Electronic and Resonance Raman Spectra of Mixed-valence, Linear-chain Complexes of Platinum and Palladium with 1,2-Diaminocycloalkanes (N–N), $[M^{II}(N–N)_2][M^{IV}(N–N)_2X_2]X_4$ (X = Halogen)

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The electronic and resonance Raman spectra of a series of halogen-bridged, linear-chain, mixed-valence complexes, $[Pt^{II}(N–N)_2][Pt^{IV}(N–N)_2X_2]X_4$ [N–N = 1,2-diaminocyclohexane (dach); X = Cl, Br, or I], as well as of the complexes $[Pd^{II}(dach)_2][Pd^{IV}(dach)_2Cl_2]Cl_4$ and $[Pt^{II}(N–N)_2][Pt^{IV}(N–N)_2Br_2]Br_4$ [N–N = 1,2-diaminocyclopentane (dacp)], have been recorded at *ca.* 295, 80, and 10 K. Excitation within the contours of the axially polarized $M^{IV}\leftarrow M^{II}$ intervalence band of each complex leads to the appearance of long overtone progressions, $v_1\nu_1$, in the resonance Raman spectrum, where ν_1 is the totally symmetric axial metal–halogen stretching mode. The excitation profile of the ν_1 band maximizes in each case on the low-energy side of the intervalence band maximum. The wavenumbers of the ν_1 band, intervalence band maximum, and excitation profile maximum of the complexes decrease in the order Cl > Br > I, Pt > Pd, and dach > dacp. Although the mixed-valence complexes are chemically pure, they form as mixtures of conformational isomers unless the resolved ligand is used in their preparations. Such conformers have different intervalence band maxima and different ν_1 values and, in consequence, as the exciting-line wavenumber ($\tilde{\nu}_0$) is changed, different conformers have their ν_1 bands resonance-enhanced, and the apparent value of ν_1 and its overtones change. These observations are discussed with reference to the steric hindrance between the cycloalkane rings in mixed-valence linear-chain complexes.

Halogen-bridged, linear-chain, mixed-valence complexes of platinum of the type $[M^{II}(N–N)_2][M^{IV}(N–N)_2X_2]Y_4$ (N–N = a bidentate or two monodentate amines; X = Cl, Br, or I; Y = ClO_4, Cl, Br, I, BF_4, HSO_4, or polymeric copper–halide chains) have recently been the subject of extensive physical studies, in particular *X*-ray diffraction, photoelectron, electronic, and resonance Raman (r.R.) spectroscopy, as well as electrical conductance studies.[1–8] Such complexes have many highly anisotropic properties, especially their conductance and their electronic and resonance Raman spectra; the last is dominated by bands attributable to the symmetric stretching mode, $\nu(X–Pt^{IV}–X)$ (ν_1), of the chain. Previous work[4] suggests that there is a close relationship between the wavenumber of ν_1, the wavenumber of the intervalence band maximum, and the $Pt^{II}\cdots Pt^{IV}$ separation along the linear chains. The recent syntheses and crystallographic studies of the complexes $[Pt^{II}\{(-)\text{-}1(R),2(R)\text{-dach}\}_2][Pt^{IV}\{(-)\text{-}1(R),2(R)\text{-dach}\}_2X_2]X_4$ (X = Cl or Br, dach = 1,2-diaminocyclohexane), which have been shown to have the shortest known $Pt^{II}\cdots Pt^{IV}$ distances,[9] have provided the opportunity further to investigate these relationships, as well as to ascertain the effects on the r.R. spectra of the presence of different conformers of the ligand. The latter effects prove to be profound.

Many fewer palladium than platinum complexes of this sort are known, since the analogous syntheses are difficult to control and the products are not very stable. However, one new complex of this type, namely $[Pd^{II}(dach)_2][Pd^{IV}(dach)_2Cl_2]Cl_4$, has been synthesised and studied. In addition, one 1,2-diaminocyclopentane (dacp) complex of platinum has also been studied for comparative purposes. This study is concerned, therefore, with the electronic and r.R. spectra of the complexes $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2Cl_2]Cl_4$ (1), $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2Br_2]Br_4$ (2), $[Pt(cis\text{-dach})_2][Pt(cis\text{-dach})_2Br_2]Br_4$ (3), $[Pt\{(-)\text{-dach}\}\{(+)\text{-dach}\}][Pt\{(-)\text{-dach}\}\{(+)\text{-dach}\}Br_2]Br_4$ (4), $[Pt\{(\pm)\text{-dach}\}_2][Pt\{(\pm)\text{-dach}\}_2Br_2]Br_4$ (5), $[Pt\{(-)\text{-dacp}\}_2][Pt\{(-)\text{-dacp}\}_2Br_2]Br_4$ (6), $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2I_2]I_4$ (7), and $[Pd(dach)_2][Pd(dach)_2Cl_2]Cl_4$ (8).

