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Mixed-Valence Palladium(II)/Platinum(IV) Chain Complexes. Infrared, Electronic, Raman, and Resonance Raman Studies

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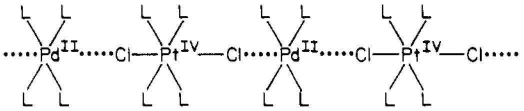
The electronic, infrared, and resonance Raman spectra of the mixed-metal, mixed-valence chain complexes $[Pd^{II}(LL)_2][Pt^{IV}(LL)_2Cl_2][ClO_4]_4$, where LL = 1,2-diaminoethane (en), 1,2-diaminopropane (pn), or 1,3-diaminopropane (tn) are reported. The electronic spectra are characterized by intense, broad intervalence bands at 26 300, 27 700, and 26 400 cm^{-1} for the en, pn, and tn complexes, respectively. The infrared spectra are near superpositions of those of the constituent palladium(II) and platinum(IV) complexes. Resolution of the axial $Cl-Pt^{IV}-Cl$ stretching modes (ν_1, symmetric, Raman active; ν_2, antisymmetric, infrared active) into their chlorine isotopic components has enabled the $Pt^{IV}-Cl$ stretching force constant to be established as ca. 2.1 mdyn Å^{-1}. The resonance Raman spectra are dominated by long overtone progressions in ν_1. The isotopic components of the members of this progression have been resolved and are tabulated up to $4\nu_1$, enabling values for ω_1 and x_{11} to be evaluated for each isotopomer. The excitation profiles of the ν_1 isotopic components for a given sample all maximize, within experimental error, at the same wavenumber, some 1700–3900 cm^{-1} below the maximum in the $Pd^{II}-Pt^{IV}$ intervalence band, as determined by transmission measurements. The Raman spectrum also reveals evidence for the existence of other emission processes, the nature of which are discussed. The spectroscopic results indicate that the mixed Pd^{II}/Pt^{IV} complexes have weaker metal center interactions, i.e. have more localized valences, than have either the analogous Pd^{II}/Pd^{IV} or Pt^{II}/Pt^{IV} complexes.

Introduction

Mixed-valence, linear-chain complexes of platinum and palladium are of interest owing to their potential as one-dimensional semiconductors.[1-4] The vibrational and electronic spectral properties of Pt^{II}/Pt^{IV} complexes of this sort have been well documented,[5,6] and information is beginning to emerge relating to analogous palladium complexes.[7,8] The present investigation is concerned with the synthesis, characterization, and detailed spectroscopic study of three mixed-metal complexes involving cation chains of the sort



where LL = 1,2-diaminoethane (en), 1,2-diaminopropane (pn), or 1,3-diaminopropane (tn). A few features of these results have appeared previously.[7-9] Bridging by chlorine in such complexes is unsymmetrical, and hence an alternation of oxidation states is produced along the chain; all such complexes are therefore regarded as class II, localized-valence species.[10] The interest in mixed-metal as compared to single-metal mixed-valence species relates to (a) relative intervalence transition energies and bandwidths, (b) the degree of localization of the valences, and (c) the infrared, Raman, and resonance Raman spectroscopy of these different sorts of chain complex.

Experimental Section

Preparations. $[M^{II}(LL)_2]Cl_2$ was prepared by the method of Bekaroglu et al.[11] and $[Pt^{IV}(LL)_2Cl_2]Cl_2$ by oxidation of $[Pt^{II}(LL)_2]Cl_2$ with chlorine gas. The mixed-valence complexes were prepared by adding $[Pd(LL)_2]Cl_2$ in aqueous solution to $[Pt(LL)_2Cl_2]Cl_2$ in aqueous solution at a 1:1 mole ratio in the presence of perchloric acid.[9] The complexes were recrystallized from dilute (ca. 0.2 M) perchloric acid solutions. Anal. Calcd for $[Pd(en)_2][Pt(en)_2Cl_2][ClO_4]_4$: C, 9.51; H, 3.19; N, 11.08; Cl, 21.05. Found: C, 9.57; H, 3.00; N, 10.90; Cl, 21.4. Calcd for $[Pd(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$: C, 13.51; H, 3.78; N, 10.50; Cl, 19.94. Found: C, 13.5; H, 3.78; N, 10.47; Cl, 20.1. Calcd for $[Pd(tn)_2][Pt(tn)_2Cl_2][ClO_4]_4$: C, 13.51; H, 3.78; N, 10.50; Cl, 19.94. Found: C, 13.6; H, 3.66; N, 10.43; Cl, 20.3. Attempts to prepare $[Pt^{II}(LL)_2][Pd^{IV}(LL)_2Cl_2][ClO_4]_4$ were unsuccessful.

