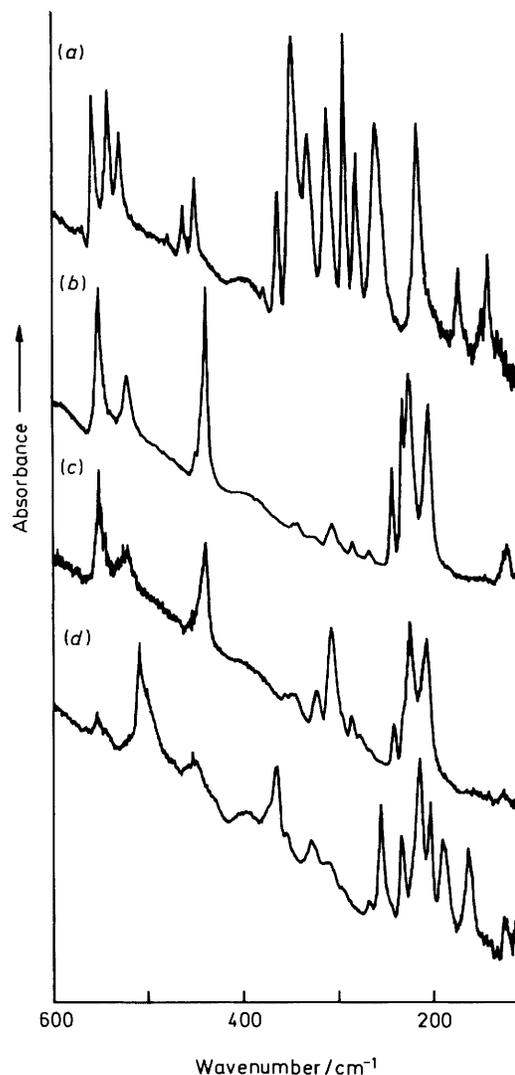
Table 2. Wavenumbers (cm^{-1}) and assignments of the bands observed in the i.r. spectra of $[\text{Pd}(\text{en})\text{Cl}_2]$ and $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$

$[\text{Pd}(\text{en})\text{Cl}_2]$	$[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$	Assignment	
614w	614w	Ring skeletal	
557vs (doublet)	556m		
540w	540m		
	528m		
517w	461w	} $\nu(\text{Pd}-\text{N})$	
456s			448w
450w (sh)			375w
	362m	$\nu_2(\nu_{\text{asym}}, \text{X}-\text{Pd}^{\text{IV}}-\text{X})?$	
344w	346s	$\nu(\text{Pd}-\text{Cl})$	
	330m	$\nu(\text{Pd}-\text{Cl})$	
309s	309s	$\nu(\text{Pd}-\text{Cl})$	
297m	292s	Ring skeletal	
273m	279m	$\nu(\text{Pd}-\text{Cl})$	
	258m	$\nu(\text{Pd}-\text{Cl}), \nu_1?$	
200s	215m	$\delta(\text{N}-\text{Pd}-\text{N})$	
197s (sh)	171w	Rotatory lattice	
157s			
141w	146w	PdX_2 skeletal lattice?	
	140w		
	103w		
82w	84w	Rotatory lattice	
68w, br			

measurements) at $17\,000\text{ cm}^{-1}$ for $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$ and between $13\,800$ and $12\,800\text{ cm}^{-1}$ for the analogous bromides. The +1 charge-type complex $[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2$ has its intervalence transition at lower wavenumber ($9\,900\text{ cm}^{-1}$) than that of any other palladium mixed-valence complex so far studied. This is in contrast to the situation for the analogous platinum complex, $[\text{Pt}(\text{dien})\text{I}][\text{Pt}(\text{dien})\text{I}_3]\text{I}_2$, whose $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$ transition is at slightly higher wavenumber than average for platinum chain complexes.⁹ However, the platinum dien complex is known to be non-linear (which may not be the case for the analogous palladium complex); non-linearity leads to more localised valences and thus to high wavenumbers for the intervalence transition. The spectra also show in each case (an) additional band(s) to the high-energy side of the intervalence band, at $23\,700\text{ cm}^{-1}$ for $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$, at $26\,250$ and $20\,750\text{ cm}^{-1}$ for $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$, at $25\,750\text{ cm}^{-1}$ for $[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]$, and at $28\,000\text{ cm}^{-1}$ for $[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2$. These bands are possibly due to $d-d$ transitions of the palladium(IV) unit^{10,11} or to ligand-to-metal charge-transfer transitions.³

Cooling the sample from room temperature to 20 K does not lead to the development of any vibrational structure to the intervalence band, a situation which also prevails for the platinum analogues. The only difference on cooling appears to be a slight increase in the peak height of the intervalence band relative to that of the other bands.

