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

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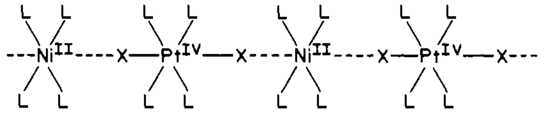
The electronic, infrared, and resonance Raman spectra of the mixed-metal, mixed-valence complexes $[Ni(en)_2][Pt(en)_2X_2][ClO_4]_4$, where X = Cl, Br, I and en = 1,2-diaminoethane, are reported. The electronic spectra are characterized by intense, broad intervalence bands at 22 000 and 19 000 cm^{-1} for X = Cl and X = Br, respectively. The infrared spectra are near-superpositions of those of the constituent Ni(II) and Pt(IV) complexes. The resonance Raman spectra are dominated by long overtone progressions in ν_1, the Raman-active, symmetric X–Pt^{IV}–X stretch, reaching $7\nu_1$ for X = Cl, Br and $4\nu_1$ for X = I. For the chloride-bridged complex, both ν_1 and ν_2 (the infrared-active, antisymmetric X–Pt^{IV}–X stretch) have been resolved into their chloride isotopic components. In addition resolution of each member of the overtone progression, up to $6\nu_1$, has enabled values for ω_1 and x_{11} to be evaluated for each isotopomer. The polarized, single-crystal spectrum of the chloride-bridged complex shows that the Raman process is polarized in the chain (z) direction. The spectroscopic results indicate that the mixed-Ni^{II}/Pt^{IV} complexes have weaker metal-center interactions, i.e. have more localized valences, than the analogous Pt^{II}/Pt^{IV} complexes but stronger interactions than the analogous Pd^{II}/Pt^{IV} complexes. The relative stabilities of mixed-valence complexes of nickel, palladium, and platinum are discussed briefly.

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} complexes,[3,4] and to a lesser extent of Pd^{II}/Pd^{IV} complexes,[5,6] have been well documented. Recently we completed an investigation of mixed-metal complexes of the type $[Pd(LL)_2][Pt(LL)_2Cl_2][ClO_4]_4$, where LL = en (1,2-diaminoethane), pn (1,2-diaminopropane), tn (1,3-diaminopropane),[7] and demonstrated that these complexes had weaker metal-center interactions, i.e. more localized valences, than the analogous Pd^{II}/Pd^{IV} or Pt^{II}/Pt^{IV} complexes. As a continuation of this work, the present investigation is concerned with the synthesis, characterization, and detailed spectroscopic study of mixed-metal complexes involving cation chains of the sort



where LL = en and X = Cl, Br, I. The complexes with X = Cl, Br have been prepared and partly characterized previously,[8] but not that with X = I, which is new. Careful Raman study of the complex with X = Cl leads to resolution of the chlorine isotopomeric components of the ν_1 and ν_2 bands (symmetric and antisymmetric Cl–Pt^{IV}–Cl stretches, respectively), from which data the Pt–Cl force constant may be evaluated.[9]

Experimental Section

(a) Preparations. The mixed-valence complexes were prepared[8] by mixing the appropriate aqueous solutions of $[Ni^{II}(en)_2]^{2+}$, $[Pt^{IV}(en)_2X_2]^{2+}$, and $Na[ClO_4]$. The ions $[Pt^{IV}(en)_2X_2]^{2+}$ were made by dihalogen oxidation of $[Pt^{II}(en)_2]^{2+}$, except for the iodide, which was made by addition of KI to an aqueous solution of $[Pt^{IV}(en)_2Br_2]^{2+}$. 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 $[Pt(en)_2][Pt(en)_2X_2][ClO_4]_4$.

The iodide complex was difficult to obtain, probably due to rapid displacement of the amine from $[Ni(en)_2]^{2+}$ by iodide. Repeated recrystallization of the Ni^{II}/Pt^{IV} complexes led to gradual reduction of the Pt^{IV} moiety to Pt^{II} and then contamination of the product with the analogous Pt^{II}/Pt^{IV} complex. Anal. Calcd for $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$: C, 9.98; H, 3.35; N, 11.64; Cl, 22.09. Found: C, 10.1; H, 3.22; N, 11.7; Cl, 22.0. Calcd for $[Ni(en)_2][Pt(en)_2Br_2][ClO_4]_4$: C, 9.13; H, 3.07; N, 10.65; total Hal as Cl, 20.2. Found: C, 9.17; H, 3.02; N, 10.5; total Hal as Cl, 20.4. Calcd for $[Ni(en)_2][Pt(en)_2I_2][ClO_4]_4$: C, 8.38; H, 2.81; N, 9.78; I, 22.15; Cl, 12.37. Found: C, 8.29; H, 2.57; N, 9.46; I, 23.3; Cl, 11.9.

(b) Instrumentation. Electronic spectra were recorded on a Cary 14 spectrometer. Spectra at 295 K were obtained as Nujol mulls of the samples, between quartz plates. The spectra of the chloride-bridged complex at ca. 20 K was recorded with use of an Air Products Displex cryostat.