Experimental

Preparative Details.—The 1,2-diaminocyclohexanes were separated into geometrical and optical isomers as described earlier.[10] 1,2-Diaminocyclopentane was prepared and resolved as described by Toftlund and Pedersen.[11] The preparations of $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2X_2]X_4$ (X = Cl or Br) have been described earlier.[9] The corresponding (±)-dach and *cis*-dach complexes were prepared analogously. The compound $[Pt\{(-)\text{-dach}\}\{(+)\text{-dach}\}]Br_2$ used to obtain the $[Pt\{(-)\text{-dach}\}\{(+)\text{-dach}\}][Pt\{(-)\text{-dach}\}\{(+)\text{-dach}\}Br_2]Br_4$ salt was prepared in two steps. First, *cis*-$[Pt\{(-)\text{-dach}\}Cl_2]$ was obtained by the reaction between $K_2[PtCl_4]$ and (−)-dach. Subsequently this salt was treated with (+)-dach and the *meso*-salt was precipitated with lithium bromide. The mixed-valence complex was obtained as above. The compound $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2I_2]I_4$ was obtained by heating an aqueous solution of the corresponding chloride complex in sodium iodide solution.

The palladium complex $[Pd(dach)_2][Pd(dach)_2Cl_2]Cl_4$ was obtained by the following method. $[Pd(dach)_2]Cl_2$ was prepared by stirring an aqueous solution of $K_2[PdCl_4]$ (1 g) with dach (*ca.* 1 g) for 15 min. A yellow-brown precipitate was obtained, which dissolved on being warmed to 50 °C. The clear solution was then evaporated to near dryness under vacuum at 40 °C. Colourless needles were obtained on cooling. To an aqueous solution of $[Pd(dach)_2]Cl_2$ (0.5 g), sodium chloride (0.5 g) was added and the solution cooled to 0 °C. Chlorine gas was then bubbled through the cold solution. Bronze-brown microcrystals of the mixed-valence complex were obtained.

Recrystallisation was not attempted due to the low stability of palladium(IV) amine complexes (Found: C, 32.0; H, 6.7;

Cl, 23.6; N, 12.5. $C_{12}H_{28}Cl_3N_4Pd$ requires C, 32.65; H, 6.4; Cl, 24.1; N, 12.7%).

Instrumental Details.—Electronic spectra were recorded using a Cary 14 spectrometer by transmission, using pressed discs of the complexes dispersed in alkali halide. Infrared spectra were measured on a Perkin-Elmer 225 spectrometer.

Raman spectra were recorded on both a Spex 1401 double monochromator (1 200 line mm^{-1} Bausch and Lomb gratings) and a Spex 14018 (R6) double/triple monochromator (1 800 line mm^{-1} Jobin-Yvon holographic gratings). Exciting radiation was provided by Coherent Radiation models CR3 Ar^+ or Kr^+ and CR15UV Ar^+ lasers. Detection was by photon counting employing cooled RCA C31034 photomultiplier tubes. Room-temperature spectra were obtained using the rotating sample technique and at *ca.* 80 K from pressed discs of the complexes. A cylindrical lens was used to prevent decomposition by line-focusing the beam. Spectra at lower temperatures (to a nominal *ca.* 10 K) were obtained by use of an Air-Products Displex cryostat.

The relative intensity data given in the Tables are based on the products of peak heights and full-widths at half-maximum. The band intensities given in Figure 2 (see below) are based on peak heights only, and were measured relative to that of the ν_1 (a_1) band of SO_4^{2-} and corrected for the response of the instrument. Band wavenumbers were determined by reference to the emission lines of neon.

Results and Discussion

Stereochemical Considerations.—1,2-Diaminocyclohexane has the ' chair ' conformation, it is chiral and stereoselective to complex formation. It has two geometrical isomers, *cis* and *trans*. In the latter (*RR*,*SS*) the amino-donor groups are either both equatorial or both axial, while in the former the amino-donor groups occupy both axial as well as equatorial positions. The ligand can be separated into the *cis* and *trans* isomers.[10,12] The *trans* isomers can each be further resolved into their (+) and (−) enantiomers [13,14] while the *cis* isomer is a *meso* form. It is worth noting that, for each enantiomer of the *trans* isomer, only one conformer (λ for *RR* and δ for *SS*) can chelate to a metal ion, whereas the *cis* isomer can do so either as λ or as δ conformers.

1,2-Diaminocyclopentane is also chiral and stereoselective. However, for *trans*-dacp, the cyclic ring becomes more strained on chelation than does that of *trans*-dach.