Instrumentation. Electronic spectra were recorded at 295 K on a Cary 14 spectrometer. Samples were made as Nujol mulls between quartz plates.

Infrared spectra were recorded on wax disks of the complexes by a Bruker IFS 113V interferometer (650–20 cm^{-1}). Spectra at ca. 80 K were obtained with the use of an RIIC liquid-nitrogen cryostat. Raman spectra were recorded on a Spex 14018/R6 spectrometer. Exciting radiation was provided by Coherent Radiation Models CR 12 and CR 3000K lasers and a Model CR 599 dye laser employing stilbene-3 as the lasing medium. Samples were in the form of single crystals (usually ca. 2 mm long), pressed disks of the pure complexes, or pressed disks of the complexes dispersed in $KClO_4$. Laser powers were kept to <10 mW. All Raman spectra were recorded at ca. 10 K on an Air Products Displex cryostat. Spectra were calibrated by reference to the Rayleigh line. Spectral slit widths were ≤1.5 cm^{-1}. Excitation profiles were measured on samples held at ca. 10 K with reference to the a_1 band of $[ClO_4]^-$ as internal intensity standard. Intensities were corrected for the spectral response of the instruments.

Results and Discussion

Electronic Spectra. Crystals of the complexes are dichroic, being yellow with the electric vector of the transmitted light parallel to the chain (*z*) axis and colorless when perpendicular to it.

The transmission spectra (Figure 1) show strong absorption in the visible region. The spectra, at room temperature, are dominated by a strong, broad, featureless band (fwhm ca. 5000 cm^{-1}) that, via a single-crystal spectrum, can be shown to be polarized along the chain axis. This band is assigned to the $Pd^{II} \rightarrow Pt^{IV}$ intervalence transition by analogy with the assignment for the corresponding band of analogous purely platinum and purely palladium complexes.[6]

The wavenumbers of the intervalence band maxima (Table I) increase (in terms of the equatorially coordinated amine) in the order en (26 300 cm^{-1}) ≤ tn (26 400 cm^{-1}) < pn (27 700 cm^{-1}). This suggests that, by analogy with previous results,[8,12,13] the $Pd^{II}\cdots Pt^{IV}$ chain distances and thus the degree of valence electron localization increases in the same order. The out-of-plane methyl

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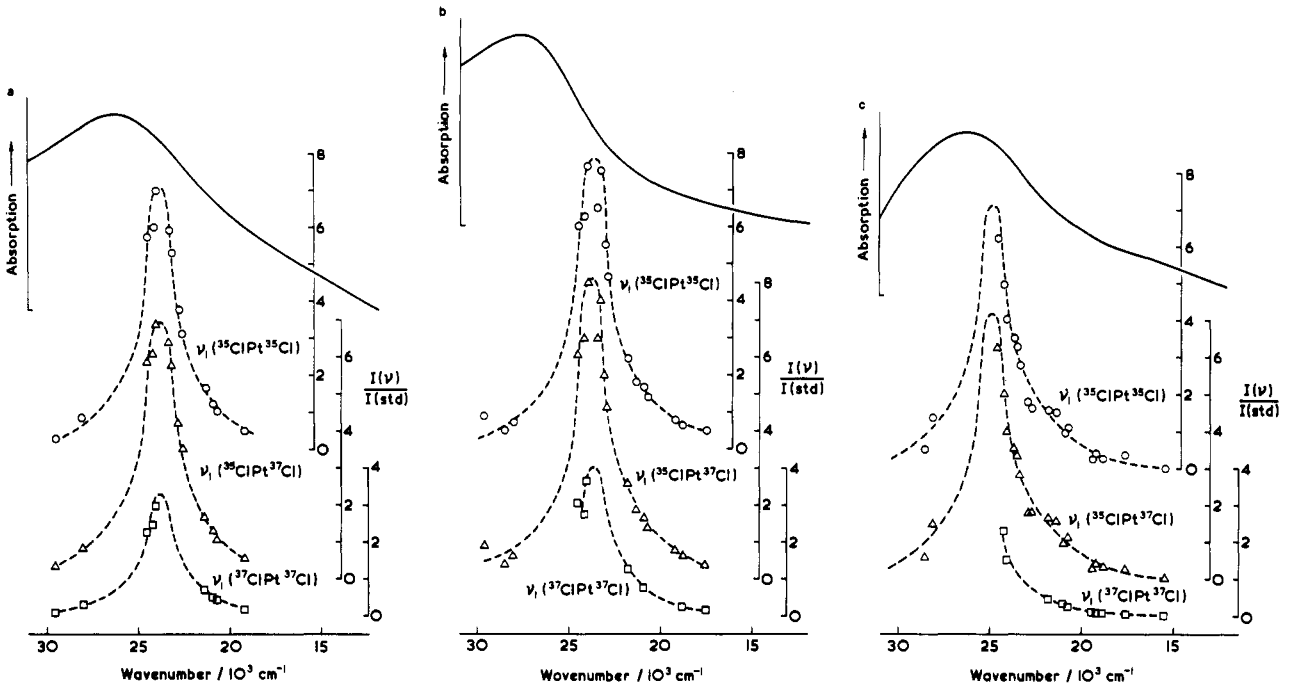

