The heuristic outline of the molecular mechanics calculation (Scheme I) illustrates the use of Δd_{MM} to scale Δd_{MC} by eq 5 and the C–C distances by eq 7 and 8. R_C corresponds to

$$R_C{}^0 = R_M{}^0 + (\cos\theta)d_{MC}{}^0 \qquad (7)$$

$$R_C = R_C{}^0 + (\cos\theta)(\tfrac{1}{2}\Delta d_{MM} + \Delta d_{MC}) \qquad (8)$$

the average radius of the spherical surface containing the carbon atoms, R_M is the average radius of the spherical surface containing the metal atoms, and the superscript corresponds to values for $[Fe_4(CO)_{13}]^{2-}$. The angle θ (35.65°) between the threefold axis and one edge of a tetrahedron is used to project the M–C distances onto the radius by eq 7 and the changes in M–M and M–C distances onto the radius in eq 8. The ratio of R_C/R_C' is then the factor by which experimental C–C distances are scaled for any arbitrary value of the M–M distance, the prime superscript corresponding to the radius for $[Fe_3Cr(CO)_{14}]^{2-}$.

Once a value of the strain-free metal–metal distance, $d_{MM}{}^0$, is picked, the calculation of energies for a series of M–M distances, d_{MM}, is performed by the procedure outlined in Figure 6. If the parameters are correctly chosen, the resulting total energy (Figure 6, curve 3) should reach a minimum at the observed iron–iron distance. In the present calculations, the d_0 parameter in the C–C nonbonding potential was varied until the total energy minimum correspond to the value of d_{MM} in $[Fe_3Cr(CO)_{14}]^{2-}$ (2.64 Å).

Supplementary Material Available: Complete listings of bond angles and distances (Table XII), positional parameters (Table XIII), anisotropic thermal parameters (Table XIV), and observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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Linear-Chain Halogen-Bridged Mixed-Valence Complexes of Palladium: Infrared, Electronic, Raman, and Resonance Raman Study

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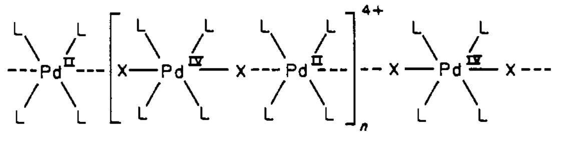
The electronic, infrared, and resonance Raman spectra of the linear-chain mixed-valence complexes $[Pd^{II}(LL)_2][Pd^{IV}(LL)_2X_2][ClO_4]_4$, where LL = 1,2-diaminoethane, 1,2-diaminopropane, and 1,3-diaminopropane and X = Cl and Br, are reported. The electronic spectra are characterized in the visible–near-infrared region by intense broad intervalence bands that decrease in wavenumber in the order Cl > Br. The infrared spectra are near-superpositions of those of the constituent ions. The resonance Raman spectra show long overtone progressions ($v_1\nu_1$) in the axial X–Pd^{IV}–X symmetric stretching mode (ν_1, which lies at $\simeq$280 cm^{-1} for X = Cl and at $\simeq$150 cm^{-1} for X = Br) and combination tones ($v_1\nu_1 + \nu_n$, where ν_n may be either δ(N–Pd–N) or ν_2, ν_{as} (X–Pd^{IV}–X)). The excitation profiles of the ν_1 and $2\nu_1$ bands of the chlorides maximize on the low-energy side of the electronic band maxima, as determined by transmission spectral measurements. For the bromides, enhancement of several bands was observed with red excitation, but none of the excitation profiles reached a maximum even with the excitation line of lowest available wavenumber (799.3 nm ≙ 12 510 cm^{-1}). The palladium complexes were found to have lower intervalence band maxima, ν_1 band excitation profile maxima, and ν_1 values than the analogous platinum complexes. The implications of these results are in agreement with those drawn from conductivity measurements, which indicate that the palladium complexes are the more conducting and thus the ones with the more delocalized valences.

Introduction

Mixed-valence, linear-chain complexes of platinum and palladium are of interest owing to their potential as one-dimensional semiconductors.[1–4] The electronic, infrared, and resonance Raman (RR) spectra of the platinum complexes have been well documented, but little information is yet available on the analogous and potentially more interesting palladium complexes.[5,6] The present investigation is concerned with a spectroscopic study of some cation-chain palladium complexes of the sort



where LL = 1,2-diaminoethane (en), 1,2-diaminopropane (pn), and 1,3-diaminopropane (tn) and X = Cl and Br. The structures of $[Pd(en)_2][Pd(en)_2X_2][ClO_4]_4$, X = Cl and Br, have been found to be similar to those of their platinum analogues.[7,8] They consist of stacks of nearly planar $[Pd(en)_2]$ units bridged by halide ions. Bridging by chlorine is unsymmetrical, producing an alternation of oxidation states, viz. Pd^{II}- - -Cl–Pd^{IV}–Cl- - -Pd^{II}- - -Cl–Pd^{IV}–Cl- - -, along the chain direction; bromine also bridges in an unsymmetrical fashion, though it tends to sit closer to the midpoint between successive Pd atoms. All the complexes are therefore class II mixed-valence species,[9] and they have been found to be more conducting than their platinum analogues, the bromides being better conductors than the chlorides.[3,10]

