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 $[Pd(en)Cl_2][Pd(en)Cl_4]$, $[Pd(en)Br_2][Pd(en)Br_4]$, $[Pd(tn)Br_2][Pd(tn)Br_4]$, and a mixed-valence complex of empirical formula $Pd_2(en)_2Br_3Cl_3$, 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, $[Pd(dien)Br_3]Br_2$, 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 Cl > Br. The resonance Raman spectra show overtone progressions (v_1v_1) in the axial X-Pd^{IV}-X symmetric stretching mode (v_1) , which lies at *ca*. 260 cm⁻¹ for X = Cl and at *ca*. 145 cm⁻¹ for X = Br, and combination tones $v_1v_1 + v_n$, where v_n is the v(Pd-X) equatorial stretching mode, or v_2 , $v_{asym}(X-Pd^{IV}-X)$, the antisymmetric chain-stretching mode. The excitation profiles of the v_1 and $2v_1$ bands of the neutral chain complexes do not reach maxima even with excitation of the lowest available wavenumber $(12 \ 510 \ cm^{-1})$. These complexes appear to be more delocalised than those of the +2 charge type. Powder diffraction data indicate that $Pd_2(en)_2Br_3Cl_3$ and $[Pd(en)Br_2][Pd(en)Br_4]$ 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, [Pd(en)Cl₂][Pd(en)Cl₄], [Pd(en)Br₂]- $[Pd(en)Br_4]$, $[Pd(tn)Br_2][Pd(tn)Br_4]$, and $Pd_2(en)_2Br_3Cl_3$ involve the diamines L-L = 1,2-diaminoethane (en) or 1,3diaminopropane (tn) co-ordinated in the equatorial plane, while the fifth, [Pd(dien)Br][Pd(dien)Br₃]Br₂, involves the terdentate ligand L-L-L = diethylenetriamine (dien) co-ordinated in the equatorial plane.

Experimental

Preparations.—(a) $[Pd(L-L)Cl_2]$ (L-L = en or tn]. The methods of Drew and Tress ⁵ and Basolo et al.^{6,7} were modified for the preparation of $[Pt(en)Cl_2]$ since that of McCormick et al.⁸ gave poor yields and impure products. Aliquots (2 cm³) of a solution of the amine (0.5 cm³ in 100 cm³ water) were added dropwise to a stirred solution of K₂[PdCl₄] (0.5 g in 30 cm³ water). The yellow precipitate of $[Pd(L-L)Cl_2]$ which is formed after several minutes was filtered off immediately, further amine added to the mother-liquor, and the procedure repeated until no more $[Pd(L-L)Cl_2]$ 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, $[Pd(L-L)_2][PdCl_4]$. By keeping a low concentration of amine the yield of the pink salt was kept to a minimum. The yellow $[Pd(L-L)Cl_2]$ was washed with cold

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

A second method for preparing $[Pd(L-L)Cl_2]$ in quantitative yield was by adding hydrochloric acid (11 mol dm⁻³) to a cold aqueous solution of $[Pd(L-L)_2]Cl_2$.

(b) $[Pd(en)Cl_2][Pd(en)Cl_4]$. Chlorine was bubbled through a suspension of $[Pd(en)Cl_2]$ 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 $C_2H_8Cl_3N_2Pd$: C, 8.80; H, 2.95; Cl, 39.0; N, 10.25%).

(c) $[Pd(en)Br_2][Pd(en)Br_4]$. Bromine in a saturated aqueous solution of KBr was added to an aqueous suspension of $[Pd(en)Cl_2]$ 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 $C_2H_8Br_3N_2Pd$: C, 5.90; H, 2.0; Br, 59.0; N, 6.90%).

(d) $[Pd(tn)Br_2][Pd(tn)Br_4]$. This complex was obtained as gold-brown crystals by method (c), the starting material being $[Pd(tn)Cl_2]$ (Found: C, 9.25; H, 2.50; Br, 57.0; N, 6.85. Calc. for $C_3H_{10}Br_3N_2Pd$: C, 8.55; H, 2.40; Br, 57.0; N, 6.65%).