Figure 1. Electronic spectra (295 K) and excitation profiles (ca. 10 K) of the chlorine isotopic components of the ν_1 band: (a) $[Pd(en)_2][Pt(en)_2Cl_2][ClO_4]_4$; (b) $[Pd(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$; (c) $[Pd(tn)_2][Pt(tn)_2Cl_2][ClO_4]_4$.

Table I. Properties of the Palladium(II)/Platinum(IV) Complexes

complex[a]	intervalence band max/cm⁻¹	EP max/cm⁻¹	ω_1[b]/cm⁻¹	x_{11}[b]/cm⁻¹	$I(2\nu_1)/I(\nu_1)$[b,c]	progn length
$[Pd(en)_2][Pt(en)_2Cl_2][ClO_4]_4$	26 300	ca. 23 900	330.0	−0.83	0.39	$11\nu_1$
			325.9	−0.89	0.26	
			322.1	−0.82	0.20	
$[Pd(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$	27 700	ca. 23 800	330.5	−0.96	0.45	$9\nu_1$
			326.3	−1.10	0.39	
			323.3	−1.29	0.27	
$[Pd(tn)_2][Pt(tn)_2Cl_2][ClO_4]_4$	26 400	ca. 24 700	333.6	−0.83	0.36	$10\nu_1$
			328.9	−0.72	0.28	
			326.7	−1.04	0.24	

[a] All three complexes form as yellow crystals, which, on being ground, form yellow powders. [b] Values are listed for each isotopic component, viz. 35/35, 35/37, and 37/37; ω_1 values are accurate to ±0.1 cm⁻¹, x_{11} values to ±0.05 cm⁻¹. [c] The intensity ratios relate to 413.1, 406.7, and 415.4 nm for the en, pn, and tn complexes, respectively.

group in the case of pn doubtless accounts for the position of pn in this series.[8]

The intervalence band is at higher energy than that of purely platinum or purely palladium complexes, implying that the mixed-metal complexes are the most valence localized of all the chain complexes and thus are likely to be the poorest electrical conductors.

Infrared Spectra. The infrared spectra of the mixed-valence complexes have been recorded at 80 K from 650 to 20 cm⁻¹. The assignments of the bands are based on those of previously reported complexes[14–16] (Table II).

The infrared spectra of these halogen-bridged complexes are, as expected for class II mixed-valence complexes, found to consist essentially of superpositions of the infrared spectra of the constituent complexes. Such differences as exist are mainly due to changes in the amine modes as a result of hydrogen-bond formation with the counterion, of changes in space group on going from the monomer to the mixed-valence complex,[8] and of changes in force constant of the axial Pt^{IV}–X bond consequent upon the interaction with the Pd^{II} centers (vide infra).

