the 5p exponent fixed at 1.4. An exponent of 1.16 was used for the H 1s atomic orbital.[48]

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Registry No. $Mo_4Cl_4^{8+}$, 113860-50-7; $Mo_4(\mu\text{-}Cl)_8^{4+}$, 113860-51-8; $Mo_4(\mu\text{-}OH)_8^{4+}$, 113860-52-9; $Mo_4(\mu\text{-}Cl)_8Cl_4$, 101349-43-3; $Mo_4(\mu\text{-}OH)_8Cl_4$, 113860-53-0.

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Mixed-Valence Nickel(II)/Platinum(IV) Chain Complexes with 1,2-Diaminopropane. Electronic, Infrared, Raman, and Resonance Raman Studies

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The synthesis and the electronic, infrared, Raman, and resonance Raman spectra of the new mixed-metal complexes $[Ni(pn)_2][Pt(pn)_2X_2][ClO_4]_4$, where X = Cl, Br, or I and pn = 1,2-diaminopropane, are reported. The electronic spectra are characterized by intense broad intervalence bands with maxima at ca. 24 200, 20 400, and 13 150 cm^{-1} for X = Cl, Br, and I, respectively. The infrared spectra are near superpositions of those of the constituent nickel(II) and platinum(IV) complexes. The resonance Raman spectra are dominated by overtone progressions in ν_1, the symmetric X-Pt^{IV}-X stretch, reaching $5\nu_1$ for X = Cl or Br and $3\nu_1$ for X = I. Structure was observed in the ν_1 and associated overtone bands for all the complexes; both this structure and the dependence of the band wavenumbers on the excitation line are discussed. The spectroscopic results indicate that the Ni^{II}/Pt^{IV} complexes have weaker metal-center interactions, i.e. more localized valences, than analogous Pt^{II}/Pt^{IV} complexes have. The nature of emission bands occurring in the resonance Raman spectra is also discussed.

Introduction

The relationship between the optical and electrical properties of mixed-valence, linear-chain complexes of platinum and palladium, which are one-dimensional semiconductors, is of considerable interest.[1,2] The vibrational and electronic spectral properties of Pt^{II}/Pt^{IV}[3] and to a lesser extent of Pd^{II}/Pd^{IV}[4,5] and Pd^{II}/Pt^{IV}[6] complexes have been well documented. It has been demonstrated that, for a given metal and halogen, the wavenumber of the symmetric X-M^{IV}-X stretching vibration (ν_1) can be correlated with the chain conductivity of the complex. Recently we completed an investigation of mixed-metal complexes of the type $[Ni(en)_2][Pt(en)_2X_2][ClO_4]_4$, where en = 1,2-diaminoethane and X = Cl, Br, or I,[7] and demonstrated that the degree of metal-center interaction was intermediate between that of analogous Pt^{II}/Pt^{IV} and Pd^{II}/Pt^{IV} complexes. In order to study further the effect of substituting Pt^{II} by Ni^{II}, we have extended our studies to Ni^{II}/Pt^{IV} complexes containing 1,2-diaminopropane as the off-axial ligand and Cl, Br, or I as the bridging group.

Experimental Section

(a) Preparations. The mixed-valence complexes were prepared by mixing the appropriate aqueous solutions of $[Ni(pn)_2]^{2+}$, $[Pt^{IV}(pn)_2X_2]^{2+}$, and $Na[ClO_4]$. The ions $[Pt^{IV}(pn)_2X_2]^{2+}$ were made by dihalogen oxidation of $[Pt^{II}(pn)_2]^{2+}$ except for the iodide, which was made by addition of KI to an aqueous solution of $[Pt^{IV}(pn)_2Br_2]^{2+}$. All platinum(IV) species were checked for complete oxidation by adding an excess of $Na[ClO_4]$ to an aqueous solution of the platinum(IV) species and looking for any color changes characteristic of the formation of the complexes $[Pt(pn)_2][Pt(pn)_2X_2][ClO_4]_4$. The iodide complex was difficult to obtain, probably due to rapid displacement of the amine from $[Ni(pn)_2]^{2+}$ by iodide.

Repeated attempts to recrystallize the Ni^{II}/Pt^{IV} complexes led to a gradual reduction of the Pt^{IV} moiety to Pt^{II} and then to contamination of the product with the analogous Pt^{II}/Pt^{IV} chain complex. As a consequence only fairly small crystals were grown, which did not prove suitable for single-crystal Raman work. Anal. Calcd for $[Ni(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$: C, 14.14; H, 3.96; Cl, 20.87; N, 11.00. Found: C, 14.2; H, 3.96; Cl, 20.6; N, 10.95. Calcd for $[Ni(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$: C, 13.01; H, 3.64; total halogen as Cl, 19.20; N, 10.11. Found: C, 13.0; H, 3.50; total halogen as Cl, 19.4; N, 10.14. Calcd for $[Ni(pn)_2][Pt(pn)_2I_2][ClO_4]_4$: C, 11.99; H, 3.35; N, 9.32; I, 21.11. Found: C, 11.7; H, 3.30; N, 9.35; I, 20.5%.

(b) Instrumentation. Electronic spectra were recorded on a Varian 2390 spectrometer as Nujol mulls of the samples, between quartz plates, at room temperature.

Infrared spectra were recorded in the region 650-20 cm^{-1} on wax disks of the complexes, by using a Bruker IFS 113 V interferometer. The spectra were obtained at ca. 80 K by using an RIIC cryostat cooled by liquid nitrogen.