Infrared Spectroscopy.—Mixed-valence complexes of the type under discussion are expected to be localised valence (class II)¹² complexes and as such their i.r. spectra should be superpositions of the spectra of the constituent ions. This is found to be essentially the case, as the change in crystallographic space group on going from the monomer $[D_2]$ for $[\text{Pd}(\text{en})\text{Cl}_2]$ ¹³ to the mixed-valence complex $[C_{2v}]$ for the analogous $[\text{Pt}(\text{en})\text{X}_3]$ ¹⁴ does not greatly alter the form of the spectrum. The main difference between the spectrum of the monomer and that of the mixed-valence complex is expected to be due to the change in force constant of the axial $\text{Pd}^{\text{IV}}-\text{X}$ bond consequent upon interaction with the palladium(II) centres. The wavenumbers and assignments of the bands observed in the i.r. spectra of the complexes are listed in Tables 2 and 3 and the

**Figure 2.** Fourier-transform i.r. spectra (wax discs at 80 K) of (a) $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$, (b) $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$, (c) $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$, and (d) $[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]$

spectra are shown in Figure 2. The assignments are based on those of previously reported complexes.¹⁵

The i.r. spectra of the mixed-valence complexes have a sloping background, from high to low wavenumber, which is not present in those of the monomers. The slope is greater for the bromides than for the chloride. This background may be the tail of the intervalence $\text{Pd}^{\text{II}} \rightarrow \text{Pd}^{\text{IV}}$ transition, and the greater slope for the bromides is in accord with the observation that their intervalence transitions are at lower wavenumbers than for the chloride. It is worth noting that this tail would be expected to be even more pronounced for an iodide-bridged complex, and this would possibly make the i.r. spectrum difficult to observe.

The $\nu_2, \nu_{\text{asym}}(\text{Cl}-\text{Pd}^{\text{IV}}-\text{Cl})$ band for $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$ does not show chlorine isotopic splitting, although this has been observed for platinum cation-chain complexes of the +2 charge type.¹⁶ This is a consequence of the larger number of isotopes of significant abundance for Pd than Pt and of their lower mass.

The spectrum of the complex $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ has bands attributable to both $\nu(\text{Pd}-\text{Cl})_{\text{eq}}$ and $\nu(\text{Pd}-\text{Br})_{\text{eq}}$ as well as to $\nu_{\text{asym}}(\text{Br}-\text{Pd}^{\text{IV}}-\text{Br})$, but none attributable to $\nu_{\text{asym}}(\text{Cl}-\text{Pd}^{\text{IV}}-\text{Cl})$; this implies that the complex is bromine bridged. This

Table 3. Wavenumbers (cm^{-1}) and assignments of bands observed in the i.r. spectra of $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$, $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$, $[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]$, and $[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2$

$[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$	$\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$	$[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]$	$[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2$	Assignment ^a
551s doublet	552m	615w 553w	615s 552m 543w	v(PdN)
520w	522w			
449w 438s	440m	509m 500 (sh) 452w,br	513w 485w	v(PdN)
			430w 386w	
		372w 365m		$\delta(\text{NCC})$
345w 325w 305w	345w 322w 307m ^b	355w 329w 314w,br		Ring modes
284w	286w 278w			v(M-Cl)
266w 242m 232s 225s 222s 204s	242w 225m 208m	268w 256m 234m 214s 203m 190m 162m 122w	230m 196s	v(M-Br) $v_2, v_{\text{asym}}(\text{Br}-\text{Pd}^{\text{IV}}-\text{Br})$
121w 106w	122w		120w	v(M-Br) PdX ₂ skeletal lattice?

^a Additional bands observed at 95w, 89w, and 66m cm^{-1} for $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$, at 84m cm^{-1} for $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$, at 68m cm^{-1} for $[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]$, and 84w cm^{-1} for $[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2$. ^b May be v(M-Cl)_{eq}.