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

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. Samples were in the form of single crystals (X = Cl, usually ca. 2 mm long) or pressed disks of the pure complexes (X = Br, I). Laser powers were kept to <50 mW. Raman spectra for the chloride- and bromide-bridged complexes were recorded at ca. 20 K on an Air Products Displex cryostat and those of the iodide-bridged complex at ca. 80 K with use of liquid nitrogen and a Dewar assembly. Spectra were calibrated by reference to the Rayleigh line or to the emission lines of neon.

All Raman band intensities were corrected for the spectral response of the instruments.

Results and Discussion

Description of the Structure. The complex $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ has been established crystallographically[10] to consist of a disordered linear chain of chloride-bridged $M(en)_2$ units, isostructural with $[Pd(en)_2][Pd(en)_2Cl_2][ClO_4]_4$.[11] Spectroscopic data (vide infra) indicate that the metal ion valences are Ni^{II}/Pt^{IV} along each chain. The Pt^{IV}–Cl distance (2.315 (6) Å) is virtually identical with that in $[Pt(en)_2][Pt(en)_2Cl_2][ClO_4]_4$

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Table I

complex	cryst color	powder color	intervalence[a] max/cm^{-1}	ω_1/cm^{-1}	x_{11}/cm^{-1}	$I(2\nu_1)/I(\nu_1)$[c] (λ_0/nm)	prog (ν_1)[c]
$[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$	red	yellow	22 200 (RT)	327.9 ± 0.1[d]	−1.0 ± 0.05[d]	0.48[d]	$7\nu_1$
			22 500[b] (~20 K)	323.1 ± 0.1	−0.99 ± 0.05	0.33	
				319.5 ± 0.1	−0.98 ± 0.05	0.32 (488.0)	
$[Ni(en)_2][Pt(en)_2Br_2][ClO_4]_4$	green metallic	blue	19 000 (RT)	195.1 ± 0.2	−0.29 ± 0.07	0.57 (520.8)	$7\nu_1$
$[Ni(en)_2][Pt(en)_2I_2][ClO_4]_4$	gold-green metallic	blue		130.8 (ν_1 value)		0.32 (676.4)	$4\nu_1$

[a] By transmission; sample held at room temperature (RT) or ~20 K. [b] Single-crystal transmission. [c] At ~20 K (chloride and bromide) and ~80 K (iodide). [d] Values of ω_1, x_{11}, and I are listed for each chlorine isotopic component, viz. 35/35, 35/37, and 37/37.

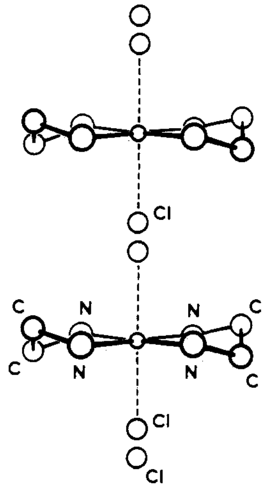

Figure 1. Coordination environment for the $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ chain.

(2.318 (7) Å),[12] while the Ni^{II}–Cl distance (3.057 (7) Å) is slightly less than the Pt^{II}–Cl distance in the pure platinum complex (3.085 (7) Å).[12] The coordination environment of the Ni^{II}/Pt^{IV} complex is shown in Figure 1, and the packing diagram (view down the z axis) is shown in Figure 2; this indicates the likely important nonbonded interactions.

Electronic Spectra. Crystals of the complexes are dichroic. The chloride is yellow with the electric vector of the transmitted light 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 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. The mull spectra are, of course, only qualitative, as it is well-known that the color of a mull can depend on particle size.

The transmission spectra (Figure 3a,b) show a strong broad band in the visible region, which is assigned to the $Ni^{II} \rightarrow Pt^{IV}$ intervalence charge-transfer transition, as for analogous platinum mixed-valence complexes.[4] It occurs (by transmission measurements, as Nujol mulls) at 22 200 cm^{-1} for X = Cl and 19 000 cm^{-1} for X = Br, at room temperature. This is higher in wavenumber than found for the Pt^{II}/Pt^{IV} analogues[4] but lower than for the Pd^{II}/Pt^{IV} ones,[7] implying that the ease of electron transfer and hence the degree of valence delocalization for Ni^{II}/Pt^{IV} complexes is intermediate between the values for the Pt^{II}/Pt^{IV} and Pd^{II}/Pt^{IV} complexes.

Figure 3c shows a single-crystal transmission spectrum of the chloride-bridged complex at ca. 20 K. The spectrum shows a distinct absorption edge when recorded for a single crystal held at low temperatures, as has been observed for other mixed-valence complexes.[13,14] The wavenumber of the maximum increases to 22 500 cm^{-1} when the complex is cooled, consistent with previous observations.[13,14]

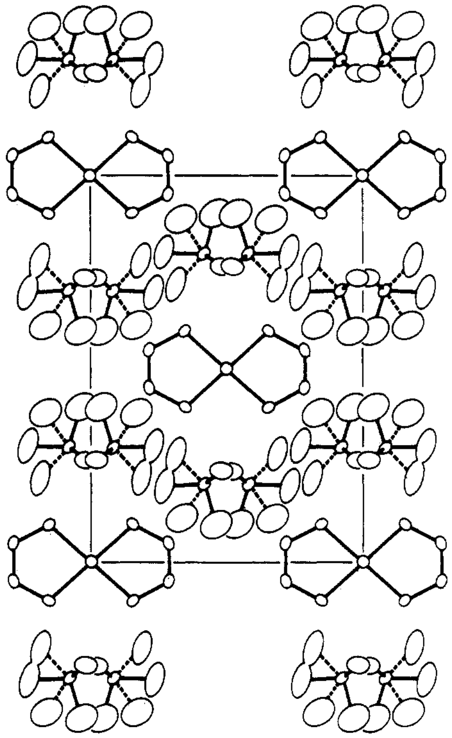

Figure 2. Packing diagram for the complex $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ (view down the z axis). Hydrogen bonding between the protons of the amines and the oxygen atoms of the $[ClO_4]^-$ counterions leads to slight modification to the vibrational band wavenumbers of the amine modes.