(e) $Pd_2(en)_2Br_3Cl_3$. By treatment of an aqueous suspension of $[Pd(en)Cl_2]$ with bromine in dilute HBr, gold-brown microcrystals of the complex $Pd_2(en)_2Br_3Cl_3$ were obtained (Found: C, 7.25; H, 2.25; Br, 34.7; Cl, 14.5; N, 8.35. Calc. for $C_4H_{16}Br_3Cl_3N_4Pd_2$: 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) [Pd(dien)Br][Pd(dien)Br₃]Br₂. 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 $C_4H_{13}Br_3N_3Pd$: C, 10.7; H, 2.90; Br, 53.3; N, 9.35%).

Attempts to prepare analogous 1,2-diaminopropane com-

Complex	Crystal colour	Powder colour	Intervalence band max. ^a / cm ⁻¹	ω_1/cm^{-1}	x_{11}/cm^{-1}	$\frac{I(2v_1)/I(v_1)}{(\lambda_0/nm)}$	Progn. v 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)	8v1
$[Pd(en)Br_2][Pd(en)Br_4]$	Gold	Blue	12 800	148.6 ± 0.3	-0.06 ± 0.1	0.53 (752.5)	6v1
$\left[Pd(tn)Br_{2}\right] \left[Pd(tn)Br_{4}\right]$	Gold	Blue	13 800	147.2 ^{<i>b</i>}	ca. 0	0.45 (752.5)	$5v_1$
$Pd_2(en)_2Br_3Cl_3$	Gold	Blue	12 800	148.6		(752.5)	6v1
[Pd(dien)Br][Pd(dien)-	Gold	Blue	9 900	147.2 <i>^b</i>		(799.3)	$3v_1$
Br ₃]Br ₂							

Table 1. Summary of data on complexes studied

^a The v₁ band excitation profiles all maximise at less than 12 500 cm⁻¹. ^b v₁ Value.



Figure 1. (a) Electronic spectrum (KCl disc at ca. 14 K) and excitation profiles (ca. 80 K) of the v_1 (\bigcirc), $2v_1$ (\triangle), and 313 cm⁻¹ (\square) 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 v_1 (\bigcirc) and $2v_1$ (\triangle) bands of [Pd(en)Br₂][Pd(en)Br₄]. (c) Electronic spectrum (KBr disc at 295 K) and excitation profile (ca. 80 K) of the v_1 (\bigcirc) band of [Pd(tn)Br₂][Pd(tn)Br₄].

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

The preparation of $[Pd(en)I_2][Pd(en)I_4]$ was attempted by treating $[Pd(en)Cl_2]$ with a solution of iodine in aqueous KI and also by treating $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$ 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 $K_2[SO_4]$ or in the appropriate alkali-metal halide. For $Pd_2(en)_2Br_3Cl_3$, only $K_2[SO_4]$ 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 $[SO_4]^2$ ($[ClO_4]^-$ 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 $2\theta = 6-120^\circ$.

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.) $ca. 5\,000 \text{ cm}^{-1}$] in the visible-near-i.r. region assigned to the Pd^{II} \rightarrow Pd^{IV} intervalence charge-transfer transition, as for analogous platinum complexes.^{1,2} It occurs (by disc transmission

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Table 2. Wavenumbers (cm ⁻¹) and assignments of the bands observed in
the i.r. spectra of [Pd(en)Cl ₂] and [Pd(en)Cl ₂][Pd(en)Cl ₄]

[Pd(en)Cl ₂]	[Pd(en)Cl ₂][Pd(en)Cl ₄]	Assignment
614w	614w	
557vs (doublet)	556m	Ring skeletal
540w	540m	c
	528m	
517w		ך ר
456s	461w	$\downarrow v(Pd-N)$
450w (sh)	448w	J
	375w	-
	362m	$v_2(v_{asym}, X-Pd^{IV}-X)?$
344w	346s	v(Pd–Cl)
	330m	v(Pd-Cl)
309s	309s	v(PdCl)
297m	292s	Ring skeletal
273m	279m	v(PdCl)
	258m	$v(Pd-Cl), v_1?$
200s	215m	$\delta(N-Pd-N)$
197s (sh)	171w	Rotatory lattice
157s		
141w	146w	PdX ₂ skeletal lattice?
	140w	
	103w	
82w	84w	Rotatory lattice
68w, br		