Raman spectra were recorded on a Spex 14018/R6 spectrometer. Exciting radiation was provided by Coherent Radiation Model CR 12 and CR 3000 K lasers, the powers being kept to <50 mW. Samples for Raman spectra were in the form of pressed disks of the pure complexes and were held at ca. 80 K with use of a liquid nitrogen and Dewar assembly and at lower temperatures by using an Air Products Displex cryostat. Spectra were calibrated by reference to the Rayleigh line.

Results and Discussion

Electronic Spectra. Crystals of the complexes are dichroic. The chloride is yellow with the electric vector of the incident beam parallel to the chain (z) axis and colorless when the vector is perpendicular to it. The bromide is likewise blue and orange, respectively, and the iodide is dark blue and red, respectively. The bromide and iodide have a strong metallic sheen, which is lost on their being ground to powders. The colors of the crystals and powders together with related spectroscopic data are given in Table I.

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Table I. Summary of Properties of Complexes Studied[a]

complex	color		$Ni^{II} \rightarrow Pt^{IV}$ band max/cm^{-1} [a]	$\omega_1{}^b$/cm^{-1} (λ_0/nm)	$x_{11}{}^b$/cm^{-1} (λ_0/nm)	progn length (λ_0/nm)	dispersion of $\nu_1{}^b$/cm^{-1}
	cryst	powder					
$[Ni(pn)_2][Pt(pn)_2Cl_2][ClO_4]$	red	orange/yellow	24 200	328.5 (457.9)	−1.48 (457.9)	$5\nu_1$ (457.9)	ca. 0[c]
$[Ni(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$	green metallic	red	20 400	195.4 (514.5)	−0.43 (514.5)	$5\nu_1$ (514.5)	2.2 for ν_1; 7.5 for ν_n[d]
$[Ni(pn)_2][Pt(pn)_2I_2][ClO_4]_4$	gold metallic	blue	13 150			$3\nu_1$ (647.1)	

[a] Recorded as Nujol mulls at room temperature. [b] For strongest ν_1 component. [c] λ_0 = 514.5–406.7 nm. [d] λ_0 = 676.4–457.9 nm.

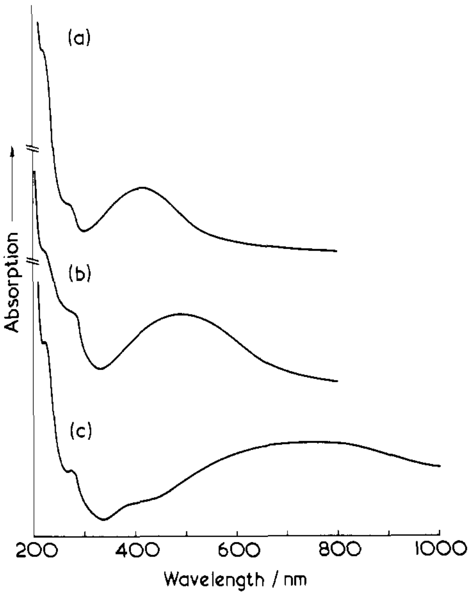

Figure 1. Electronic spectra of (a) $[Ni(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$, (b) $[Ni(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$, and (c) $[Ni(pn)_2][Pt(pn)_2I_2][ClO_4]_4$ as Nujol mulls at 295 K.

The transmission spectra (Figure 1) show an intense, broad band that is assigned to the $Ni^{II} \rightarrow Pt^{IV}$ charge-transfer transition. The maximum occurs for X = Cl (by transmission measurements as Nujol mulls) at ca. 24 200 cm^{-1}, which is lower in wavenumber than is the case for either the analogous Pt^{II}/Pt^{IV} [8] (25 000 cm^{-1}) or Pd^{II}/Pt^{IV} complex[6] (27 700 cm^{-1}). This situation differs from that noted for the analogous complexes containing diaminoethane (en), for which the wavenumber of the $Ni^{II} \rightarrow Pt^{IV}$ transition was intermediate between those of the Pt^{II}/Pt^{IV} and Pd^{II}/Pt^{IV} complexes (but closer to that of the former).[7] This difference may be due to difficulties associated with estimating electronic band maxima for these strongly absorbing complexes as Nujol mulls. It has already been shown that particle size can affect the wavenumber of the intervalence band maximum and this effect seems particularly marked with complexes containing pn as the off-axis ligand.[8] Single-crystal polarized electronic spectra provide the most accurate measure of the transition wavenumbers, the value obtained from the absorption edge being equal to the band gap for these semiconductors. Unfortunately the small size of the crystals obtained precluded such studies.

The intervalence maximum for the bromide-bridged complex occurs at ca. 20 400 cm^{-1}, greater than that (ca. 19 600 cm^{-1})[8] of the analogous Pt^{II}/Pt^{IV} complex, implying a weaker metal-center interaction for the Ni^{II}/Pt^{IV} complex than for the analogous Pt^{II}/Pt^{IV} complex. No accurate data are available for the analogous Pd^{II}/Pt^{IV} complex.

For the iodide-bridged complex, the intervalence maximum occurs at ca. 13 150 cm^{-1}, again at a higher wavenumber than that of the analogous Pt^{II}/Pt^{IV} complex for which it lies at ca. 12 800 cm^{-1}.[8]

For all three complexes a second weaker band occurs, at ca. 38 760, 36 760 and 36 500 cm^{-1} for X = Cl, Br, or I, respectively, which can be assigned[4-8] to a d–d transition of the Pt^{IV} entity.