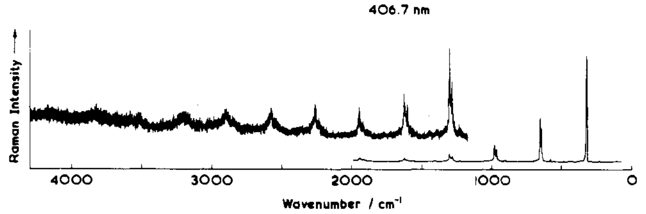

Figure 2. Resonance Raman spectrum of $[Pd(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ as a solid disk at ca. 10 K, λ_0 = 406.7 nm, showing vibrational Raman spectrum only.

It is possible to resolve the chlorine isotopic splitting of the ν_2 band (attributed to the antisymmetric Cl–Pt^{IV}–Cl stretching mode) by using the conditions specified in the Experimental Section. The results are listed in Table II, the component bands having the intensity ratio of 9:6:1 expected for the model based on an isolated linear Cl–Pt^{IV}–Cl unit.[17] For the tn complex the closeness of an amine ligand mode to the ν_2 band has precluded the resolution of all the isotopic components. The amine modes are virtually insensitive to the metal.

There is no evidence for any band attributable to a Pd–Cl stretching mode, thus confirming that the metal atom valences are Pd^{II}/Pt^{IV} rather than vice versa.

Resonance Raman Spectra. The Raman and resonance Raman spectra of the mixed-valence complexes were recorded for single crystals (where possible) and as polycrystalline disks (pure or

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Table II. Wavenumbers/cm^{-1} and Assignments of the Bands Observed in the Infrared Spectra of the Complexes $[Pd(LL)_2][Pt(LL)_2Cl_2][ClO_4]_4$ in the Region 650–20 cm^{-1} (LL = en, pn, tn)[a]

en	pn	tn	assgnt
625 vs	625 vs	625 vs	$[ClO_4]^-$
595 w	600 sh		
577 m	576 w		
560 m		552 w	M–N str
	534 w	531 w	
512 m		502 m	
483 w			ring bends
474 w	479 w		
470 w	471 m	466 m	$[ClO_4]^-$
459 w	461 wbr		
456 w	455 wbr		ring bends
446 w			
369 m		367 w	δ(NCCN)
360.8 s	358.5 s	359.3 m	ν_2, $\nu_{as}(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
358.4 s	356.1 s	355.8 s	ν_2, $\nu_{as}(^{37}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
355.0 m	352.6 s	*b*	ν_2, $\nu_{as}(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
	342 w	347.2 s	
333 w	333 m		ring bends
	307 m		
		289 sh	
296 s	292 s	280 vs	in-plane δ(N–M–N)
290 sh	275 w	274 m	
247 s	251 m	258 s	in-plane δ(N–M–N)
		245 w	
	228 m	224 s	

[a] Additional bands occur for the en complex at 184 m, 165 s, 154 s, 145 s, 124 w, 115 s, 96 w, 90 w, 80 w, 76 w, and 68 w cm^{-1}, for the pn complex at 160 m, 125 m, 108 m, 83 w, and 64 w cm^{-1}, and for the tn complex at 170 w, 138 w, and 108 m cm^{-1}. [b] ν_1 of the $^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl$ isotopomer for LL = tn is not observed probably due to its close proximity to the amine band at 347.2 cm^{-1}. This may also alter the expected isotopomer ratio of 9:6:1 to that observed (the 35/37 band is in fact the most intense).

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

$\tilde{\nu}$/cm^{-1}	$I(\nu_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	assgnt
227.8			δ(N–Pt–N)
320.7	1.0	3.4	ν_1, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
324.1	1.0	3.4	ν_1, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
328.4	1.0	3.6	ν_1, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
360.3			ν_2?
581.7			ν(Pt–N)
638.7	0.20	4.0	$2\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
646.4	0.26	4.8	$2\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
655.0	0.39	6.2	$2\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
681.6			
908			$\rho(CH_2)$?, ν_1 + ν(Pt–N)?
956.1	0.06	5.0	$3\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
967.2	0.07	5.2	$3\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
980.2	0.15	7.2	$3\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
1262.7			$\delta(CH_2)$
1272.7	<0.01	>5.0	$4\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
1285.5	0.04	7.2	$4\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
1303.8	0.08	8.8	$4\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$

[a] Recorded as a solid disk at ca. 10 K with 413.1-nm excitation, <10 mW at source, slits 80/150/80 μm (spectral slit width ca. 1.2 cm^{-1}).