measurements) at 17 000 cm⁻¹ for [Pd(en)Cl₂][Pd(en)Cl₄] and between 13 800 and 12 800 cm⁻¹ for the analogous bromides. The +1 charge-type complex $[Pd(dien)Br][Pd(dien)Br_3]Br_2$ has its intervalence transition at lower wavenumber (9 900 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, [Pt(dien)I][Pt(dien)I₃]I₂, whose $Pt^{II} \rightarrow Pt^{IV}$ 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 cm⁻¹ for $[Pd(en)Cl_2][Pd(en)Cl_4]$, at 26 250 and 20 750 cm⁻¹ for [Pd(en)Br₂][Pd(en)Br₄], at 25 750 cm^{-1} for [Pd(tn)Br₂][Pd(tn)Br₄], and at 28 000 cm⁻¹ for $[Pd(dien)Br][Pd(dien)Br_3]Br_2$. These bands are possibly due to d-d transitions of the palladium(IV) unit ^{10,11} or to ligand-tometal 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 Pd(en)Cl₂]¹³ to the mixed-valence complex $[C_{2v}$ for the analogous Pt(en)X₃]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 Pd^{IV}–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) $[Pd(en)Cl_2][Pd(en)Cl_4],(b)[Pd(en)Br_2][Pd(en)Br_4],(c)Pd_2(en)_2Br_3Cl_3, and (d) [Pd(tn)Br_2][Pd(tn)Br_4]$

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 $Pd^{II} \rightarrow Pd^{IV}$ 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 v_2 , $v_{asym}(Cl-Pd^{IV}-Cl)$, band for [Pd(en)Cl₂][Pd(en)Cl₄] 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 $Pd_2(en)_2Br_3Cl_3$ has bands attributable to both $v(Pd-Cl)_{eq}$ and $v(Pd-Br)_{eq}$ as well as to $v_{asym}(Br-Pd^{IV}-Br)$, but none attributable to $v_{asym}(Cl-Pd^{IV}-Cl)$; 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 $[Pd(en)Br_2][Pd(en)Br_4]$, $Pd_2(en)_2Br_3Cl_3$, $[Pd(tn)Br_2][Pd(tn)Br_4]$, and $[Pd(dien)Br_3]Br_2$

$[Pd(en)Br_2][Pd(en)Br_4]$	$Pd_2(en)_2Br_3Cl_3$	$[Pd(tn)Br_2][Pd(tn)Br_4]$	$[Pd(dien)Br][Pd(dien)Br_3]Br_2$	Assignment "
		615w	615s	
551s doublet	552m	553w	552m	v(PdN)
			543w) í í
520w	522w			
		509m	513w	
		500 (sh)	485w	v(Pan)
449w		452w,br		
438s	440m	,	430w	
			386w	δ(NCC)
		372w		
		365m		
345w	345w	355w		
325w	322w	329w		> Ring modes
305w	307m ^b	314w,br		
284w	286w			J
	278w			v(M-Cl)
266w		268w		
242m	242w	256m		
232s		234m	230m	v(M-Br)
225s	225m	214s	196s	v ₂ ,v _{sevm} (Br-Pd ^{IV} -Br)
222s				
204s	208m	203m		v(M-Br)
		190m		
		162m		
121w	122w	122w	120w	
106w				PdX ₂ skeletal lattice?

^a Additional bands observed at 95w, 89w, and 66m cm⁻¹ for $[Pd(en)Br_2][Pd(en)Br_4]$, at 84m cm⁻¹ for $Pd_2(en)_2Br_3Cl_3$, at 68m cm⁻¹ for $[Pd(tn)Br_2][Pd(tn)Br_4]$, and 84w cm⁻¹ for $[Pd(dien)Br_3]Br_2$. ^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 $[Pd(en)Cl_2][Pd(en)Cl_4]^*$

$\tilde{\nu}/cm^{-1}$	$I(v_1v_1)/I(v_1)$	$\Delta \tilde{v}_{\frac{1}{2}}/cm^{-1}$	Assignment
258.3	1.00	11.4	ν ₁
273)
289.5			(Pd Cl)
313.4			v(ru-Ci) _{eq}
348			J
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	8v1
tained for	a KICIO I dis	c held at co	7 80 K with 676 4-m

* Obtained for a K[ClO₄] 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 $[Pd(en)Cl_2]$ and $[Pd(en)Br_3]$ (a possibility from the method of preparation).