Table II. Wavenumbers (cm^{-1}) and Assignments of the Bands Observed in the Infrared Spectra of the Complexes $[Ni(pn)_2][Pt(pn)_2X_2][ClO_4]_4$ (X = Cl, Br, I) and $[Ni(pn)_2]Cl_2$ in the Region 650–20 cm^{-1}

$[Ni(pn)_2][Pt(pn)_2X_2]$-$[ClO_4]_4$			$[Ni(pn)_2]Cl_2$	assignt[a]
X = Cl	X = Br	X = I		
624 vs	623 vs	615 vs		$[ClO_4]^-$
			612 w	
593 w	593 w			$\nu(Pt^{IV}–N)$
577 w	575 m			
		569 s		
		562 s		
			544 vw	ν(Ni–N)?
	546 m			$\nu(Pt^{IV}–N)$
	539 w		543 s	ν(Ni–N)?
			536 w	ν(Ni–N)
			534 w	
			522 w	
			518 w	
486 w	486 m			ring bends
480 w	478 w	482 s	478 m	
460 w	459 m			
	452 w	455 s		
449 w	449 w	447 s		
			437 s	
			432 m	
	389 w	388 w	383 s	
			377 m	
353.7 s				ν_2, $\nu_{as}(Cl–Pt^{IV}–Cl)$
352.5 s				
351.6 m				
	342.5 vw			ring bends
333 w	332 s		335 w	
326 w	327 m	329 s		
308 w		308 w	312 m	
	304 m	303 m	300 m	
292 s	293 s	296 m		$\delta(N–Pt^{IV}–N)$
277 w			289 m	
258 m	262 s	271 s		$\delta(N–Pt^{IV}–N)$
		248 w	250 s	
	239 s			ν_2, $\nu_{as}(Br–Pt^{IV}–Br)$
232 w	222 w		222 m	
		208 m		ν_2, $\nu_{as}(I–Pt^{IV}–I)$?
		191 m		ν_2, $\nu_{as}(I–Pt^{IV}–I)$?
160 s				$\delta(Cl–Pt^{IV}–Cl)$
148 s		148 m	149 vs	
	138 w			
	125 s			$\delta(N–Pt^{IV}–Br)$?

[a] Also bands at 90 w, 80 w, 74 m, and 68 w cm^{-1} for X = Cl; 74 w and 68 w cm^{-1} for X = Br; and 118 vs and 92 m for $[Ni(pn)_2]Cl_2$.

Infrared Spectra. The infrared spectra of the mixed-valence complexes and of $[Ni(pn)_2]^{2+}$ were recorded at ca. 80 K in the region 650–20 cm^{-1}. The wavenumbers and assignments of the observed bands (Table II) are based on those for related complexes.[9-11]

As expected for class II mixed-valence complexes[12] the infrared spectra are found to consist essentially of superpositions of those of the constituent ions. Hydrogen bond formation between the

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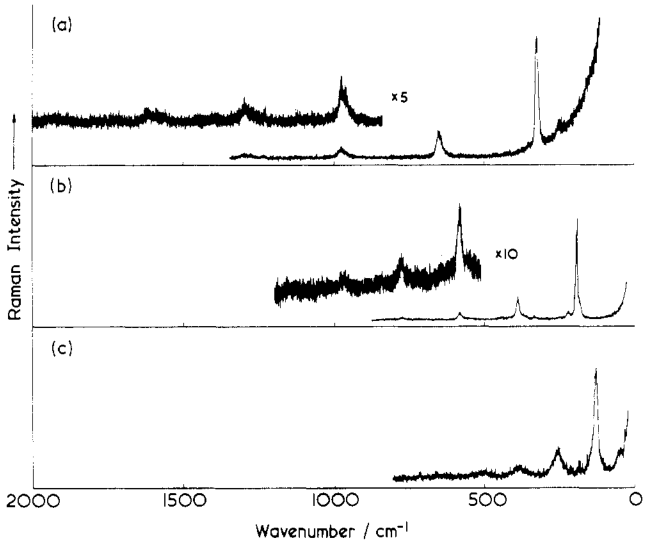

Figure 2. Resonance Raman spectra of (a) $[Ni(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$, $\lambda_0 = 406.7$ nm, (b) $[Ni(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$, $\lambda_0 = 514.5$ nm, and (c) $[Ni(pn)_2][Pt(pn)_2I_2][ClO_4]_4$, $\lambda_0 = 799.3$ nm. Each sample was held as a disk of the pure material at ca. 80 K.

amine and counterion, changes in the force constants of the axial X–Pt^{IV}–X bonds upon interaction with the Ni^{II} centers, and changes in space group on formation of the chain complex, account for any differences that exist.

For the chloride-bridged complex, it is possible partially to resolve the band assigned to ν_2, ν_{as}(Cl–Pt^{IV}–Cl), into three components at ca. 353.7, 352.5 and 351.6 cm^{-1}. However neither the relative intensities nor the peak separations of the components are compatible with their being chlorine isotopic in origin, as has been found to be the case for other analogous complexes.[13] The ν_2 value for the Ni^{II}/Pt^{IV} complex is lower than that found for the analogous Pt^{II}/Pt^{IV} complex[8] (ca. 356 cm^{-1}), implying a stronger metal-center interaction for the former. The infrared spectra of the Ni^{II}/Pt^{IV} and Pt^{II}/Pt^{IV} complexes were, however, recorded at different temperatures (ca. 80 and 300 K, respectively), which precludes the placing of much reliance on this conclusion since the wavenumber of ν_2 is known[14] to be temperature dependent. Nevertheless, the conclusion is in agreement with that drawn from the electronic spectra (vide supra).