Table 4. Wavenumbers, relative intensities, full widths at half maximum, and assignments of bands observed in the resonance Raman spectrum of $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$ *

$\tilde{\nu}/\text{cm}^{-1}$	$I(v_1 v_1)/I(v_1)$	$\Delta\tilde{\nu}_3/\text{cm}^{-1}$	Assignment
258.3	1.00	11.4	v_1
273			v(Pd-Cl) _{eq}
289.5			
313.4			
348			
517.8	0.57	23.7	$2v_1$
534			$v_1 + 273$
544			$v_1 + 289.5$
773.3	0.33	33.7	$3v_1$
800			$2v_1 + 289.5$
1 030	0.26	54	$4v_1$
1 052			$3v_1 + 289.5$
1 282	0.22	76	$5v_1$
1 535	0.12	86	$6v_1$
1 792	0.08	92	$7v_1$
2 084	ca. 0.01	120	$8v_1$

* Obtained for a $\text{K}[\text{ClO}_4]$ disc held at ca. 80 K with 676.4-nm excitation. Spectral slit width ca. 1 cm^{-1} .

conclusion is borne out by the resonance Raman spectrum (see below). The complex does not, from the i.r. spectrum, appear to be a mixture of unreacted $[\text{Pd}(\text{en})\text{Cl}_2]$ and $[\text{Pd}(\text{en})\text{Br}_3]$ (a possibility from the method of preparation).

It is noteworthy that the i.r. spectrum of $[\text{Pd}(\text{en})\text{Cl}_2]-[\text{Pd}(\text{en})\text{Cl}_4]$ has more bands than that of the corresponding bromide. In addition it appears that the v_1 band is i.r. active for the chloride (at 258 cm^{-1}) but not for the bromide. It would therefore seem that $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$ crystallises in a different space group from that of $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$.

Table 5. Wavenumbers, relative intensities, full widths at half maximum, and assignments of bands observed in the resonance Raman spectrum of $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$ *

$\tilde{\nu}/\text{cm}^{-1}$	$I(vv_1)/I(v_1)$	$\Delta\tilde{\nu}_3/\text{cm}^{-1}$	Assignment
145.3	1.00	8.3	v_1
187.5			
221.5			v(Pd-Br) _{eq}
293.3	0.53	17.0	$2v_1$
369			$v_1 + 221.5$
438.9	0.25	20.0	$3v_1$
488			v(Pd-N)
517			$2v_1 + 221.5$
582.1	0.13	26	$4v_1$
723.4	0.08	37	$5v_1$
866	0.04	48	$6v_1$

* Obtained for a KBr disc held at ca. 80 K with 752.5-nm excitation. Spectral slit width ca. 1 cm^{-1} . The spectral data for $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ are essentially the same as those of $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$.

X-Ray Diffraction.—X-Ray powder diffraction patterns indicate that $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$ is not isostructural with $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$, but that both the latter as well as $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ are isostructural with $[\text{Pt}(\text{en})\text{X}_2][\text{Pt}(\text{en})\text{X}_4]$, X = Cl, Br, or I,¹⁴ and hence belong to space group *Ama*2 (C_{2v}^{18}). The compound $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ has been indexed to this group, the lattice parameters being $a = 10.43$, $b = 13.89$, and $c = 5.59$ Å; the diffraction pattern is such that this complex could not be a mixture of $[\text{Pd}(\text{en})\text{Cl}_2]$ and the mixed-valence bromide. As the c axis is the chain axis in this space group, the results indicate that the $\text{Pd}^{\text{II}} \cdots \text{Pd}^{\text{IV}}$ distance is 5.59 Å, a value which is only compatible with bromide bridging along the chain.² The 1,2-diaminoethane ligands must be eclipsed when viewed along the chain direction in the palladium bromo-

Table 6. Wavenumbers, relative intensities, full widths at half maximum, and assignments of bands observed in the resonance Raman spectrum of $[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]^*$