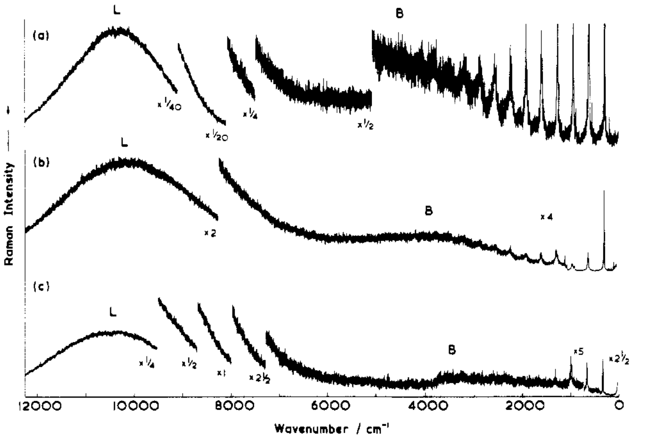

Figure 3. Resonance Raman spectra of $[Pd(LL)_2][Pt(LL)_2Cl_2][ClO_4]_4$, LL = (a) en, (b) pn, and (c) tn, at ca. 10 K, λ_0 = 406.7 nm, showing vibrational Raman spectrum together with bands L and B (diagram uncorrected for spectral response of the instrument).

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

$\tilde{\nu}$/cm^{-1}	$I(\nu_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	assgnt
225.3			
320.9	1.0	4.8	ν_1, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
324.1	1.0	3.4	ν_1, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
328.6	1.0	3.4	ν_1, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
339.0			
357.3			ν_2?
638.4	0.27	8.0	$2\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
645.8	0.39	6.8	$2\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
654.9	0.45	6.8	$2\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
953.9	0.10	9.2	$3\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
965.8	0.16	8.4	$3\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
980	0.18	8.4	$3\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
1268	<0.10	>11.0	$4\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
1283	0.08	11.0	$4\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
1303	0.14	11.0	$4\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$

[a] Recorded as a single crystal at ca. 10 K, with 406.7-nm excitation, <10 mW at source, slits 100/150/100 μm (spectral width ca. 1.5 cm^{-1}).

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

$\tilde{\nu}$/cm^{-1}	$I(\nu_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	assgnt
100 br			
208 (w)			δ(N–Pt–N)
324.5	1.0	3.6	ν_1, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
327.5	1.0	3.8	ν_1, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
332.1	1.0	3.6	ν_1, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
345.7			
483			δ(NCCN)
528			ν(Pt–N)
647.3	0.24	7.2	$2\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
653.6	0.28	7.2	$2\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
661.8	0.36	7.2	$2\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
673			
679			ν_1 + 345
967.8	0.11	ca. 10	$3\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
978.0	0.11	10.0	$3\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
991.2	0.17	10.0	$3\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$
1128			$[ClO_4]^-$? or $\delta(NH_2)$
1223.5			$\delta(CH_2)$?
1285.8	0.07	ca. 16	$4\nu_1$, $\nu_s(^{37}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
1301.7	0.07	15.4	$4\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{37}Cl)$
1317.8	0.15	15.2	$4\nu_1$, $\nu_s(^{35}Cl\text{-}Pt^{IV}\text{-}^{35}Cl)$

[a] Recorded as a solid disk at ca. 10 K, with 415.4-nm radiation, <10 mW at source, slits 100/150/100 μm (spectral slit width ca. 1.5 cm^{-1}).

mixed with $KClO_4$) at ca. 10 K. The spectra are shown in Figures 2–4, and the band wavenumbers and assignments are given in Tables III–V.