The band at 239 cm^{-1} in the spectrum of the bromide-bridged complex is assigned to ν_2; in comparison for the Ni^{II}/Pt^{IV} en bromide complex, ν_2 is at ca. 242 cm^{-1}.[7] The assignment of the band at 191 cm^{-1} for the analogous iodide-bridged complex to ν_2 is not certain; in comparison for the analogous Ni^{II}/Pt^{IV} en complex, ν_2 is at 188 cm^{-1}.[7]

No band was observed that could be attributed to ν_{as}(X–Ni^{IV}–X) for any of the complexes under study here, thus confirming that the metal atom valences are Ni^{II}/Pt^{IV} rather than vice versa.

Resonance Raman Spectra. The resonance Raman spectra were recorded on samples as polycrystalline disks and obtained at ca. 80 and ca. 40 K for the chloride-bridged complex and at ca. 80 K for the bromide- and iodide-bridged complexes. It was noted that grinding the complexes with any material suitable as an internal intensity standard, such as $K_2[SO_4]$ or $K[ClO_4]$, alters the profile of the band attributed to ν_1; moreover, the intensity of the ν_1 band of the Ni^{II}/Pt^{IV} complex decreases and that of a band at ca. 315 cm^{-1} ($\lambda_0 = 468$ nm) increases if the sample is ground with such a matrix material (cf. the similar situation for the Ni^{II}/Pt^{IV} en complexes).[7] The assignment of the 315-cm^{-1} band is not clear. One possibility is that it arises from the formation of some of the analogous Pt^{II}/Pt^{IV} complex ($\nu_1 = 312.5$ cm^{-1}, $\lambda_0 = 476.5$ nm) within the matrix. This being said, it is important to note that the 315-cm^{-1} band does not develop if the Ni^{II}/Pt^{IV} complex is ground in the absence of such inorganic salts, either on its own (for Raman/fluorescence work) or with a mulling agent (for FT-IR work). Thus genuine spectra (Raman, infrared, fluorescence) of the pure Ni^{II}/Pt^{IV} complex can be obtained, but not excitation profiles (which require an internal standard).

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

$\tilde{\nu}$/ cm^{-1}	$\Delta\tilde{\nu}_{1/2}$/ cm^{-1}	I	$I(n\nu_1)$/ $I(\nu_1)$	assignt	
126.1					
248.9					
318	4.5	0.3	1.0	ν_c	ν_1, ν_s(Cl–Pt^{IV}–Cl)
322.5	4.5	0.9	1.0	ν_b	
326.2	4.5	1.0	1.0	ν_a	
635	11.2	0.1	0.5	$2\nu_c$	$2\nu_1$
643.2	11.2	0.4	0.4	$2\nu_b$	
650.9	11.2	0.5	0.5	$2\nu_a$	
946	15.5	<0.1	<0.4	$3\nu_c$	$3\nu_1$
960	15.5	0.1	0.1	$3\nu_b$	
973.2	15.5	0.2	0.2	$3\nu_a$	
1283	>15.5	<0.2	<0.2	$4\nu_a$, $4\nu_1$	

[a] Recorded as a solid disk at ca. 40 K, with slits of 150/200/150 μm $\lambda_0 = 406.7$ nm, and <50 mW of power.

The resonance Raman spectra of the complexes, as polycrystalline disks of the pure materials, were found to be dominated by overtone progressions in ν_1, reaching $5\nu_1$ for the chloride- and bromide-bridged complexes and $3\nu_1$ for the iodide-bridged complex (Figure 2). No evidence was obtained for a band attributable to a symmetric (X–Ni^{IV}–X) mode, and thus the valences are certainly Ni^{II}/Pt^{IV} rather than vice versa.

For the chloride-bridged complex the ν_1, $2\nu_1$, and $3\nu_1$ band profiles are partially resolved into three peak maxima (Table III) whose structure is independent of the sample, extent of grinding, disk pressure, etc. The structure differs somewhat from that which might be expected if it arose from chlorine isotopic effects, and it also differs from the predictions of factor group analysis. For the overtone bands the lower wavenumber components lose intensity faster than the higher ones as the vibrational quantum number (v_n) of the overtone increases. Single-crystal Raman spectroscopy would have enabled better resolution of the $v_1\nu_1$ profiles[15-17] to be achieved, but unfortunately the crystals of the complex obtained were of insufficient size for this to be practicable although they did prove to be big enough for single-crystal X-ray crystallography.[15] Recent work on analogous Pt^{II}/Pt^{IV} en complexes on well-resolved ν_1 band profiles has shown that these partially resolved maxima are actually made up of further narrower components[16,17] (fwhm ca. 1.2 cm^{-1} for X = Cl).