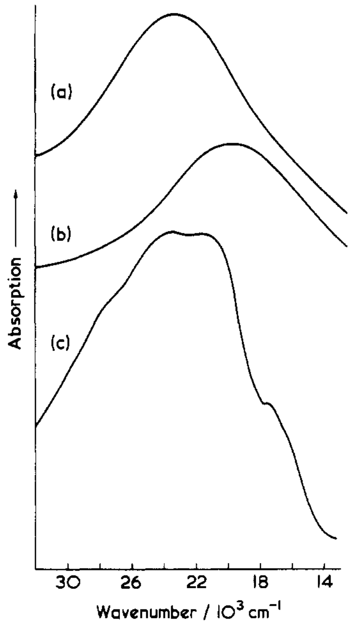

Figure 3. Electronic absorption spectra of (a) $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ at 295 K as a Nujol mull, (b) $[Ni(en)_2][Pt(en)_2Br_2][ClO_4]_4$ at 295 K as a Nujol mull, and (c) $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ at ca. 20 K as a single crystal.

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Table II. Wavenumbers (cm^{-1}) and Assignments of the Bands Observed in the Infrared Spectra of the Complexes $[Ni(en)_2][Pt(en)_2X_2][ClO_4]_4$ (X = Cl, Br, I) and $[Ni(en)_2]^{2+}$ in the Region 650–20 cm^{-1}

$[Ni(en)_2][Pt(en)_2X_2][ClO_4]_4$				
X = Cl	X = Br	X = I	$[Ni(en)_2]^{2+}$	assignt
		630 vs		
625 vs	625 vs	624 vs		$[ClO_4]^-$
613 m	612 vs	614 vs	613 w	
595 sh				$\nu(Pt^{IV}–N)$
592 m	592 m	590 w		
			570 w	
562 m				
554 w	557 m	557 m		
551 w				
	543 w	546 w		
534 m	534 w	534 w	535 w	$\nu(Ni–N)$?
			521 vs	$\nu(Ni–N)$
		508 m	510 m	$\nu(Ni–N)$
493 m	492 m	493 w		$\nu(Ni–N)$?
484 m	481 w			ring bends
474 w	474 w	474 m		
468 w, br		468 sh		
457 w	456 w			
447 w	446 w		443 w	
		430 w	427 w	
407 m	407 m			
405 w	404 m	404 w		
	390 w, br			
364 m	360 s		360 m	$\delta(NCCN)$?
		356 s		
355.5 m				ν_2, $\nu_{as}(^{35}Cl–Pt^{IV}–^{35}Cl)$
353.2 m				ν_2, $\nu_{as}(^{37}Cl–Pt^{IV}–^{35}Cl)$
349.9 m				ν_2, $\nu_{as}(^{37}Cl–Pt^{IV}–^{37}Cl)$
334 m	336 w			ring bends
	330 w		329 w	
	326 w	324 w		
306 sh	306 m		310 w	
		298 w	300 w	
295 s	294 m	294 sh		in-plane $\delta(N–Pt^{IV}–N)$
291 sh				
261 s	264 s	267 s		in-plane $\delta(N–Pt^{IV}–N)$
			252 m	
	242.7 s			ν_2, $\nu_{as}(Br–Pt^{IV}–Br)$
			237 m	
	222 w		222 w	
		208 w	200 w	
194 m	195 m		195 w	
		188 m		ν_2, $\nu_{as}(I–Pt^{IV}–I)$?
			183 w	
		178 s		ν_2, $\nu_{as}(I–Pt^{IV}–I)$?
	177 m		175 w	
			168 w	
163 m			163 w	
152 m, br	150 m		150 w	
			144 s	
	138 w	135 s, br	139 w	
	123 m			
118 m		118 m, br		
	112 m		110 m	
	94 w	98 m		
82 m				
66 w	68 w, br			

Infrared Spectra. The infrared spectra of the mixed-valence complexes, along with that of $[Ni(en)_2]^{2+}$, have been recorded at ca. 80 K in the region 650–20 cm^{-1}. The wavenumbers and assignments of the bands are listed in Table II. The assignments are based on those of related complexes.[15-17]

The infrared spectra of these halogen-bridged complexes are found, as expected for localized-valence complexes, to consist essentially of superpositions of the infrared spectra of the constituent complexes. Changes in the amine modes as a result of hydrogen-bond formation with the counterion (cf. Figure 2), changes in space group on going from the monomer to the mixed-valence complex, and changes in force constant of the axial $Pt^{IV}–X$ bond consequent upon the interaction with the Ni^{II} centers are responsible for such differences as exist.