Experimental Section

Preparations. Monomers. $[Pd(LL)_2]Cl_2$ was prepared by the method of Bekaroglu et al.[11] $[Pd(en)_2Cl_2][ClO_4]_2$ was obtained by a method different from that originally given by Mason;[12] chlorine gas was bubbled through an aqueous solution of $[Pd(en)_2]Cl_2$ containing an excess of perchloric acid in an ice bath. Addition of cold absolute ethanol led to the slow precipitation of the yellow complex

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Table I. Summary of Data on Complexes Studied

complex	cryst color[a]	powder color[b]	intervalence max[b]/ cm^{-1}	EP max[c]/ cm^{-1}	ω_1[c]/cm^{-1}	x_{11}[c]/cm^{-1}	$I(2\nu_1)/I(\nu_1)$[c] (λ_0/nm)	prog (ν_1)[c]
$[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$	gold-green	purple	17 800	13 000	273.9 ± 0.3	−1.01 ± 0.09	0.68 (676.4)	$11\nu_1$
$[Pd(pn)_2][Pd(pn)_2Cl_2][ClO_4]_4$	gold-green	purple	20 000	14 700	279.9 ± 0.3	−1.54 ± 0.07	0.56 (676.4)	$7\nu_1$
$[Pd(tn)_2][Pd(tn)_2Cl_2][ClO_4]_4$	gold-green	purple	17 000	13 300	283.4 ± 0.2	−0.93 ± 0.05	0.65 (676.4)	$8\nu_1$
$[Pd(en)_2][Pd(en)_2Br_2][ClO_4]_4$	gold	blue	13 500	⩽12 500	152.5[d]		~0.2 (752.5)	$3\nu_1$
$[Pd(pn)_2][Pd(pn)_2Br_2][ClO_4]_4$	gold	blue	14 800	⩽12 500	150.6 ± 0.3	−0.18 ± 0.02	0.55 (752.5)	$5\nu_1$
$[Pd(tn)_2][Pd(tn)_2Br_2][ClO_4]_4$	gold	blue	13 500	⩽12 500	143.4[d]		<0.2 (752.5)	$3\nu_1$

[a] By reflection. [b] By transmission. [c] At ca. 80 K. [d] ν_1 value.

$[Pd(en)_2Cl_2][ClO_4]_2$. Care must be taken not to chlorinate for too long, otherwise an orange, air-stable but unidentified solid is formed in large quantities. The palladium(IV) complex is stable if it is crystalline or if it is held in a solution containing an excess of halogen for periods of 12–24 h.

Mixed-Valence Complexes. The mixed-valence complexes $[Pd(LL)_2][Pd(LL)_2X_2][ClO_4]_4$ were prepared by partial oxidation of $[Pd(LL)_2]Cl_2$ with dihalogen in perchloric acid.[13] They were recrystallized by being dissolved in the minimum amount of warm water, to which perchloric acid was then added. Recrystallization can be repeated several times with only a slight loss of yield.

Large crystals of $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$ were obtained by allowing a solution of $[Pd(en)_2Cl_2][ClO_4]_2$ in dilute perchloric acid to decompose slowly over a few days in a refrigerator. Large crystals of the bromo complex were obtained by introducing bromine water into the bottom of a beaker containing a solution of $[Pd(en)_2]Cl_2$ in perchloric acid and allowing the bromine to diffuse upward undisturbed over a few hours. Once formed, the mixed-valence complexes were found to be stable in air. Their purity was checked by elemental analyses for C, H, N, and halogen. Attempts to prepare analogous iodine-bridged complexes were unsuccessful.

Instrumentation. Electronic spectra were recorded at 295 K on a Cary 14 spectrometer. Samples were made up by dispersing the complexes in $K[ClO_4]$ disks.

Infrared spectra were recorded as wax disks of the complexes with a Bruker IFS 113V interferometer (700–20 cm^{-1}). Spectra at ca. 80 K were obtained with the use of a RIIC liquid-nitrogen cryostat.

Raman spectra were recorded on a Spex 1401 or a Spex 14018/R6 spectrometer. Exciting radiation was provided by Coherent Radiation Models CR3, CR500K, and CR3000K lasers. Samples were in the form of single crystals (usually ~3 mm long), pressed disks of the pure complexes, or pressed disks of the complexes dispersed in $K[ClO_4]$. Laser powers were usually less than 50 mW for $K[ClO_4]$ disks and about 5–10 mW for crystals and for pressed disks of the pure complex. A Dewar assembly using liquid nitrogen was used for measurements at ca. 80 K[14] and an Air Products Displex cryostat for those at ca. 10 K. Spectra were calibrated by reference to the emission spectrum of neon or to the Rayleigh line. Excitation profile measurements were made on samples held at ca. 80 K, with the a_1 band of $[ClO_4]^-$ as internal intensity standard. Intensities were corrected for the spectral response of the instruments.