Relationship between ν_1 Band Components and the Band Gap. It has previously been noted for analogous complexes that, for ν_0 greater than the band gap (E_g), the wavenumber of the unresolved ν_1 band increases as ν_0 increases.[18,19] This feature is characteristic of these linear-chain, halogen-bridged complexes and is now known to be due to changes in the relative intensities of the narrow components (and hence of the wavenumbers of the partially resolved or unresolved peak maxima) of the $v_1\nu_1$ profiles with ν_0.[16,17,25] The higher wavenumber components have their greatest relative intensities with $\nu_0 \gg E_g$ and the lower wavenumber components with ν_0 nearest to, or at, E_g, each component having its own excitation profile maximum. Thus the ν_0 depen-

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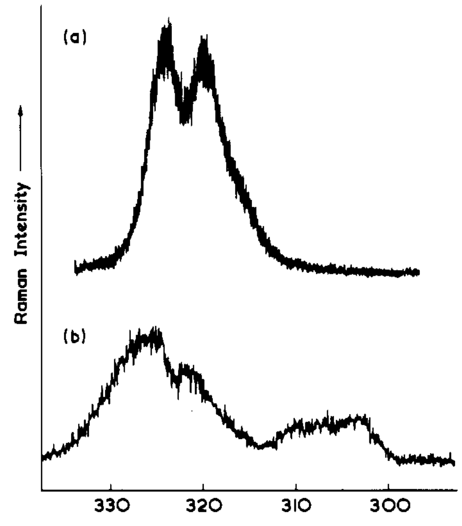

Figure 3. ν_1 band of $[Ni(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$ recorded as a disk of the pure material at ca. 80 K with (a) 514.5- and (b) 363.8-nm excitation.

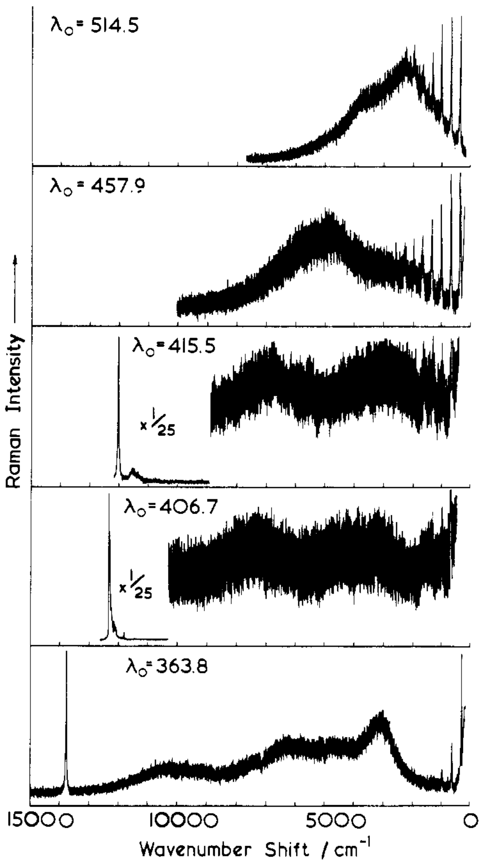

Figure 4. Luminescence bands of $[Ni(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$, recorded for different exciting lines, as solid disks at ca. 80 K. Diagram uncorrected for spectral response. The abscissa is the wavenumber shift from the specified excitation line (λ_0 in nm).

dence of the relative intensities of the ν_1 profile components can be used as a crude method of locating E_g.[20] For the chloride-bridged Ni^{II}/Pt^{IV} pn complex there was no change in the wavenumber of the unresolved $v_1\nu_1$ band maxima (and thus of the relative intensities of the narrow components to the profile) for exciting lines with λ_0 ranging from 514.5 to 406.7 nm, indicating that $E_g > 24\,600$ cm^{-1}; cf. the approximate value of 24 200 cm^{-1} for E_g obtained from the electronic spectrum at room temperature (Table I). Unfortunately the only exciting lines available of wavenumber > E_g occur in the ultraviolet region for which there is a loss of spectral resolution with slits physically wide enough to achieve a recordable signal (which is weak, being off-resonance) with the laser power at <50 mW. For λ_0 = 363.8 nm two peak maxima (at ca. 326.0 and 321.6 cm^{-1}) are observed for the ν_1 band profile. The 321.6-cm^{-1} and obviously the non-observed 318-cm^{-1} components to ν_1 have lost intensity relative to the 326.0-cm^{-1} one (Figure 3) with this excitation line, the lower wavenumber components having their maximum relative intensity for λ_0 nearer to or at E_g (vide supra).

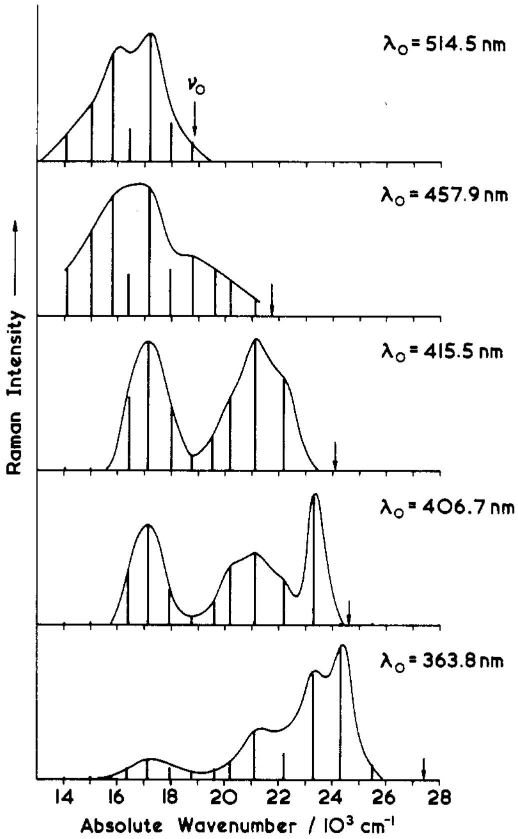

Figure 5. Luminescence bands of $[Ni(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$ as solid disks at ca. 80 K, recorded for different exciting lines, after correcting for the spectral response of the instrument. The vertical lines indicate the approximate wavenumbers and intensities of the components. (↓ denotes ν_0.)