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

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$[b]	$\Delta\tilde{\nu}^{1/2}$/cm^{-1}	assignt
28.4[c]		<1.0	plasma?
90.8[c]		<1.0	
214 w[c]			$\delta(N–Pt^{IV}–N)$
224 w[c]			$\delta(N–Pt^{IV}–N)$
313.5 w			
317.4	1.0	2.4	ν_1, $\nu_s(^{37}Cl–Pt^{IV}–^{37}Cl)$
320.8	1.0	2.4	ν_1, $\nu_s(^{37}Cl–Pt^{IV}–^{35}Cl)$
325.3	1.0	2.4	ν_1, $\nu_s(^{35}Cl–Pt^{IV}–^{35}Cl)$
353.5 w			ν_2?
583			$\nu(Pt–N)$
633.0	0.32	3.4	$2\nu_1$, $\nu_s(^{37}Cl–Pt^{IV}–^{37}Cl)$
640.4	0.33	3.2	$2\nu_1$, $\nu_s(^{37}Cl–Pt^{IV}–^{35}Cl)$
649.6	0.48	3.4	$2\nu_1$, $\nu_s(^{35}Cl–Pt^{IV}–^{35}Cl)$
672.2 vw			
946.6	0.09	4.0	$3\nu_1$, $\nu_s(^{37}Cl–Pt^{IV}–^{37}Cl)$
957.9	0.14	4.0	$3\nu_1$, $\nu_s(^{37}Cl–Pt^{IV}–^{35}Cl)$
968.1 sh			
971.5	0.26	4.8[d]	$3\nu_1$, $\nu_s(^{35}Cl–Pt^{IV}–^{35}Cl)$
1258.1	0.08	>6.0	$4\nu_1$, $\nu_s(^{37}Cl–Pt^{IV}–^{37}Cl)$
1272.7	0.09	6.0	$4\nu_1$, $\nu_s(^{37}Cl–Pt^{IV}–^{35}Cl)$
1290.9	0.22	8.0[d]	$4\nu_1$, $\nu_s(^{35}Cl–Pt^{IV}–^{35}Cl)$
1295 sh			CH_2 twist
1565		>9.4	$5\nu_1$, $\nu_s(^{37}Cl–Pt^{IV}–^{37}Cl)$
1587	0.07	>9.4	$5\nu_1$, $\nu_s(^{37}Cl–Pt^{IV}–^{35}Cl)$
1609	0.19	9.4	$5\nu_1$, $\nu_s(^{35}Cl–Pt^{IV}–^{35}Cl)$
1896			$6\nu_1$, $\nu_s(^{37}Cl–Pt^{IV}–^{35}Cl)$
1924	0.10	>10.0	$6\nu_1$, $\nu_s(^{35}Cl–Pt^{IV}–^{35}Cl)$
2240	<0.1	>10.0	$7\nu_1$, $\nu_s(^{35}Cl–Pt^{IV}–^{35}Cl)$

[a] Recorded as a single crystal at ca. 20 K with 488.0-nm excitation, power <20 mW at source, and slit widths 110/150/110 μm (spectral slit width ca. 1.4 cm^{-1}). [b] Intensity corrected for the spectral response of the instrument. [c] Recorded with 482.5-nm excitation with the spectrometer in the triple mode. [d] There is suspected to be an interfering peak on the low-wavenumber side.

For the chloride-bridged complex it is possible to resolve the chloride isotopic splitting of the ν_2 band by using the conditions specified by Allen et al.[9] The results are listed in Table II, the component bands having the intensity ratio 9:6:1 expected for a model based on an isolated, linear $X–Pt^{IV}–X$ entity.

The choice of which band to assign to ν_2 for the iodide-bridged complex is not certain. That at 178 cm^{-1} would be in line with the assignment made for $[Pt(en)_2][Pt(en)_2I_2][ClO_4]_4$.[18]

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

Resonance Raman Spectra. The Raman and resonance Raman spectra were recorded for single crystals (where possible) and as polycrystalline disks. The spectra were recorded at ca. 20 K for the chloride- and bromide-bridged complexes and at ca. 80 K for the iodide-bridged complex. The spectra of the chloride- and bromide-bridged complexes are shown in Figure 4, and the band wavenumbers and assignments are listed in Tables III–V.

It was noted that the Ni^{II}/Pt^{IV} complexes, on being ground with any material suitable as an internal intensity standard, such as $K[ClO_4]$ or $K_2[SO_4]$, decomposed to the analogous Pt^{II}/Pt^{IV} complex (Figure 5a–c); thus excitation profiles of the complexes could not be obtained. In addition it was found that with time (ca. 1 year) the percentage of Pt^{II}/Pt^{IV} complex contaminating the Ni^{II}/Pt^{IV} complex increased (Figure 5d).