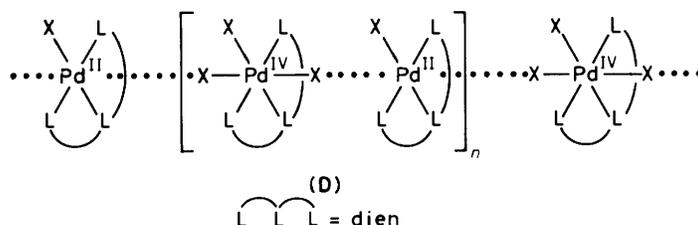
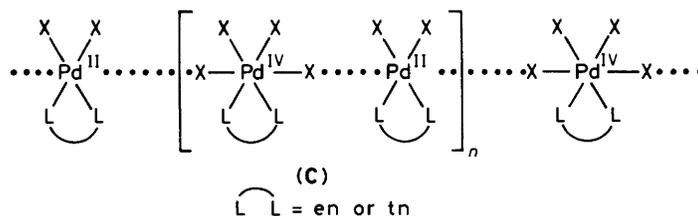
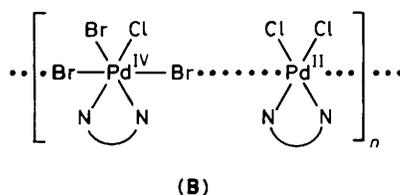
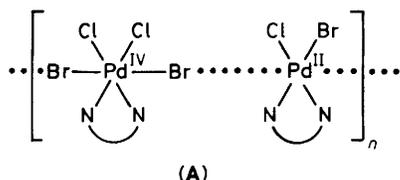
$\tilde{\nu}/\text{cm}^{-1}$	$I(v_1 v_1)/I(v_1)$	$\Delta\tilde{\nu}_{1/2}/\text{cm}^{-1}$	Assignment
147.2	1.00	8.5	ν_1
205.5			$\delta(\text{N-Pd-N})$
257.5			$\nu(\text{Pd-Br})$
296.1	0.45	15.7	$2\nu_1$
407.5			$\nu_1 + \nu(\text{Pd-Br})$
445	0.22	24	$3\nu_1$
502			$\nu(\text{Pd-N})$
592	0.09	36	$4\nu_1$
741	<0.09	>40	$5\nu_1$

* Obtained for a $\text{K}[\text{ClO}_4]$ disc held at ca. 80 K with 752.5-nm excitation. Spectral slit width ca. 1 cm^{-1} .

Table 7. Wavenumbers and assignments of bands observed in the resonance Raman spectrum of $[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2^*$

$\tilde{\nu}/\text{cm}^{-1}$	Assignment
147.2	ν_1
198.4	$\delta(\text{N-Pd-N})$
293	$2\nu_1$
438	$3\nu_1$

* Obtained from a $\text{K}[\text{ClO}_4]$ disc held at ca. 80 K with 799.3-nm excitation. Spectral slit width ca. 1 cm^{-1} .



complexes, owing to their being isostructural with $[\text{Pt}(\text{en})\text{X}_2][\text{Pt}(\text{en})\text{X}_4]$, for which this feature has already been established.¹⁴ It has not yet been possible to index the diffraction pattern for $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$ to the same d -spacing precision ($\pm 0.03 \text{ \AA}$) as for $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$. The complex $[\text{Pd}(\text{tn})\text{Br}_2][\text{Pd}(\text{tn})\text{Br}_4]$ is not isostructural with the other bromides.

There are two $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$ formula units per unit cell in space group $\text{Ama}2$ but, since this cell is non-primitive, there is only one formula unit per Bravais cell. The 1,2-diaminoethane rings are non-planar (hence the choice of $\text{Ama}2$ rather than Cmcm or $\text{Cmc}2_1$). If the conformations of consecutive (eclipsed) amines are the same, then the line-group symmetry is C_2 , irrespective of whether or not the bridging halogen atom is centrally placed.

Raman and Resonance Raman Spectra.—The wavenumbers and assignments of the observed bands are given in Tables 4–7.