Luminescence Bands. Two luminescence bands are generally observed superimposed on the resonance Raman spectra of halogen-bridged mixed-valence complexes,[6,21] and these have been stated to be due to light emitted during electron-hole recombination during and after relaxation of the excited electrons to a self-trapped state following the charge-transfer excitation.[21]

The more intense (ca. 10^3 times) luminescence band (denoted L), considered to be due to electron-hole recombination of the relaxed self-trapped state is only observed for $\nu_0 > E_g$ and, for the complexes studied so far, occurs at an energy of ca. half that of the band gap.[6,21] We were unable to detect such a band in this region (ca. 12 000 cm^{-1}) for the Ni^{II}/Pt^{IV} pn chloride complex or even observe its tail. This result is at variance with those obtained for analogous Pt^{II}/Pt^{IV},[20,21] Pd^{II}/Pt^{IV},[6] and Pd^{II}/Pd^{IV}[22] complexes previously studied but it is in agreement with the result obtained for the analogous Ni^{II}/Pt^{IV} en complex.[17]

The luminescence band (denoted B) purportedly caused by electron-hole recombination *during* relaxation to the self-trapped state is typically rather weak and occurs under the vibrational Raman bands, extending into the band gap. This band is broad

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Table IV. Absolute Wavenumbers and Relative Intensities of Bands Present in the Luminescence Spectra of $[Ni(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$ with Different Exciting Lines[a]

	$\tilde{\nu}$/cm^{-1}													
λ_0/nm	14 100	15 000	15 800	16 400	17 200	17 900	18 700	19 600	20 200	21 200	22 200	23 200	24 300	25 500
363.8				0.9	1.4	0.8	0.6	0.8	1.3	3.7	1.9	7.7	10	1.3
406.7				4.0	7.2	2.5	0.5	1.7	4.5	5.2	3.3	10.0		
415.5				5.4	9.1	4.8	1.0	2.5	5.3	10.0	6.7			
457.9	3.4	6.4	9.8	3.1	10.0	3.5	4.5	3.7	2.5	1.1				
514.5	2.0	4.3	8.8	2.4	10.0	2.9	1.7							

[a] Recorded as a solid disk at ca. 80 K. Incident laser power <50 mW.

and flat and has a ν_0 dependence of its Stokes shift, the latter increasing as ν_0 increases. It is only observed for $\nu_0 > E_g$.[21]

We have observed a weak, broad luminescence occurring under the vibrational Raman bands of the Ni^{II}/Pt^{IV} pn chloride complex (Figure 4). However some features of this differ significantly from that previously reported for band B. First, the luminescence is clearly observed for $\nu_0 < E_g$ (see Figure 4, λ_0 = 514.5 nm). The same observation holds for other mixed-metal complexes,[17,20] casting some doubt on the correctness of the assignment[21] of this luminescence band. Second, the observed luminescence profile is clearly dependent on ν_0 (Figures 4 and 5) and can be seen to consist of several components. Indeed it would appear that, in a manner reminiscent of the apparent dispersion of ν_1 with ν_0, the B-type luminescence consists of several components of *fixed* absolute wavenumber whose relative intensities are ν_0 dependent. The lower wavenumber components have their maximum intensity for ν_0 with the highest wavenumber (i.e. the opposite behavior to that displayed by the ν_1 band components). The enhancement apparently occurs at a Stokes shift of ca. 3000–4000 cm^{-1}. The band B components have a fwhm of ca. 1100 cm^{-1} and approximate absolute wavenumbers as given in Table IV; a representation of the component intensities is given in Figure 5. The Stokes shift of the *overall* profile still increases as ν_0 increases in wavenumber in line with the previous observation for band B of the analogous Pd^{II}/Pt^{IV} and Pt^{II}/Pt^{IV} complexes.

The nonappearance of band L at an energy of $E_g/2$ must be connected with the mixed-metal nature of this complex and, more specifically, with the change in the metal(II) from Pd or Pt to Ni, with its much smaller d_{z^2} orbital.

Relationship with the Nasu Model. According to the work of Nasu[23] on an extended Peierls–Hubbard model of linear-chain complexes, there are two possible reasons for band L not to occur at an energy of ca. $E_g/2$. The model looks at the interrelationships between four parameters, namely S, the electron–phonon coupling energy, T, the transfer energy of an electron between two neighboring metal sites, U, the intrasite electron–electron repulsive energy, and V, the intersite electron–electron repulsive energy.

When the relationships $2T \simeq S$ (and $U \lesssim S$) do not hold, band L will not occur at an energy of ca. $E_g/2$. If T/S is small, the relevant "luminescent" states are metastable and the energy of L is very small, i.e. $<E_g/2$. However if T/S is large, then the luminescence will not have an appreciable Stokes shift. Another situation for which L may not occur at an energy of $E_g/2$ is that in which V is small. In this case the self-trapped electron and self-trapped hole will localize independently, and the resulting state will not be luminescent; i.e., the luminescent self-trapped exciton with the electron and hole localized on adjacent sites will not be formed, which precludes the occurrence of band L. Which situation obtains here is not certain.