The resonance Raman spectra of the complexes are dominated by long overtone progressions in ν_1, the totally symmetric X–

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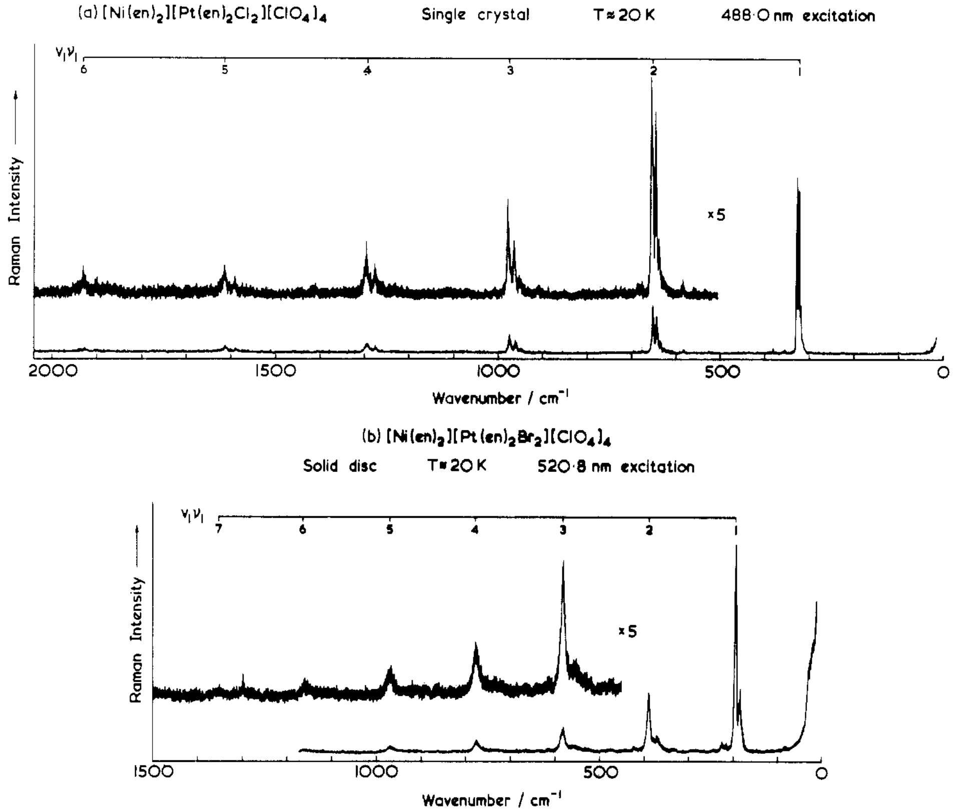

Figure 4. Resonance Raman spectra. (a) $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$: single crystal, λ_0 = 488.0 nm. (b) $[Ni(en)_2][Pt(en)_2Br_2][ClO_4]_4$: $K[ClO_4]$ disk, λ_0 = 520.8 nm. Each sample was held at ca. 20 K.

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

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$[b]	$I(v_1\nu_n)/I(\nu_n)$	$\Delta\tilde{\nu}^{1/2}$/cm^{-1}	assignt
183.8		1.0	~6.8	ν_n
194.5	1.0		4.5	ν_1, ν_s(Br–Pt^{IV}–Br)
214				δ(N–Pt–N)
223.6				δ(N–Pt–N)
242				ν_2?
279.5				
292.6				
333				
367.6		0.58	~15	$2\nu_n$
388.7	0.57		8.4	$2\nu_1$
419				ν_1 + 223.6
471				ν_1 + 279
481				ν_1 + 292?
553		0.24	~21	$3\nu_n$
581.6	0.29		12.4	$3\nu_1$
612				$2\nu_1$ + 223.6
635				ClO_4^-?
665				$2\nu_1$ + 279
731		<0.24	>21	$4\nu_n$
774.6	0.12		14.4	$4\nu_1$
825				
914		<0.24	>21	$5\nu_n$
967	0.12		23	$5\nu_1$
1160	0.06		28	$6\nu_1$
1350	<0.06		>28	$7\nu_1$

[a] Recorded as a solid disk at ca. 20 K, with 520.8-nm excitation, power <10 mW at source, and slit widths 150/200/150 μm (spectral slit width ca. 1.75 cm^{-1}). [b] Corrected for the spectral response of the instrument.

Table V. Wavenumbers, Relative Intensities, and Assignments of Bands Observed in the Resonance Raman Spectrum of $[Ni(en)_2][Pt(en)_2I_2][ClO_4]_4$[a]

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	assignt
130.8	1.0	ν_1, ν_s(I–Pt^{IV}–I)
164		
251.5	0.32	$2\nu_1$
364.5	0.20	$3\nu_1$
494.9	0.13	$4\nu_1$

[a] Recorded as a solid disk at ca. 80 K, with 676.4-nm excitation and slit widths 200/250/200 μm (spectral slit width ca. 1.1 cm^{-1}).

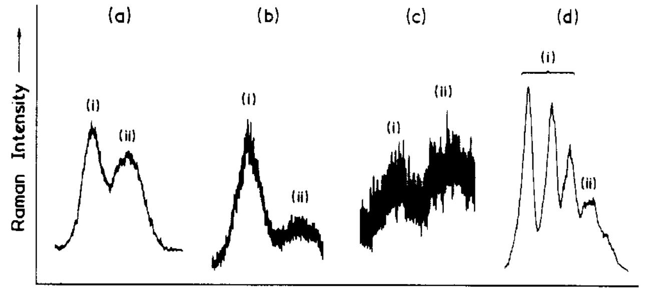

Figure 5. (a)–(c) ν_1 band of $[Ni(en)_2][Pt(en)_2Br_2][ClO_4]_4$: (a) sample ground with $K_2[SO_4]$ and pressed as a disk, λ_0 = 568.2 nm; (b) sample ground with $K[ClO_4]$ and pressed as a disk, λ_0 = 468.0 nm; (c) sample ground with $K[ClO_4]$, left for a few hours, and then ground with more $K[ClO_4]$ and pressed as a disk, λ_0 = 468.0 nm. (d) ν_1 band of $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$: single-crystal sample 1 year after the sample was first prepared, λ_0 = 647.1 nm ((i) Ni^{II}/Pt^{IV} component; (ii) Pt^{II}/Pt^{IV} component).