The resonance Raman spectra are dominated by long overtone progressions in ν_1, the totally symmetric $Cl\text{-}Pt^{IV}\text{-}Cl$ stretching mode; they are thus characteristic of chain complexes. No evidence was obtained for the presence of a band attributable to a symmetric $Cl\text{-}Pd^{IV}\text{-}Cl$ mode, and thus the metal atom valences are certainly Pd^{II}/Pt^{IV} rather than vice versa. Other subsidiary

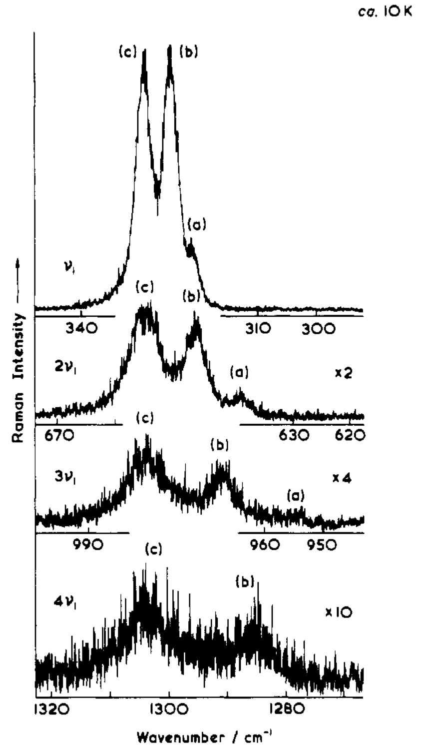

Figure 4. Isotopomer band intensities for ν_1, $2\nu_1$, $3\nu_1$, and $4\nu_1$ of [Pd(en)$_2$][Pt(en)$_2$Cl$_2$][ClO$_4$]$_4$, λ_0 = 413.1 nm, slit widths 80/150/80 μm. For ease of presentation, the ^{35}ClPt^{35}Cl component (c) of each harmonic is lined up with the same abscissa value; (b) and (a) refer to the ^{35}ClPt^{37}Cl and ^{37}ClPt^{37}Cl components, respectively.

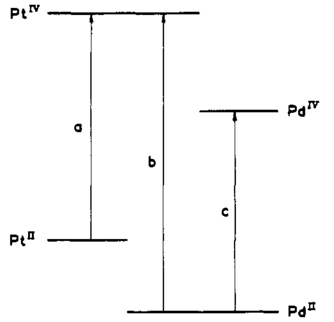

Figure 5. Approximate relative energy levels for the mixed-valence complexes. a, b, and c represent the Pt^{II} → Pt^{IV}, Pd^{II} → Pt^{IV}, and Pd^{II} → Pd^{IV} charge-transfer transitions, respectively.

progessions $\upsilon_1\nu_1 + \nu_n$, where ν_n is another Raman-active mode, are either weak or absent. By recording the spectra at ca. 10 K with <10-mW laser power source and a spectral slit width of $\leq$1.5 cm^{-1}, we have been able to resolve the chlorine isotopic splitting for the ν_1 band and its associated overtones, the results being listed for ν_1, $2\nu_1$, $3\nu_1$, and $4\nu_1$ in Tables III–V. For a linear Pt^{IV}Cl$_2$ unit a 9:6:1 triplet band structure is predicted. Surprisingly however, the fundamental has an observed isotopomer ratio different from 9:6:1, although this ratio is approached for the higher overtones (Table VI; and Figure 5). The reasons for this are unclear. The harmonic band wavenumbers (ω_1) and anharmonicity constants (x_{11}) of the complexes have been calculated[18] for each isotopomer and are listed in Table I. The chlorine isotopic splitting is easier to resolve for the mixed-metal complexes than either for the purely platinum or especially for the purely palladium ones.[8] The reason for this could be that, on changing from the mixed-metal complexes to the more delocalized palladium complexes, the vibrational model based on a linear, isolated Cl–M–Cl unit becomes less appropriate.

Table VI. Observed Isotopomer Band Ratios for $n\nu_1$ (n = 1–4) for [Pd(LL)$_2$][Pt(LL)$_2$Cl$_2$][ClO$_4$]$_4$ (LL = en, pn, tn)

n	35/35	35/37	37/37
	LL = en		
1	4.1	4.0	1
2	7.8	5.1	1
3	10.8	5.5	1
	LL = pn		
1	2.6	2.4	1
2	4.2	3.5	1
3	4.5	3.7	1
4	4.9	2.8	1
	LL = tn		
1	3.2	3.4	1
2	4.8	3.9	1
3	5.0	3.4	1
4	6.4	3.3	1

In addition to the normal Raman bands there are two other features evident in the Raman spectra at ca. 10 K. There is under the Raman bands an almost flat continuous band (B) of low intensity that extends into the band gap and is immediately followed by a large featureless emission band (L) that maximizes in the red. Such bands were first observed by Tanino et al.[19] for mixed-valence platinum complexes and discussed by these authors in terms of self-trapping in a quasi-one-dimensional crystal.