Electronic Spectra

Crystals of the complexes show remarkable dichroism, the chlorides being blue with the electric vector of the transmitted light parallel to the z (chain) axis and colorless when perpendicular to it. The bromides are likewise dark blue and light yellow, respectively. The crystals have a strong metallic sheen, which is lost when they are ground to a powder. The colors of the crystals and powders are given in Table I.

The transmission spectra (Figures 1 and 2) show strong absorption in the visible/near-infrared region. The spectrum in each case is dominated by a strong, broad band (~5000 cm^{-1} fwhm) which is slightly asymmetric by virtue of a shoulder or ill-defined band on the high-energy side. Both bands are halogen dependent, decreasing in wavenumber on going from chloride to bromide (Table I). The strong band of lower energy, polarized along the chain axis, is assigned to the $Pd^{IV} \leftarrow Pd^{II}$ intervalence transition by analogy with the corresponding band of analogous platinum complexes.[5]

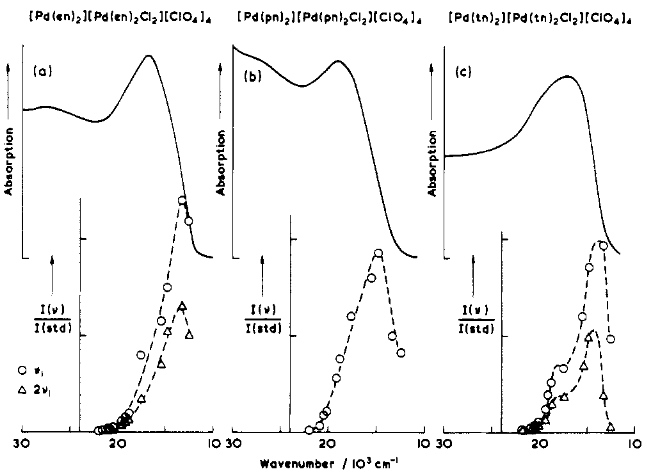

Figure 1. Electronic spectra (295 K) and excitation profiles (ca. 80 K) of the ν_1 (and in some cases $2\nu_1$) bands of (a) $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$, (b) $[Pd(pn)_2][Pd(pn)_2Cl_2][ClO_4]_4$, and (c) $[Pd(tn)_2][Pd(tn)_2Cl_2][ClO_4]_4$.

The wavenumbers of the intervalence band maxima increase (in terms of the equatorially coordinated amines) in the order en ≤ tn < pn. This suggests, by analogy with earlier results on linear-chain platinum complexes,[15,16] that the Pd^{II}- - -Pd^{IV} chain distance and thus the degree of valence localization increases in the same order; the out-of-plane methyl group in the pn case doubtless accounts for the position of pn in this series.

Infrared Spectra

The infrared spectra of the monomers, $[Pd(LL)_2]Cl_2$ and $[Pd(en)_2Cl_2][ClO_4]_2$, and of the mixed-valence complexes $[Pd(LL)_2][Pd(LL)_2X_2][ClO_4]_4$ have been recorded at 80 K from 600 to 20 cm^{-1}. The assignments of the bands are based on those of previously reported complexes.[19-21] The mixed-valence complexes are regarded as being in class II,[9] and their infrared spectra are expected, and found, to consist essentially of the superpositions of the infrared spectra of the constituent complexes. Such differences as exist are expected to be mainly due to the change in force constant of the axial Pd^{IV}–X bond

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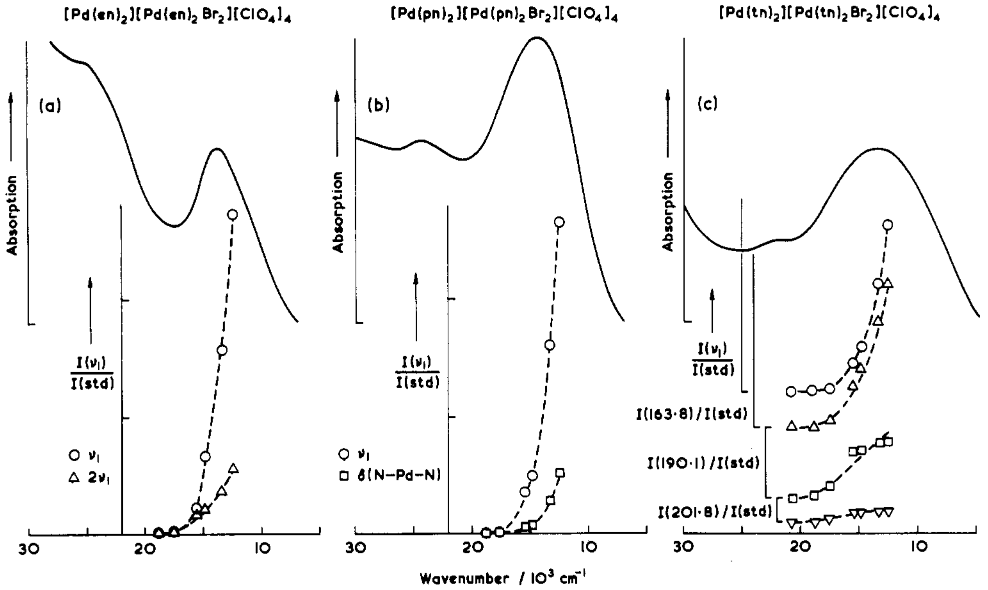