Pt^{IV}–X stretching mode. No evidence was obtained for the presence of a band attributable to a symmetric X–Ni^{IV}–X mode, and thus the metal atom valences are certainly Ni^{II}/Pt^{IV} rather than vice versa.

For the chloride-bridged complex, only a progression in ν_1 was observed with no other subsidiary progressions (Figure 4a). By recording the spectra at ca. 20 K with a spectral slit width of <1.5 cm^{-1}, we have been able to resolve the chlorine isotopic structure of the ν_1 band and its associated overtones up to $6\nu_1$, the results being listed in Table III. For a linear $Pt^{IV}Cl_2$ unit a 9:6:1 triplet band structure is predicted; however, the observed band structure for the fundamental differs from this, only approaching 9:6:1 for the higher overtone bands (Table VI, Figure 6). The reason for

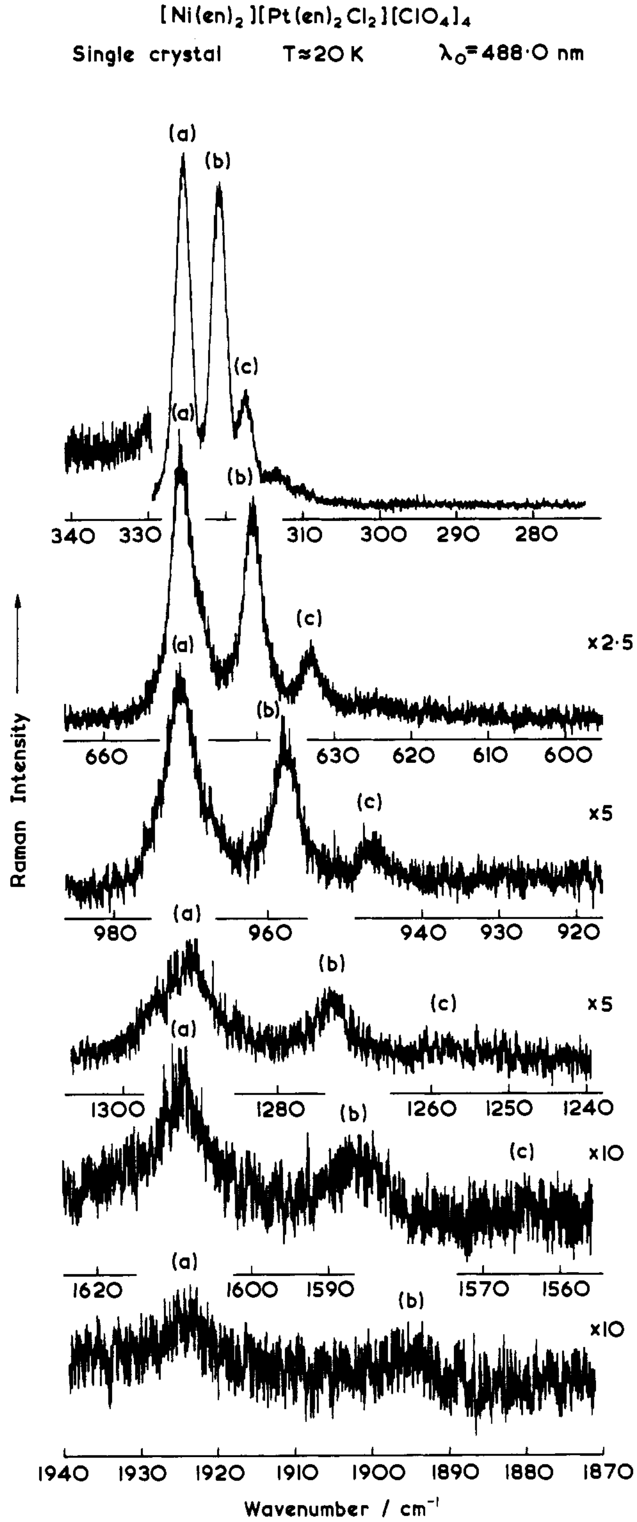

Figure 6. Isotopomer band intensities for ν_1 to $6\nu_1$ of a single crystal of $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ (λ_0 = 488.0 nm, slit widths 120/150/120 μm). For ease of presentation, the $^{35}ClPt^{35}Cl$ component (a) of each harmonic is lined up with the same abscissa value; (b) and (c) refer to the $^{35}ClPt^{37}Cl$ and $^{37}ClPt^{37}Cl$ components, respectively.