The comparatively better orbital overlap between the Ni^{II} $3d_{z^2}$ orbital and the chloride $3p_z$ orbital may increase T if the electron transfer between Ni^{II} and Pt^{IV} occurs through the halogen, leading to an increase in T/S. The parameter S is determined by the change of electrostatic potential seen by an electron at the metal lattice site due to the displacement of the X^- ions from their position in the hypothetical Ni^{III}/Pt^{III} state. For complexes containing the same metal ion in both sites the deviation of the ratio of M^{IV}–X/M^{II}–X distances (ρ), obtained from X-ray data, away from unity gives the required information. For the Pt^{II}/Pt^{IV} pn chloride complex the value of ρ is 0.73,[24] which is the same as that obtained for the Ni^{II}/Pt^{IV} pn chloride complex.[15] However, for the latter, the halogen would not sit centrally, even in the hypothetical Ni^{III}/Pt^{III} state, but rather be displaced off-center toward the nickel; hence, the ρ value of this complex indicates a greater degree of valence localization than is the case for the Pt^{II}/Pt^{IV} analogue. This implies a decrease in S for the Ni^{II}/Pt^{IV} complex relative to that for the Pt^{II}/Pt^{IV} complex, similarly leading to an increase in T/S. However as the magnitude of the band gap is mainly determined by $(2S + 4V - U)/2T$ and either T has increased or S decreased in order that T/S be larger than is the case for the Pt^{II}/Pt^{IV} and Pd^{II}/Pt^{IV} analogues, then the values of V and mainly U must also have changed in the appropriate direction (the band gap of the Ni^{II}/Pt^{IV} complexes is comparable with that of the Pt^{II}/Pt^{IV} and Pd^{II}/Pt^{IV} analogues). U will decrease with a decrease in d_{z^2} orbital extension occurring for Ni^{II} substitution, which is the desired direction of change. Thus, if the above is correct, L should occur at an energy $> E_g/2$ and one of the components in the band B profile (presumably that of lowest absolute wavenumber if L arises from electron-hole recombination for the *relaxed* self-trapped state) is L. However none of the band B components has an intensity comparable with that previously observed for band L.

Table V. Wavenumbers, Fwhm, Relative Intensities, and Assignments of Bands Observed in the Resonance Raman Spectrum of $[Ni(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$[a]

$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	$I(\nu_i)/I(\nu_1)$	assignt
94.6			
186.8	14.5	0.46	ν_n
194.4	5.6	1.0	ν_1, ν_s (Br–Pt^{IV}–Br)
221.5			δ(N–Pt–N)
250			
291.9			
371.8	24.8	0.13	$2\nu_n$
388.2	10.0	0.38	$2\nu_1$
417			$\nu_1 + 221$
442			$\nu_1 + 250$
529			$\nu_1 + 332$
554	>25	<0.13	$3\nu_n$
578	14.5	0.14	$3\nu_1$
612			$2\nu_1 + 221$
637			$2\nu_1 + 250$
746.8	>25	<0.13	$4\nu_n$
773.8	24	0.05	$4\nu_1$
964.2	>24	<0.05	$5\nu_1$

[a] Recorded as a solid disk at ca. 80 K, with slits of 150/200/150 μm, λ_0 = 514.5 nm, and <50 mW of power at source. For λ_0 = 476.5 nm, ν_n = 187.9, ν_1 = 194.7, $2\nu_n$ = 371.7, $2\nu_1$ = 389.2, $3\nu_n$ = 557.6, and $3\nu_1$ = 582.4 cm^{-1}, where ν_n is possibly a component of ν_1 (see text).

Bromide-Bridged Complex. The resonance Raman spectrum of the bromide-bridged complex (Figure 2b, Table V) is strongly dependent on ν_0, as the exciting lines available with which to study this complex are of wavenumber $\geqslant E_g$ (ca. 19 000 cm^{-1} by electronic transmission spectroscopy). For ν_0 toward the blue a band at ca. 194 cm^{-1}, and its overtones, dominate the spectrum, and

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(23) Nasu, K.; *J. Phys. Soc. Jpn.* **1983**, *52*, 3865; **1984**, *53*, 302; **1984**, *53*, 427; **1985**, *54*, 1933.

(24) Matsumoto, N.; Yamashita, M.; Ueda, I.; Kida, S. *Mem. Fac. Sci., Kyushu Univ., Ser. C* **1978**, *11*, 209.

Table VI. Wavenumbers of the Resolved Components in the ν_1 Region of $[Ni(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$ with Change in Exciting Line[a]

λ_0/nm	$\tilde{\nu}_1$/cm^{-1}		
676.4	172.1	180.3	193.2
647.1	173.7	180.9	193.5
514.5		184.7	193.7
488.0		185.9	193.7
476.5		186.9	194.2
457.9		187.9	195.4

[a] Recorded as solid disk at ca. 80 K, with slits of 200/250/200 μm.