It is noteworthy that the i.r. spectrum of $[Pd(en)Cl_2]$ -[Pd(en)Cl₄] has more bands than that of the corresponding bromide. In addition it appears that the v₁ band is i.r. active for the chloride (at 258 cm⁻¹) but not for the bromide. It would therefore seem that $[Pd(en)Cl_2][Pd(en)Cl_4]$ crystallises in a different space group from that of $[Pd(en)Br_2][Pd(en)Br_4]$. **Table 5.** Wavenumbers, relative intensities, full widths at half maximum, and assignments of bands observed in the resonance Raman spectrum of $[Pd(en)Br_2][Pd(en)Br_4]$ *

$\tilde{\nu}/cm^{-1}$	$I(vv_1)/I(v_1)$	$\Delta \tilde{v}_{\frac{1}{2}}/cm^{-1}$	Assignment
145.3	1.00	8.3	v,
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	5v1
866	0.04	48	6v1

* 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 $Pd_2(en)_2Br_3Cl_3$ are essentially the same as those of [Pd(en)Br_2][Pd(en)Br_4].

X-Ray Diffraction.—X-Ray powder diffraction patterns indicate that $[Pd(en)Cl_2][Pd(en)Cl_4]$ is not isostructural with $[Pd(en)Br_2][Pd(en)Br_4]$, but that both the latter as well as $Pd_2(en)_2Br_3Cl_3$ are isostructural with $[Pt(en)X_2][Pt(en)X_4]$, X = Cl, Br, or I,¹⁴ and hence belong to space group Ama2 (C_{2v}^{18}) . The compound $Pd_2(en)_2Br_3Cl_3$ 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 $[Pd(en)Cl_2]$ and the mixed-valence bromide. As the c axis is the chain axis in this space group, the results indicate that the $Pd^{II} \cdots Pd^{IV}$ 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 $[Pd(tn)Br_2][Pd(tn)Br_4]^*$

$\tilde{\nu}/cm^{-1}$	$I(v_1v_1)/I(v_1)$	$\Delta \tilde{v}_{rac{1}{2}}/cm^{-1}$	Assignment
147.2	1.00	8.5	v ₁
205.5			$\delta(N-Pd-N)$
257.5			v(Pd-Br)
296.1	0.45	15.7	$2v_1$
407.5			$v_1 + v(Pd-Br)$
445	0.22	24	$3v_1$
502			v(Pd-N)
592	0.09	36	$4v_1$
741	< 0.09	>40	5v ₁

* Obtained for a K[ClO₄] 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 $[Pd(dien)Br_3]Br_2^*$

v∕cm ⁻¹	Assignment
147.2	v ₁
198.4	$\delta(N-Pd-N)$
293	$2v_1$
438	$3v_1$

* Obtained from a K[ClO₄] 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 $[Pt(en)X_2]$ -[Pt(en)X₄], for which this feature has already been established.¹⁴ It has not yet been possible to index the diffraction pattern for [Pd(en)Br₂][Pd(en)Br₄] to the same *d*-spacing precision (±0.03 Å) as for Pd₂(en)₂Br₃Cl₃. The complex [Pd(tn)Br₂][Pd(tn)Br₄] is not isostructural with the other bromides.

There are two $[Pd(en)Br_2][Pd(en)Br_4]$ formula units per unit cell in space group Ama2 but, since this cell is non-primitive, there is only one formula unit per Bravais cell. The 1,2diaminoethane rings are non-planar (hence the choice of Ama2 rather than Cmcm or Cmc2₁). 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 v_1 , the totally symmetric X-Pd^{IV}-X axial stretching mode. The progressions are long for the neutral complexes (to $8v_1$ for X = Cl and to $5v_1$ or $6v_1$ for X = Br) but only reach $3v_1$ for [Pd(dien)Br][Pd-(dien)Br₃]Br₂. This is because even the exciting line of lowest wavenumber available (799.3 nm \doteq 12 510 cm⁻¹) barely falls within the contour of the intervalence band ($\tilde{v}_{max} = 9\,900$ cm⁻¹). Other subsidiary progressions, $v_1v_1 + v_n$, are also apparent in the spectra of the neutral-chain complexes. The modes designated v_n are identified as $v(Pd-Cl)_{eq}$ for [Pd(en)Cl₂][Pd(en)Cl₄] and as $v(Pd^{IV}-Br)_{eq}$ or v_2 , v_{asym} -(Br-Pd^{IV}-Br), for the bromine-bridged complexes. The neutral-chain bromides and the +1 charged chain bromide show a band attributed to $\delta(N-Pd-N)$ but, unlike the +2 cationchain complexes³ studied previously, have no detectable progression involving this mode. The appearance of subsidiary progressions involving v_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 $\cdots Pd^{II} \cdots X - Pd^{IV} - X \cdots Pd^{II} \cdots$ to the excited-state geometry $\cdots Pd^{III} \cdots X \cdots Pd^{III} \cdots X \cdots Pd^{III} \cdots$. It is also likely that the $v(Pd-X)_{eq}$ modes, having similar wavenumber and symmetry to those of v_1 , have borrowed intensity therefrom. No chlorine isotopic splitting is observed for v_1 . The v_1 band for Pd(tn)Br₃ is asymmetric to the high-wavenumber side. The harmonic band wavenumbers for v_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