Table VI. Observed Isotopomer Band Ratios for $n\nu_1$ (n = 1–4) for $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$[a]

n	35/35	35/37	37/37
1	2.9	3.1	1.0
2	4.4	3.3	1.0
3	8.2	4.9	1.0
4	8.2	3.5	1.0

[a] Corrected for the spectral response of the instrument.

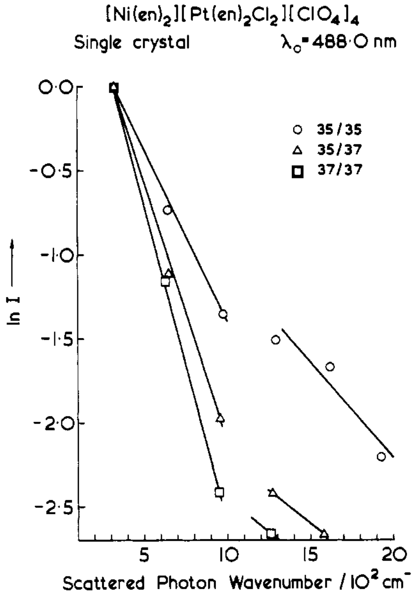

Figure 7. Data from a single-crystal spectrum of $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ (ca. 20 K, λ_0 = 488.0 nm) presented as a plot of the logarithm of the intensity of the fundamental and overtone bands vs. scattered photon wavenumber.

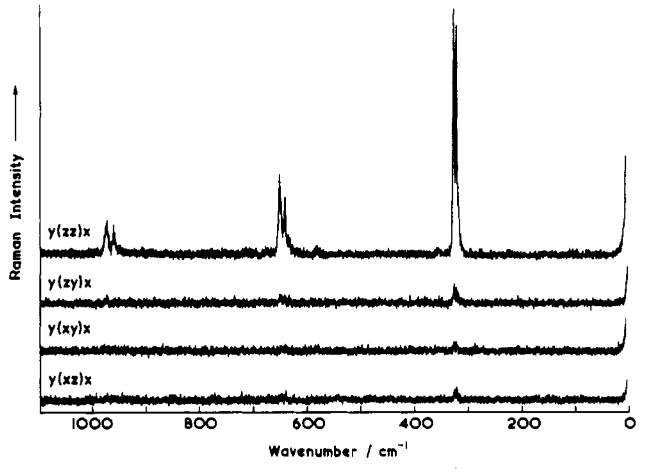

Figure 8. Polarized single crystal spectra of $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ (ca. 20 K, λ_0 = 488.0 nm) (Porto notation).

this behavior, which is the same as that observed for Pd^{II}/Pt^{IV} complexes,[7] is unclear. The harmonic band wavenumbers (ω_1) and anharmonicity constants (x_{11}) have been calculated for each isotopomer and are listed in Table I. There are two peaks assignable to δ(N–Pt–N) modes, as predicted from line-group analysis.[5] A plot of the logarithm of the intensity of the fundamental and overtone bands vs. scattered photon wavenumber has a discontinuity at 19 200–19 500 cm^{-1} (Figure 7), which is close to, or at, the band gap.[13,14] There is a very weak peak at ca. 313.5 cm^{-1} (λ_0 = 488.0 nm) possibly due to a trace of Pt^{II}/Pt^{IV} impurity in the complex.

There is a slight (ca. 1.0 cm^{-1} for ν_1, ca. 0.5 cm^{-1} for $2\nu_1$) decrease in the wavenumber of ν_1 on increasing the sample temperature from ca. 20 to ca. 80 K. The polarized single-crystal spectrum recorded at ca. 20 K (Figure 8) shows that the ν_1 progressions (and the component isotopomer bands) are polarized in the chain (z) direction.

The resonance Raman spectrum of the bromide-bridged complex (Figure 4b) shows not only a progression in ν_1 (194.5 cm^{-1}) but also a progression to five members in an unassigned band at 183.8 cm^{-1} (Table IV). This band is not due to impurities of $[Pt^{IV}(en)_2Br_2]^{2+}$ (ν_1 = 212 cm^{-1}) or Pt^{II}/Pt^{IV} chain (ν_1 ca. 178 cm^{-1}), but it may be due to domains of $Ni^{II}\cdots X–Pt^{IV}–X\cdots Ni^{II}\cdots X–Pt^{IV}–X\cdots Pt^{II}\cdots X–Pt^{IV}–X\cdots Ni^{II}$ within the chain. A weak peak at 177.8 cm^{-1} is possibly due to a trace of the Pt^{II}/Pt^{IV} complex as an impurity. Other subsidiary progressions, $v_1\nu_1 + \nu_n$, where

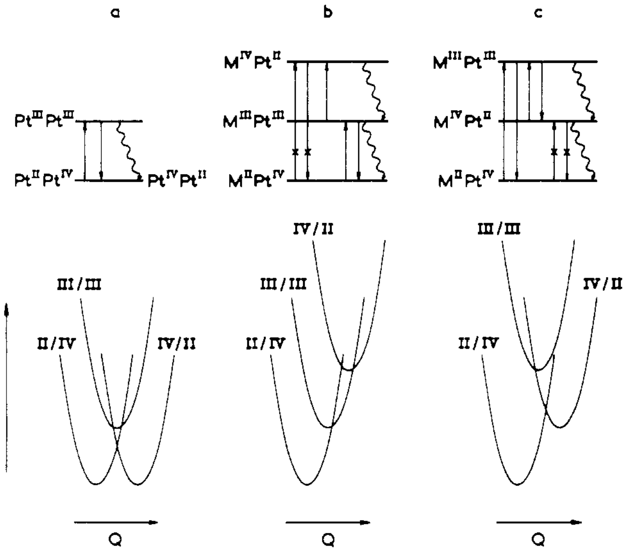

Figure 9. Representation of the relative energy levels and possible electronic transitions in linear-chain M^{II}/M^{IV} complexes.