Figure 2. Electronic spectra (295 K) and excitation profiles (ca. 80 K) of (a) the ν_1 and $2\nu_1$ bands of $[Pd(en)_2][Pd(en)_2Br_2][ClO_4]_4$, (b) the ν_1 and δ(N-Pd-N) bands of $[Pd(pn)_2][Pd(pn)_2Br_2][ClO_4]_4$, and (c) the ν_1 and 163.8-, 190.1-, and 201.8-cm^{-1} bands of $[Pd(tn)_2][Pd(tn)_2Br_2][ClO_4]_4$.

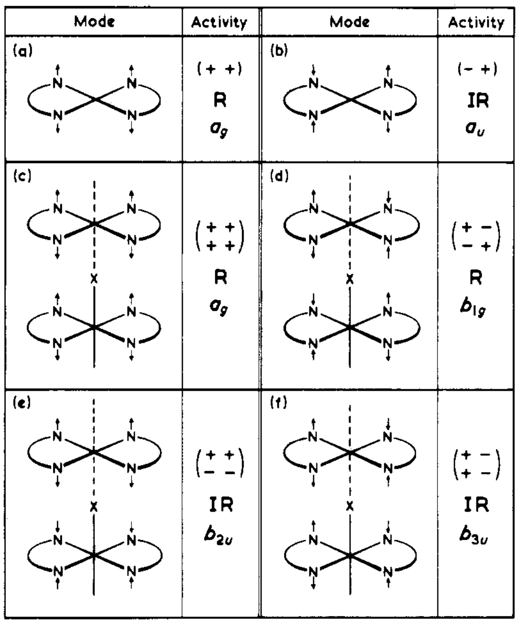

Figure 3. Approximate description of the bending modes, δ(N-Pd-N), of the monomers (a and b) and of the mixed-valence complexes (c-f).

consequent upon the interaction with the Pd^{II} centers and to changes in the amine modes as a result of hydrogen-bond formation with the perchlorate counterion. However, further differences are observed due to a change in space group on going from the monomer to the mixed-valence complex. As an illustration, the effect of this on the in-plane (chelate) δ(N-Pd-N) modes (Figure 3) follows. The space group of $[Pd(en)_2]Cl_2$ is $P\bar{1}$ ($Z = 1$),[22] and hence the Bravais unit cell contains only one $[Pd(en)_2]^{2+}$ unit and two Cl^- ions. The symmetry is isomorphous with C_i, with the molecular symmetry being approximately C_{2h}. Therefore, no correlation field splitting is predicted and the number of intramolecular vibrations for the complex in the crystal is the same as that for the isolated ion. Factor group analysis for the in-plane (chelate), δ(N-Pd-N) modes predicts one Raman-active (a_g) (Figure 3a) and one infrared-active (a_u) mode (Figure 3b). Table II shows that only one band is assigned to this mode in the infrared spectrum of the monomers.

Table II. Wavenumbers ($\tilde{\nu}$/cm^{-1}) and Assignments of Bands Observed in the Infrared Spectra of Some Palladium Monomers in the Range 650-20 cm^{-1} [a,b]

$[Pd^{II}(pn)_2]Cl_2$	$[Pd^{II}(en)_2]Cl_2$	$[Pd^{IV}(en)_2Cl_2][ClO_4]_2$	assignt
630 w	645 w		
		625 vs	ClO_4^-, ν_4
593 vw		599 m	Pd-N str
	581 s	582 s	
557 w	559 w	549 w	
536 w		539 s	
532 w			
	520 s	523 s	
		507 m	
487 w		480 s	ring bends
470 w	474 s		
467 m		466 m	
456 w			
437 w			
		382 s	ν_2 antisym ($Cl-Pd^{IV}-Cl$)
380 w	377 s	369 sh	ring torsional mode
342 w		333 w	ring bends
321 w			
312 w			
295 s	287 s, br	283 vs	in-plane δ(N-Pd-N)
279 w			
265 w			
249 w	248 w	237 w	
	226 w	218 w	
		214 w	
184 m	199 w	190 w	
	176 s	176 w	
160 vs	162 s	159 m	

[a] Obtained as wax disks of the complexes at ca. 80 K. [b] Also, bands appear for $[Pd(pn)_2]Cl_2$ at 75 w cm^{-1}, for $[Pd^{II}(en)_2]Cl_2$ at 105 w, 80 m, and 30 vw cm^{-1}, and for $[Pd^{IV}(en)_2Cl_2][ClO_4]_2$ at 151 w, 136 w, 118 w, 115 w, 110 w, 104 w, 86 w, 75 w, 62 w, and 57 w cm^{-1}.