There are two suggested interpretations of the intense band (L) in the red region of the spectrum of Wolffram's red. Tanino and Kobayashi interpreted it in terms of a luminescence caused by the collection of self-trapped excited states, whereas Wong et al.[20] predict the band from the PKS model of mixed-valence complexes[21] and consider it to arise from an electronic Raman process.

The results of Tanino and Kobayashi on Wolffram's red at 4.2 K show that the band is of approximately constant intensity regardless of the exciting line wavenumber (ν_0) and that its absolute wavenumber is nearly but not completely independent of ν_0. For luminescence the absolute wavenumber of the band would be expected to be completely independent of ν_0.

The band predicted by the PKS model is intrinsically dependent on ν_0 with regard to intensity but not absolute wavenumber if it is due to an electronic Raman process. Our own observations on an unoriented sample of [Pd(pn)$_2$][Pt(pn)$_2$Cl$_2$][ClO$_4$]$_4$ indicate that the wavenumber of the band L is at about 14 500 cm^{-1} with 406-nm excitation and decreases to about 13 000 cm^{-1} with 520-nm excitation. Band L is broad (fwhm ca. 2500 cm^{-1}) and, at ca. 10 K with 406-nm excitation, is about 10, 70, and 80 times as intense as band B for the pn, en, and tn complexes, respectively. With this same excitation, ν_1 is about 20 times as intense as band B for both the pn and the tn complexes.

The flat, weak band B is found to have a Raman shift dependent on the exciting line. For the pn complex with 406.7-nm excitation it occurs at ca. 4500 cm^{-1}, but it has dropped to ca. 1700 cm^{-1} for 520.8-nm excitation. This band, which is not predicted by the PKS model, is considered by Tanino and Kobayashi to be due to light emitted during relaxation of self-trapped states by annihilation of an electron and hole.

For Wolffram's red salt, Tanino and Kobayashi found that band L was ca. 10^3 times as intense as band B, whereas for the complexes under study here the difference in intensity between the bands is much smaller. However the results on the three (unoriented) samples under study here agree with their observation that band L shifts to higher energy with increasing energy of excitation.

The PKS model describes a mixed-valence system in terms of three parameters. We shall here briefly discuss the bearing of our results on these parameters in comparison with those found suitable for Wolffram's red salt (WRS).[21] The parameter ϵ, which

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[20] Wong, K. Y.; Schatz, P. N. *Chem. Phys. Lett.* **1981**, *80*, 172.

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measures the electronic coupling between the two subunits, would be expected to be smaller for the mixed-metal complexes than for WRS as the spectroscopic data indicate a weaker metal center interaction in the former. According to the PKS model this should result in an increase in the intensity of band L relative to that of the vibrational Raman bands in comparison to the situation for WRS; however, the spectra indicate the reverse.

The parameter λ is directly proportional to the equilibrium difference in normal coordinate in the two oxidation states. As λ increases, the separation between the vibrational Raman bands and band L increases and the relative intensity of band L to the vibrational Raman bands increases. In the case of the mixed-metal complexes the separation between the vibrational Raman bands and band L is actually less than that in WRS, indicating a smaller value of λ.

The parameter ω measures the difference in zero-point energy of the two oxidation states, and in view of the spectroscopic results, it would be predicted to be larger for the mixed-metal complexes than for WRS. By using the PKS equation

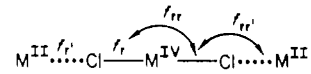
$$\nu_{\max} = 2\nu_{-}(\lambda^2 + \omega)$$

where $\nu_{\max}$ is the intervalence transition energy and ν_{-} is the ν_1 value, it follows that for λ to be less than its value for WRS ω must indeed be larger than for WRS. The predicted effect of this on the spectrum will be to decrease the intensity of band L relative to the vibrational Raman bands and to increase (slightly) the separation between the two.