ν_n is another Raman-active (though unassigned) mode at 223 or 279 cm^{-1}, are observed.

There is a 0.7-cm^{-1} drop in the wavenumber of ν_1 of the bromide on changing the exciting line from 520.8 to 647.1 nm. This dispersion of ν_1 with change in exciting line is characteristic of halogen-bridged mixed-valence complexes of platinum[19] and palladium.[20] A plot of the logarithm of the intensity of the ν_1 fundamental and its overtones vs. scattered photon wavenumber appears to show a discontinuity at ca. 18 300 cm^{-1}, cf. earlier discussion of the behavior of the analogous chloride.

The resonance Raman spectrum of the iodide-bridged complex has a weak, four-membered progression in ν_1 (130 cm^{-1}, Table V). The progression members give rise to asymmetric bands with more than one component, and thus there is no justification in attempting to calculate ω_1 and x_{11}.

Conclusion

The present project has led to the isolation and the spectral characterization of Ni^{II}/Pt^{IV} halogen-bridged chain complexes, directly analogous to the Pt^{II}/Pt^{IV}, Pd^{II}/Pd^{IV}, and Pd^{II}/Pt^{IV} ones already characterized. The energetics of the M^{II}/M^{IV} complexes are usually represented as in Figure 9a; the degenerate ground states M^{II}/M^{IV} and M^{IV}/M^{II} are interconvertible via the symmetric excited state M^{III}/M^{III} by successive one-electron transfers and are accompanied by suitable displacement of the halogen atom along the halogen–metal coordinate, Q_1 (the mode giving rise to the long resonance Raman progressions). The halogen would be expected to the centrally placed in the M^{III}/M^{III} state for the pure metal complexes, but not for the mixed-metal analogues. Three possible cases can be envisaged for the energetics of the mixed-metal complexes (cf. Figure 9). The first case (Figure 9a) corresponds to that in which both M^{II}/Pt^{IV} and M^{IV}/Pt^{II} (M = Ni, Pd) have the same energy. This is highly unlikely for M = Pd, Ni; indeed, for all mixed-metal complexes studied in this project and elsewhere, M^{II}/Pt^{IV} is established to be the ground state. Of the two remaining cases (Figure 9b,c) our expectation is that the situation is best represented by Figure 9c, the actual population of the M^{IV}/Pt^{II} state being effectively zero.

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Registry No. $[Ni(en)_2][Pt(en)_2Cl_2][ClO_4]_4$, 84076-61-9; $[Ni(en)_2][Pt(en)_2Br_2][ClO_4]_4$, 84076-62-0; $[Ni(en)_2][Pt(en)_2I_2][ClO_4]_4$, 101695-47-0; $[Ni(en)_2][Pt(en)_2{}^{35}Cl_2][ClO_4]_4$, 101695-49-2; $[Ni(en)_2][Pt(en)_2{}^{35}Cl^{37}Cl][ClO_4]_4$, 101695-51-6; $[Ni(en)_2][Pt(en)_2{}^{37}Cl_2][ClO_4]_4$, 101695-53-8.

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Chemistry of Trivalent Uranium Metallocenes: Electron-Transfer Reactions with Carbon Disulfide. Formation of $[(RC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$

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The trivalent uranium metallocenes $(MeC_5H_4)_3U{\cdot}THF$ and $(Me_3SiC_5H_4)_3U$ react with CS_2 to form the binuclear U(IV) complexes $[(RC_5H_4)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$ (**1**, R = Me; **2**, R = $SiMe_3$). Crystals of **1** are monoclinic, $P2_1/n$, with a = 14.127 (4) Å, b = 14.182 (4) Å, c = 8.123 (2) Å, and β = 92.36 (3)° at 23 °C; for Z = 2 the calculated density is 2.097 g/cm^3. The structure was refined by full-matrix least-squares to a conventional R factor of 0.025, for 1402 data with $F^2 > 2\sigma(F^2)$. The central carbon atom of the complex is disordered across a center of symmetry. The geometry about the CS_2 ligand (U–S = 2.973 (3) Å and U–C = 2.53 (2) Å), as well as NMR and susceptibility data, is consistent with two full one-electron transfers into the CS_2. There is no measurable magnetic interaction between the paramagnetic ions to 5 K.

Introduction

The transition-metal coordination chemistry of heteroallenes (CS_2, SCO, and CO_2) has been extensively studied since the first report of an η^2-CS_2 complex,[1] relative to activating these linear, 16-electron molecules for further reaction chemistry.[2] Though the insertion of carbon dioxide into actinide–carbon σ bonds[3] and the insertion of CO_2 or CS_2 into f-element amide bonds has been developed,[4] no example of a heteroallene acting as a coordinating ligand to an actinide metal center has been described.

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