The resonance Raman spectra for all the complexes are dominated by overtone progressions in ν_1 , the totally symmetric $\text{X-Pd}^{\text{IV}}\text{-X}$ axial stretching mode. The progressions are long for the neutral complexes (to $8\nu_1$ for $\text{X} = \text{Cl}$ and to $5\nu_1$ or $6\nu_1$ for $\text{X} = \text{Br}$) but only reach $3\nu_1$ for $[\text{Pd}(\text{dien})\text{Br}][\text{Pd}(\text{dien})\text{Br}_3]\text{Br}_2$. This is because even the exciting line of lowest wavenumber available ($799.3 \text{ nm} \hat{=} 12\,510 \text{ cm}^{-1}$) barely falls within the contour of the intervalence band ($\tilde{\nu}_{\text{max}} = 9\,900 \text{ cm}^{-1}$). Other subsidiary progressions, $\nu_1\nu_1 + \nu_n$, are also apparent in the spectra of the neutral-chain complexes. The modes designated ν_n are identified as $\nu(\text{Pd-Cl})_{\text{eq}}$ for $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$ and as $\nu(\text{Pd}^{\text{IV}}\text{-Br})_{\text{eq}}$ or $\nu_2, \nu_{\text{asym}}(\text{Br-Pd}^{\text{IV}}\text{-Br})$, for the bromine-bridged complexes. The neutral-chain bromides and the +1 charged chain bromide show a band attributed to $\delta(\text{N-Pd-N})$ but, unlike the +2 cation-chain complexes³ studied previously, have no detectable progression involving this mode. The appearance of subsidiary progressions involving ν_n , a metal-halogen stretching mode, implies that Pd-X_{eq} bonds are affected by changes consequent upon transforming the chain from the ground-state geometry $\dots\text{Pd}^{\text{II}}\dots\text{X-Pd}^{\text{IV}}\text{-X}\dots\text{Pd}^{\text{II}}\dots$ to the excited-state geometry $\dots\text{Pd}^{\text{III}}\dots\text{X}\dots\text{Pd}^{\text{III}}\dots\text{X}\dots\text{Pd}^{\text{III}}\dots$. It is also likely that the $\nu(\text{Pd-X})_{\text{eq}}$ modes, having similar wavenumber and symmetry to those of ν_1 , have borrowed intensity therefrom. No chlorine isotopic splitting is observed for ν_1 . The ν_1 band for $\text{Pd}(\text{tn})\text{Br}_3$ is asymmetric to the high-wavenumber side. The harmonic band wavenumbers for ν_1 and the anharmonicity constants, x_{11} , for the neutral-chain complexes (Table 1) are lower than for the +2 cation-chain complexes, cf. the comparable situation for platinum-chain complexes.²

The resonance Raman spectrum obtained for $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ confirms that this compound is bromine-bridged. The only difference between the resonance Raman spectrum of $\text{Pd}(\text{en})\text{Br}_3$ and $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ is that the latter has an $I(221.5)/I(\nu_1)$ value of approximately half that of $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$, i.e. it has a less intense $\nu(\text{Pd}-\text{Br})_{\text{eq}}$ band, due to the fact that $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$ has only half the bromine content of $[\text{Pd}(\text{en})\text{Br}_2][\text{Pd}(\text{en})\text{Br}_4]$. One might have expected to see a band due to $\nu(\text{Pd}-\text{Cl})_{\text{eq}}$ in the resonance Raman spectrum of $\text{Pd}_2(\text{en})_2\text{Br}_3\text{Cl}_3$, but this would be obscured by the $2\nu_1$ band. The spectroscopic evidence therefore indicates that the structure of $\text{Pd}_2(\text{en})_2\text{Cl}_3\text{Br}_3$ is either as in (A) or (B). This is confirmed by the X-ray results (see above) which, in addition, indicate the 1,2-diaminoethane ligands to be eclipsed. We were unable to confirm a previous report¹⁰ of the preparation of $[\text{Pd}(\text{en})\text{I}_2][\text{Pd}(\text{en})\text{I}_4]$.

Excitation Profiles.—The excitation profiles of all the bands measured show monotonic enhancement using exciting lines of wavenumber from ca. 20 000 to 12 500 cm^{-1} (Figure 1), with no maximum being reached even in the case of $[\text{Pd}(\text{en})\text{Cl}_2][\text{Pd}(\text{en})\text{Cl}_4]$. The excitation profiles of the +2 cation-chain chlorides do maximise at wavenumbers greater than 12 500 cm^{-1} , implying a lesser degree of valence delocalisation for these than for neutral-chain complexes; this is in agreement with the slightly lower wavenumbers for both the intervalence bands and the ν_1 bands of the neutral-chain than the cation-chain complexes.

Conclusions

The spectroscopic and X-ray evidence indicates that the complexes prepared are mixed-valence chain complexes of the types (C) and (D). The lower values for the intervalence bands of the neutral-chain complexes described herein than for the analogous complexes of the +2 charge type previously studied^{2,17} suggests that the former would be the better semiconductors.

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