Table VII. Wavenumbers, Fwhm, Relative Intensities, and Assignments of Bands Observed in the Resonance Raman Spectrum of $[Ni(pn)_2][Pt(pn)_2I_2][ClO_4]$[a]

$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	assignt
	(i) $\lambda_0 = 676.4$ nm		
132.4	17.2	1.00	ν_1, ν_s (I–Pt^{IV}–I)
147	12.8		
176			
189			
210			
269.6	~40	0.48	$2\nu_1$
	(ii) $\lambda_0 = 647.1$ nm		
133.6	17.6	1.0	ν_1
148	14.0		
210			
271.1	40	0.48	$2\nu_1$

[a] Solid disk, at ca. 80 K, with slits of 200/250/200 μm.

for ν_0 toward the red, a band at 173 cm^{-1} dominates (Figure 2b). A third band at ca. 186 cm^{-1} has its maximum relative intensity for a value of ν_0 intermediate between those appropriate to the 196 and 173 cm^{-1} bands; i.e., there is a sequential achievement of resonance for all three resolved bands, with the higher the band wavenumber the further to the blue its resonance position. This behavior is identical with that observed for the Ni^{II}/Pt^{IV} en analogue.[7] The origin of these well-separated peaks in the ν_1 region is not known. The peak at 196 cm^{-1} is certainly of a wavenumber expected for ν_1 of a bromide-bridged Ni^{II}/Pt^{IV} species. The peak at 186 cm^{-1} does not correspond to ν_1 of $[Pt^{IV}(pn)_2Br_2]^{2+}$ or of the Pt^{II}/Pt^{IV} analogue.[8] The peak at 173 cm^{-1} ($\lambda_0 = 647.1$ nm) is close to that observed for the Pt^{II}/Pt^{IV} analogue (ca. 171 cm^{-1} for $\lambda_0 = 647.1$ nm)[8,18] and therefore could conceivably be due to a trace impurity of the Pt^{II}/Pt^{IV} complex. No combination bands are observed between these components in the overtone region. The wavenumbers of these three well-resolved bands have the ν_0 dependence typical of linear-chain halogen-bridged complexes (Figure 6, Table VI). The three well-resolved components are likely themselves to consist of further narrower components whose relative intensities are ν_0 dependent, as previously indicated. From studies of the analogous Pt^{II}/Pt^{IV} en Br complex the "spread" of component band wavenumbers is ca. 20 cm^{-1} (fwhm ca. 4 cm^{-1}),[17,25] and so it is not inconceivable that all three well-resolved peaks observed here arise solely from the Ni^{II}/Pt^{IV} pn complex. The greatest dispersion is for the 184-cm^{-1} band, indicating that this band is more on resonance with $\lambda_0 = 676.4$–457.9 nm than the 196-cm^{-1} band for which lines to the blue are favorable and the 173-cm^{-1} band for which lines to the red give the greatest enhancement.

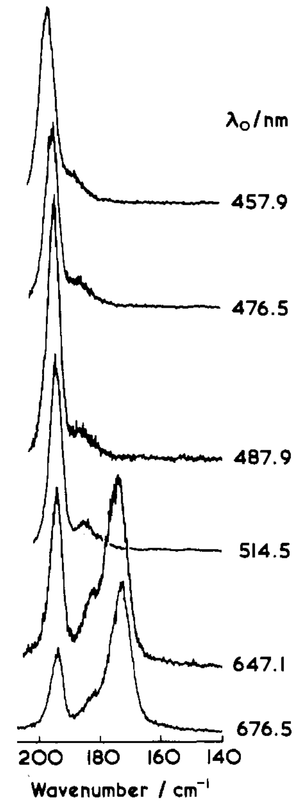

Figure 6. ν_1 band profile of $[Ni(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$, recorded as a solid disk at ca. 80 K showing components and apparent "dispersion" of components on changing ν_0.

Iodide-Bridged Complex. There is only a progression to $3\nu_1$ observed in the resonance Raman spectrum of the iodide-bridged complex with the ν_1 band profile maximum being 132 cm^{-1} for $\lambda_0 = 676.4$ nm (Figure 2c, Table VII). All of the exciting lines used to study this complex were of wavenumber greater than E_g (ca. 13 000 cm^{-1}, Table I), and so the wavenumber of the unresolved ν_1 profile maximum is significantly ν_0 dependent; e.g., a change from 676.4- to 647.1-nm excitation results in a 1.2-cm^{-1} increase in the ν_1 profile maximum. A band to the high wavenumber side at 147 cm^{-1} ($\lambda_0 = 676.4$ nm) is evident, and its wavenumber dependence on ν_0 suggests that it is due to the Ni^{II}/Pt^{IV} mixed-valence species and not to $[Pt^{IV}(pn)_2I_2]^{2+}$ impurity (a possibility from the peak wavenumber). A further resolution of the structure was not possible due to the breadth of the underlying components to ν_1.[17]

Conclusion

In all cases the wavenumbers of the unresolved ν_1 profiles of the Ni^{II}/Pt^{IV} complexes are higher than those of the analogous Pt^{II}/Pt^{IV} complexes for any given λ_0, indicating that the former complexes have the weaker metal-center interaction and thus will be the poorer conductors. The inclusion of Ni at the M^{II} sites has radically altered the emission spectra of the complexes.

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Registry No. $[Ni(pn)_2][Pt(pn)_2Cl_2][ClO_4]_4$, 113794-57-3; $[Ni(pn)_2][Pt(pn)_2Br_2][ClO_4]_4$, 113794-59-5; $[Ni(pn)_2][Pt(pn)_2I_2][ClO_4]_4$, 113794-61-9; $[Ni(pn)_2]Cl_2$, 15522-52-8; $[Ni(pn)_2]^{2+}$, 20037-68-7; $[Pt^{IV}(pn)_2Cl_2]^{2+}$, 65650-85-3; $[Pt^{IV}(pn)_2Br_2]^{2+}$, 87525-38-0; $[Pt^{IV}(pn)_2I_2]^{2+}$, 62569-63-5; $[Pt^{II}(pn)_2]^{2+}$, 45844-25-5; Br_2, 7726-95-6; Cl_2, 7782-50-5.

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