In conclusion, if the effect on the intensity of band L relative to that of the vibrational Raman bands of a decrease in ϵ can be overcome by a smaller value of λ and a larger value of ω, then the PKS model may be applicable to these complexes.

Excitation Profiles. The excitation profiles of the ν_1 bands of the isotopomers at ca. 10 K have been constructed (Figure 1). The excitation profiles maximize at 1700–3900 cm^{-1} on the low-wavenumber side of the electronic band maximum, a well-understood situation typical of halogen-bridged mixed-valence platinum and palladium complexes.[22-24] In addition, all the isotopomers of a complex have ν_1 band excitation profiles that maximize, within experimental error, at the same wavenumber. Although use of a dye laser and stilbene-3 enabled intensity points between 420 and 460 nm to be located, the absence of lines between 406.7 and 356.4 nm meant that the wavenumber of the maximum is slightly uncertain.

Force Constants. The resolution of the isotopic components of the ν_1 and ν_2 bands has enabled force constant calculations to be performed by using the model of an isolated linear MCl_2 unit discussed by Allen et al.[17]



The values of the force constants f_r and f_{rr} are 2.105 and 0.121 mdyn Å^{-1}, respectively, for the en complex and 2.099 and 0.142 mdyn Å^{-1}, respectively, for the pn complex. For the tn complex the f_r and f_{rr} values are approximately 2.1 and 0.18 mdyn Å^{-1}, respectively, but these values cannot be defined more precisely owing to uncertainty in the ν_2 values arising from the presence of interfering amine modes. Comparison of these values with those obtained for pure platinum complexes[17] and Ni/Pt complexes[17] shows that the Pt^{IV}–Cl force constants decrease in the order Pt^{IV}(monomer) > Pd/Pt > Ni/Pt > Pt/Pt, in line, as expected, with the similar trend in the intervalence band maxima.

Conclusions

The mixed-valence palladium(II)–platinum(IV) complexes have been shown to have a weaker metal center interaction than either analogous pure platinum or pure palladium complexes, and hence they would be expected to be the poorer semiconductors. This at first seemingly surprising result may be understood if we consider the metal d_{z^2} orbitals to be ordered as in Figure 5. With knowledge of the $Pt^{II} \rightarrow Pt^{IV}$, $Pd^{II} \rightarrow Pd^{IV}$ and $Pd^{II} \rightarrow Pt^{IV}$ intervalence transition energy this diagram leads us to predict that the intervalence transition for a mixed-metal Pt^{II}/Pd^{IV} complex would occur at a wavenumber (ca. 15 000 cm^{-1}) less that that of any of the former complexes. There are two consequences of this. First, the existence of such a Pt^{II}/Pd^{IV} complex would be difficult to establish spectroscopically. Excitation within the contours of such a low-energy intervalence charge-transfer band is not practicable as the commonly available laser exciting lines are not of sufficiently low energy. In addition, spectrometer response in this region is poor. Hence, the characteristic resonance Raman spectrum could not be obtained. Information obtained from infrared spectra has to be treated cautiously due to the difficulty in unambiguously assigning the ν_2 mode. This leaves the electronic spectrum which, although easily recorded, only shows a broad unstructured band. This feature, however, is not unique to mixed-valence, halogen-bridged complexes.

Second, if the intervalence transition was of low energy, then one would expect the transition from the Pt^{II}/Pd^{IV} complex to the more stable Pd^{II}/Pt^{IV} analogue to be favorable. Hence, one would predict the Pt^{II}/Pd^{IV} complex to be unstable and therefore difficult to isolate. The claimed synthesis of the Pt^{II}/Pd^{IV} en complex[7] was not supported by analytical data, and the reported value of ν_1, $\nu_{sym}(Cl{-}Pd^{IV}{-}Cl)$ (315 cm^{-1}), is much greater than expected (ca. 270 cm^{-1}) on the basis of established results[8] for Pd^{II}/Pd^{IV} complexes.

Registry No. $[Pd(en)_2][Pt(en)_2Cl_2][ClO_4]_4$, 73436-71-2; $[Pd(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$, 67890-96-4; $[Pd(tn)_2][Pt(tn)_2Cl_2][ClO_4]_4$, 67825-46-1.

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