The space group of $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$ and $[Pd(en)_2][Pd(en)_2Br_2][ClO_4]_4$ is *Ibam* ($Z = 2$),[7,8] there being two $X-Pd^{IV}-X---Pt^{II}$ units per unit cell. The symmetry is isomorphous with D_{2h}. The line-group symmetry[23] of such a linear-chain complex is approximately C_{2h} and that of the site

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Table III. Wavenumbers and Assignments of Bands Observed in the Infrared Spectra of $[Pd(LL)_2][Pd(LL)_2Cl_2][ClO_4]_4$ in the Range 600–20 cm^{-1} [a,b]

$\tilde{\nu}$/cm^{-1}			
en	pn	tn	assignt
590 w			Pd–N str
578 m			
553 m	556 w		
538 m	542 s	542 w	
514 m		519 w	
		501 s	
480 w			ring bends
474 w	476 w		
470 m	470 m	465 m	ClO_4^-, ν_2
458 w	460 w	460 w	ring bends
447 w	450 s	453 w	
429 w	432 s		
394 w, br	395 w, br	385 s	
377 w		370 m	
364 m	362 s	358 m	ν_2, antisym Cl–Pd^{IV}–Cl str
	352 w	354 w	ring bends
334 w	340 s	346 m	
	312 s	321 w	
	298 sh	299 w	
289 s	284 vs	287 s	in-plane δ(N–Pd–N)
	270 vs	284 sh	
249 s	250 m	262 s	in-plane δ(N–Pd–N)
		246 w	
		228 w	
188 m	184 m	196 w, br	
		176 w, br	
165 m	164 m	170 w	Cl–Pd^{IV}–Cl bend?

[a] See footnote to Table II. [b] Also bands appear for LL = en at 153 m, 115 w, 84 w, and 70 w cm^{-1}, for LL = pn at 152 m, 128 w, and 84 w, br cm^{-1}, and for LL = tn at 144 w, 137 w, 125 w, 110 w, and 88 w, br cm^{-1}.

Table IV. Wavenumbers and Assignments of Bands Observed in the Infrared Spectra of $[Pd(LL)_2][Pd(LL)_2Br_2][ClO_4]_4$ in the Range 600–20 cm^{-1} [a,b]

$\tilde{\nu}$/cm^{-1}			
en	pn	tn	assignt
587 m			Pd–N str
578 m			
552 w, br	553 w		
533 m	538 w	538 w	
515 m		513 w	
		500 s	
485 w, br			ring bends
478 w			
473 w			
470 m	471 m	465 w	ClO_4^-, ν_2
457 w	457 w	455 w	ring bends
446 w	450 w		
	434 w		
404 s (asym to low $\tilde{\nu}$ side)			
383 s	392 m, br	382 w	
368 sh		372 vw	
	348 w	355 vw	
	342 w	345 w	
323 w	324 w	327 w	
309 w	311 m		
284 w		288 w	
276 m	278 m	278 m	in-plane δ(N–Pd–N)
256 m	258 m	258 m	
237 m	227 m	226 vs	ν_2, antisym Br–Pd^{IV}–Br str
211 vw			
185 sh			
180 m		180 w, br	
169 w	162 sh	168 w	
140 w, br	146 s	125 w	
109 m	115 m	109 w	Br–Pd^{IV}–Br bend?

[a] See footnote to Table II. [b] Also bands appear for LL = en at 89 w, 81 w, 75 w, and 69 w cm^{-1}, for LL = pn at 90 m, 81 sh, 75 m, and 69 m cm^{-1}, and for LL = tn at 89 w and 72 w cm^{-1}.

group is likewise C_{2h}. Line group analysis for the in-plane (chelate) δ(N–Pd–N) modes predicts four Raman-active (2 a_g + 2 b_{1g}) and four infrared-active (2 b_{2u} + 2 b_{3u}) modes, leading to correlation field splittings (not necessarily resolved) (Figure 3c–f).

Tables III and IV show that, for the mixed-valence complexes, two bands can be assigned to the in-plane (chelate) δ(N–Pd–N) modes.

The general trends noted in the infrared spectra of the mixed-valence complexes are that (a) ν(Pd–Cl) > ν(Pd–Br), (b) ν(Pd–X) in the mixed-valence complexes < ν(Pd–X) in the constituent monomers,[24] and (c) δ(N–Pd–N) is less sensitive than the chelate ring modes to changes in the amine. The ν_2 (antisymmetric X–Pd^{IV}–X stretch) band is observed at 382 cm^{-1} for $[Pd(en)_2Cl_2][ClO_4]_2$ and between 358 and 364 cm^{-1} for the mixed-valence chloro complexes. This drop in wavenumber on bridging is larger than that observed for the platinum analogoues,[25] a result which indicates that there is greater interaction between Pd^{II} and Cl than between Pt^{II} and Cl in chain complexes. The ν_2 band has been found to display chlorine isotopic splitting for the platinum complexes.[25] However, the analogous palladium complexes do not show any splitting even at 80 K and the highest resolution possible, an observation which is a consequence of the larger number of isotopes of significant abundance for Pd than Pt and of their lower mass. A band at ca. 230 cm^{-1} is attributed to the ν_2 fundamental of the chain bromides.