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The resonance Raman spectrum obtained for $Pd_2(en)_2Br_3Cl_3$ confirms that this compound is bromine-bridged. The only difference between the resonance Raman spectrum of $Pd(en)Br_3$ and $Pd_2(en)_2Br_3Cl_3$ is that the latter has an $I(221.5)/I(v_1)$ value of approximately half that of $[Pd(en)Br_2][Pd(en)Br_4]$, *i.e.* it has a less intense $v(Pd-Br)_{eq}$ band, due to the fact that $Pd_2(en)_2Br_3Cl_3$ has only half the bromine content of $[Pd(en)Br_2][Pd(en)Br_4]$. One might have expected to see a band due to $v(Pd-Cl)_{eq}$ in the resonance Raman spectrum of $Pd_2(en)_2Br_3Cl_3$, but this would be obscured by the $2v_1$ band. The spectroscopic evidence therefore indicates that the structure of $Pd_2(en)_2Cl_3Br_3$ 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 report ¹⁰ of the preparation of $[Pd(en)I_2][Pd(en)I_4]$.

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 $[Pd(en)Cl_2][Pd-(en)Cl_4]$. 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 v₁ 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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References

- 1 M. Kurmoo, Ph.D. Thesis, University of London, 1983.
- 2 R. J. H. Clark, in 'Advances in Infrared and Raman Spectroscopy,' eds. R. J. H. Clark and R. E. Hester, Wiley-Heyden, Chichester, 1984, vol. 11, p. 95.
- 3 R. J. H. Clark, V. B. Croud, and M. Kurmoo, *Inorg. Chem.*, 1984, 23, 2499.
- 4 R. J. H. Clark and V. B. Croud, *Inorg. Chem.*, submitted for publication.
- 5 H. D. K. Drew and H. J. Tress, J. Chem. Soc., 1935, 1244.
- 6 F. Basolo, J. C. Bailar, jun., and B. R. Tarr, J. Am. Chem. Soc., 1950, 72, 2433.
- 7 F. Basolo, H. B. Gray, and R. B. Pearson, J. Am. Chem. Soc., 1960, 82, 4200.
- 8 B. J. McCormick, E. N. Jaynes, and R. Kaplan, *Inorg. Synth.*, 1972, 13, 216.
- 9 R. J. H. Clark, M. Kurmoo, A. M. R. Galas, and M. B. Hursthouse, J. Chem. Soc., Dalton Trans., 1983, 1583.
- 10 D. Layek and G. C. Papavassiliou, Z. Naturforsch., Teil B, 1981, 36, 83.
- 11 H. Tanino and K. Kobayashi, J. Phys. Soc. Jpn., 1983, 52, 1446.
- 12 M. B. Robin and P. Day, Adv. Inorg. Chem. Radiochem., 1967, 10, 247.
- 13 D. S. Martin, R. A. Jacobsen, L. D. Hunter, and J. E. Benson, *Inorg. Chem.*, 1970, 9, 1276.
- 14 K. W. Browall, J. S. Kasper, and L. V. Interrante, *Acta Crystallogr.*, *Sect. B*, 1974, **30**, 1649.
- 15 R. W. Berg and K. Rasmussen, Spectrochim. Acta, Part A, 1973, 29, 319.
- 16 S. D. Allen, R. J. H. Clark, V. B. Croud, and M. Kurmoo, *Philos. Trans. R. Soc., London, Ser.A*, in the press.
- 17 R. J. H. Clark, Chem. Soc. Rev., 1984, 13, 219.

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