Raman and Resonance Raman Spectra

The Raman and RR spectra of the mixed-valence complexes were recorded for single crystals (where possible) and for polycrystalline disks (pure or material mixed with $K[ClO_4]$) at ca. 80 and 10 K. The spectra are shown in Figures 4 and 5, and the wavenumbers and assignments are given in Tables V–VIII.

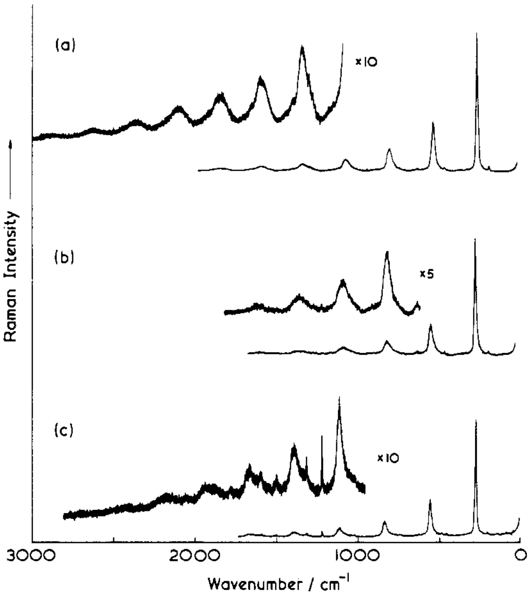

Figure 4. Resonance Raman spectra of (a) $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$, (b) $[Pd(pn)_2][Pd(pn)_2Cl_2][ClO_4]_4$, and (c) $[Pd(tn)_2][Pd(tn)_2Cl_2][ClO_4]_4$ as $K[ClO_4]$ disks at ca. 80 K (λ_0 = 647.1 nm, spectral slit width ~2 cm^{-1}).

Resonance Raman spectra for the three chloride complexes (Figure 4) are dominated by long overtone progressions in ν_1, the totally symmetric Cl–Pd^{IV}–Cl stretching mode. Other

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Table V. Wavenumbers, Relative Intensities, Fwhm, and Assignments of Bands Observed in the RR Spectrum of $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$[a]

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	assignt
197.6			δ(N–Pd–N)
272.0	1.00	12.1	ν_1, ν_s(Cl–Pd^{IV}–Cl)
330.7			
372.4			ν_2, ν_{as}(Cl–Pd^{IV}–Cl)
542.2	0.68	23.3	$2\nu_1$
809.1	0.49	38.8	$3\nu_1$
1073.3	0.35	54	$4\nu_1$
1271.6			
1291.1			δ_t(H–C–H)
1339	0.29	70	$5\nu_1$
1394			δ_s(H–C–H)
1566			$\nu_1 + \delta_t$
1584			δ_s(H–N–H)
1600	0.21	90	$6\nu_1$
1834			$2\nu_1 + \delta_t$
1854			$\nu_1 + \delta_s$(H–N–H)
1863	0.15	100	$7\nu_1$
1931			
2100	0.10	120	$8\nu_1$
2350	~0.06	>120	$9\nu_1$
2630	~0.03	>120	$10\nu_1$
2880	~0.01	>120	$11\nu_1$

[a] Obtained as a K[ClO$_4$] disk at ca. 80 K with 647.1-nm excitation. Slit widths were 180/220/180 μm (~2 cm^{-1}).

Table VI. Wavenumbers, Relative Intensities, Fwhm, and Assignments of Bands Observed in the RR Spectrum of $[Pd(pn)_2][Pd(pn)_2Cl_2][ClO_4]_4$[a]

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	assignt
195			δ(N–Pd–N)
233.3			
276.7	1.00	13.5	ν_1, ν_s(Cl–Pd^{IV}–Cl)
325			
362			ν_2, ν_{as}(Cl–Pd^{IV}–Cl)
551.3	0.56	27.5	$2\nu_1$
606			$\nu_1 + 325$
628.1			
634.7			
821.4	0.41	45	$3\nu_1$
922.5			
1087	0.29	61	$4\nu_1$
1121			
1219			
1255			
1354	0.17	86	$5\nu_1$
1396			
1607	~0.10	~100	$6\nu_1$
1874	<0.10	>100	$7\nu_1$

[a] Obtained as a K[ClO$_4$] disk at ca. 80 K with 647.1-nm excitation. Slit widths were 100/120/100 μm (~1 cm^{-1}).

subsidiary progressions, $v_1\nu_1 + \nu_n$, are also apparent. These ν_n modes have been identified as δ(N–Pd–N), ν_2(Cl–Pd^{IV}–Cl), and ligand modes (see Tables V–VIII). The harmonic band wavenumbers (ω_1) and anharmonicity constants[26] are listed in Table I; the likely accuracies of such values, and the constraints on them, are discussed elsewhere.[27a]

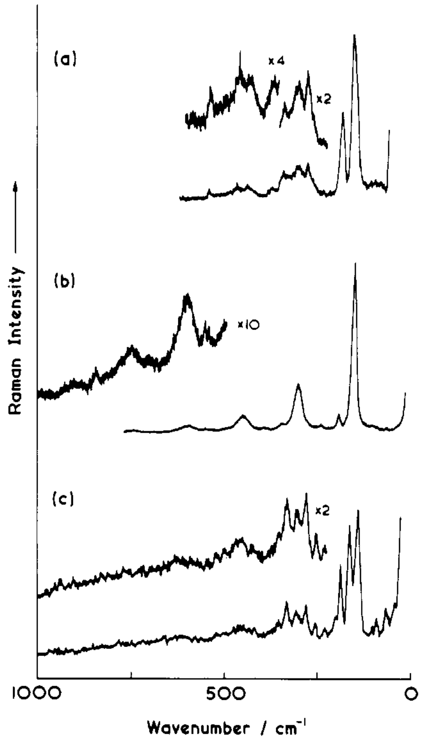

Figure 5. Resonance Raman spectra of (a) $[Pd(en)_2][Pd(en)_2Br_2][ClO_4]_4$, (b) $[Pd(pn)_2][Pd(pn)_2Br_2][ClO_4]_4$, and (c) $[Pd(tn)_2][Pd(tn)_2Br_2][ClO_4]_4$ as K[ClO$_4$] disks at ca. 80 K ($\lambda_0 = 752.5$ nm, spectral slit width ~2.5 cm^{-1}).

Table VII. Wavenumbers, Relative Intensities, Fwhm, and Assignments of Bands Observed in the RR Spectrum of $[Pd(tn)_2][Pd(tn)_2Cl_2][ClO_4]_4$[a]

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	assignt
206.3			δ(N–Pd–N)
281.4	1.00	10.2	ν_1, ν_s(Cl–Pd^{IV}–Cl)
460.0			ν(Pd–N)
488.4			$\nu_1 + \delta$(N–Pd–N)
561.6	0.65	21.2	$2\nu_1$
740			$\nu_1 + \nu$(Pd–N)
770.1			$2\nu_1 + \delta$(N–Pd–N)
820			
839.2	0.40	29.8	$3\nu_1$
842			
1113.4	0.26	35.3	$4\nu_1$
1218.9[b]			
1287			
1312			δ_t(H–C–H)
1387	0.21	56	$5\nu_1$
1499			
1595			$\nu_1 + \delta_t$
1663	0.12	69	$6\nu_1$
1777			
1873			$2\nu_1 + \delta_t$
1934	0.07	80	$7\nu_1$
2047			
2146			$3\nu_1 + \delta_t$
2197	0.05	100	$8\nu_1$
2337			
2410			$4\nu_1 + \delta_t$
2465	0.03	120	$9\nu_1$

[a] Obtained as a K[ClO$_4$] disk at ca. 80 K with 647.1-nm excitation. Slit widths were 150/200/150 μm (~1.5 cm^{-1}). [b] The 1218.9-cm^{-1} band is possibly a δ(H–C–H) twist.

Chlorine isotopic splitting is expected for the ν_1 mode (unlike ν_2) since the Q_1 normal coordinate does not involve motion of the central metal atom. For a linear Pd^{IV}Cl$_2$ unit a triplet band structure (9:6:1) is expected. The ν_1 band of a single crystal of $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$ held at ca. 10 K was resolved into a triplet at 275.8 w, 272.7 s, and 267.6 m cm^{-1}. Using the model described by Allen et al.[25] and choosing the 364-cm^{-1} infrared band as ν_2 and the 272.7 cm^{-1} Raman band as ν_1(Pd^{35}Cl$_2$) to describe the force field, we calculate ν_1(Pd^{35}Cl^{37}Cl) to be 268 cm^{-1}, cf. observed value 267.6 cm^{-1};

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(26) Herzberg, G. "Infrared and Raman Spectroscopy of Polyatomic Molecules"; Van Nostrand: Princeton, 1945; p 265.

(27) (a) Clark, R. J. H.; Stewart, B. *Struct. Bonding (Berlin)* **1979**, *36*, 1. (b) Siebrand, W.; Zgierski, M. Z. *Excited States* **1979**, *4*, 1.

Table VIII. Wavenumbers and Assignments of Bands Observed in the RR Spectra of $[Pd(LL)_2][Pd(LL)_2Br_2][ClO_4]_4$[a]

$\tilde{\nu}/cm^{-1}$	assignt	$\tilde{\nu}/cm^{-1}$	assignt
LL = en			
152.5	ν_1, $\nu_s(Br-Pd^{IV}-Br)$	343.5	$\nu_1 + \delta$(N-Pd-N)
188.9	δ(N-Pd-N)	432	ν_1 + 276.5
236.9	ν_2, $\nu_{as}(Br-Pd^{IV}-Br)$	464	$3\nu_1$
276.5		541	
301	$2\nu_1$	622	
306		630	
LL = pn			
150.1	ν_1	390.2	$\nu_1 + \nu_2$
191.3	δ(N-Pd-N)	449.3	$3\nu_1$
240.3	ν_2	499.6	$2\nu_1 + \delta$(N-Pd-N)
300.3	$2\nu_1$	599.6	$4\nu_1$
345.2	$\nu_1 + \delta$(N-Pd-N)	747	$5\nu_1$
LL = tn			
143.4	ν_1	353	ν_1 + 201.8
163.8		375	
190.1	δ(N-Pd-N)	424	$3\nu_1$
201.8		446	$2\nu_1$ + 163.8
225	ν_2	456	ν(Pd-N)
257		592	$3\nu_1$ + 163.8
281.6	$2\nu_1$	609	
305	ν_1 + 163.8	629	
331.3	$\nu_1 + \delta$(N-Pd-N)		

[a] Obtained as $K[ClO_4]$ disks at ca. 80 K with 752.5-nm excitation. Slit widths were 250/300/250 μm (~2.5 cm^{-1}).

$\nu_1(Pd^{37}Cl_2)$ is too weak to be observed experimentally. Although the discrepancy of 0.4 cm^{-1} is within experimental error, the agreement is not as good as that obtained for the platinum analogues, for which chlorine isotopic splitting has been observed for both ν_1 and ν_2.[25] The alternative choice of the band at 275.8 cm^{-1} instead of that at 272.7 cm^{-1} for ν_1-$(Pd^{35}Cl_2)$ is clearly incorrect, since it gives a poor fit to the model and is relatively too weak. In the case of the pn and tn complexes, measurements were only possible on polycrystalline disks, as attempts to grow large crystals were unsuccessful. Measurements made under these conditions result in only poor resolution of the (albeit asymmetric) ν_1 band.

It is worth noting that the ν_1 band for the en complex shows a wavenumber dependence on the exciting line and that the relative intensities of the isotopomer bands also change. For the pn and tn complexes this was only detected as changes in the shape of the band with change of exciting line.

For the bromide complexes, RR spectra were only obtained for the pn complex as resonance could not be achieved for the en and tn complexes even with the exciting line of lowest energy at our disposal (799.3 nm ≙ 12 510 cm^{-1}) (Figure 5). The spectrum of the pn complex is likewise dominated by a progression in ν_1 (up to $5\nu_1$ maximum) and a combination tone progression $v_1\nu_1 + \delta$(N–Pd–N). For the en and tn complexes several fundamentals were observed to give rise to overtones and combination tones. Unlike the pn complex, for which the band assignments were unambiguous, those for the en and tn complexes were less so. The ν_1 band was assigned to the one showing maximum enhancement at or near resonance.

Excitation Profiles

The excitation profiles (EP) of the ν_1 and $2\nu_1$ bands of the chlorides and several bands of the bromides at ca. 80 K have been constructed (Figures 1 and 2). The EP for ν_1 and $2\nu_1$ of the chlorides maximize on the low-energy side of the electronic band maxima, a situation typical of halogen-bridged platinum complexes.[28] In the case of the tn complex a shoulder is observed on the high-energy side. The EP of all the strong bands of the bromides show continuous enhancement from 20 000 to 12 500 cm^{-1} with no sign of any maxima being reached.

The large enhancement of ν_1 and its overtones on excitation within the contour of the intervalence band is consistent with the large change in the Pd^{IV}–X bond length expected on transforming the chain from the ground state, ---Pd^{II}---X–Pd^{IV}–X---Pd^{II}---, to the excited state, –Pd^{III}–X–Pd^{III}–X–Pd^{III}–. The small enhancement of the other modes is mainly due to slight changes in the geometry accompanying this transformation.

The EP maxima for the chlorides have the same trend as the intervalence band maxima, viz. en ≃ tn < pn.

Conclusion

The mixed-valence halogen-bridged complexes of palladium have been found to display optical properties similar to those of platinum. The ν_2 band wavenumber of isolated $[M(en)_2X_2]^{2+}$ is lowered more for palladium than platinum on the formation of linear-chain complexes ---$[M(en)_2]$---$[M(en)_2X_2]$---$[M(en)_2]$---. The intervalence band maxima, EP maxima, and ν_1 values of the palladium complexes are all lower in wavenumber than those of the corresponding platinum complexes. Since conductivity in these materials is believed to be phonon-assisted,[3] low ν_1 values and low intervalence transition energies would indicate higher conductances for the complexes of palladium than for the platinum. These conclusions are in complete agreement with the conductance data of Kida et al.[3,10]

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(28) Clark, R. J. H.; Kurmoo, M. *J. Chem. Soc., Dalton Trans.* **1983**, 761.