Structural Considerations.—The structures of only two of these complexes have been solved completely, namely [Pt{(−)-dach}$_2$][Pt{(−)-dach}$_2$X$_2$]X$_4$ (X = Cl or Br).[9] The structure consists in both cases of long chains, made up of stacks of alternate $[Pt^{II}(dach)_2]^{2+}$ in square-planar coordination and $[Pt^{IV}(dach)_2X_2]^{2+}$ in square-bipyramidal coordination. The halogens in the latter bridge the units together into chains. Differences between complexes containing *cis* or *trans* ligands would be expected mainly in the orientation of the cycloalkane rings with respect to the MN_4 plane. Some selectivity in the complex formation from the $[MCl_4]^{2-}$ and a *cis–trans* mixture of diamines is expected. For dach, the *trans* isomer is a better ligand than *cis*, but the opposite is true for dacp.

For complexes containing only the *trans-RR* isomer the C_6 cyclohexane ring will lie in the MN_4 plane [Figure 1(*a*)—(*c*)]. This has been shown to be the case for complexes (1) and (2) by Larsen and Toftlund [9] [Figure 1(*a*)]. In the crystal structure [15] of *cis*-[Pt(*cis*-dach)Cl$_2$] the cyclohexane ring is in the chair conformation, resulting in a nearly perpendicular orientation of the C_6 ring plane with respect to the MN_4 plane [compare Figure 1(*d*)—(*h*)]. For complexes containing two *cis* ligands, two orientations of the dach rings with respect to the MN_4 plane are possible. These are shown in Figure 1(*g*) and (*h*). No structural information is available for the bis-*cis*-dach platinum complex but both stereochemistries have been shown to exist for copper(II) chelates [16] of *cis*-1,3-diaminocyclohexane.

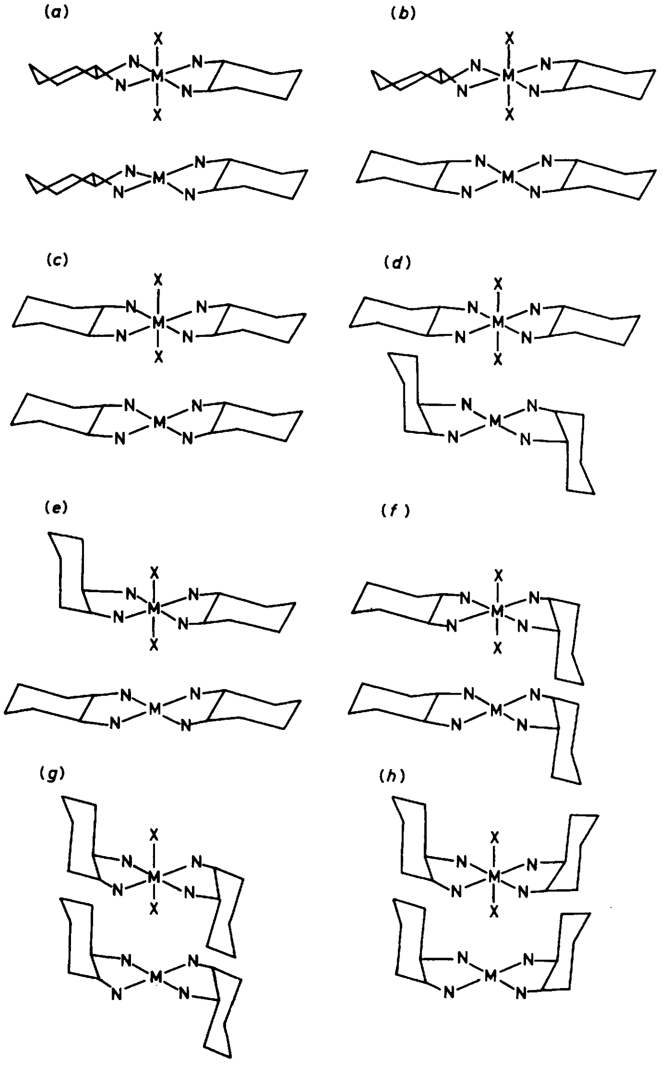

Figure 1. Representations of some of the possible structures of linear-chain 1,2-diaminocycloalkane (N–N) complexes (X = halogen)

Finally, the orientation of the C^1–C^2 bond in relation to the MN_4 plane would define the conformations (δ or λ) of the chelates. For a given chirality of a *trans*-1,2-diamine, the conformation of the chelate ring is defined and no conformational inversions are possible in the complex. If the ligands (N–N) are both (+) or (−)(*RR*), a λλ or δδ conformation is obtained [Figure 1(*a*)]. If, however, one is (−) and the other (+) a λδ (*meso*) conformation [Figure 1(*c*)] is expected. Since the *cis* isomer cannot be resolved, conformations λλ, δδ, and λδ are all possible; in the case of $[Pt(en)_2]^{2+}$, a λδ conformation is observed in the crystal.[17]

Electronic Spectra.—The crystals of the complexes are dichroic and have a metallic sheen which disappears on their being ground. The colours of the crystals and those of their

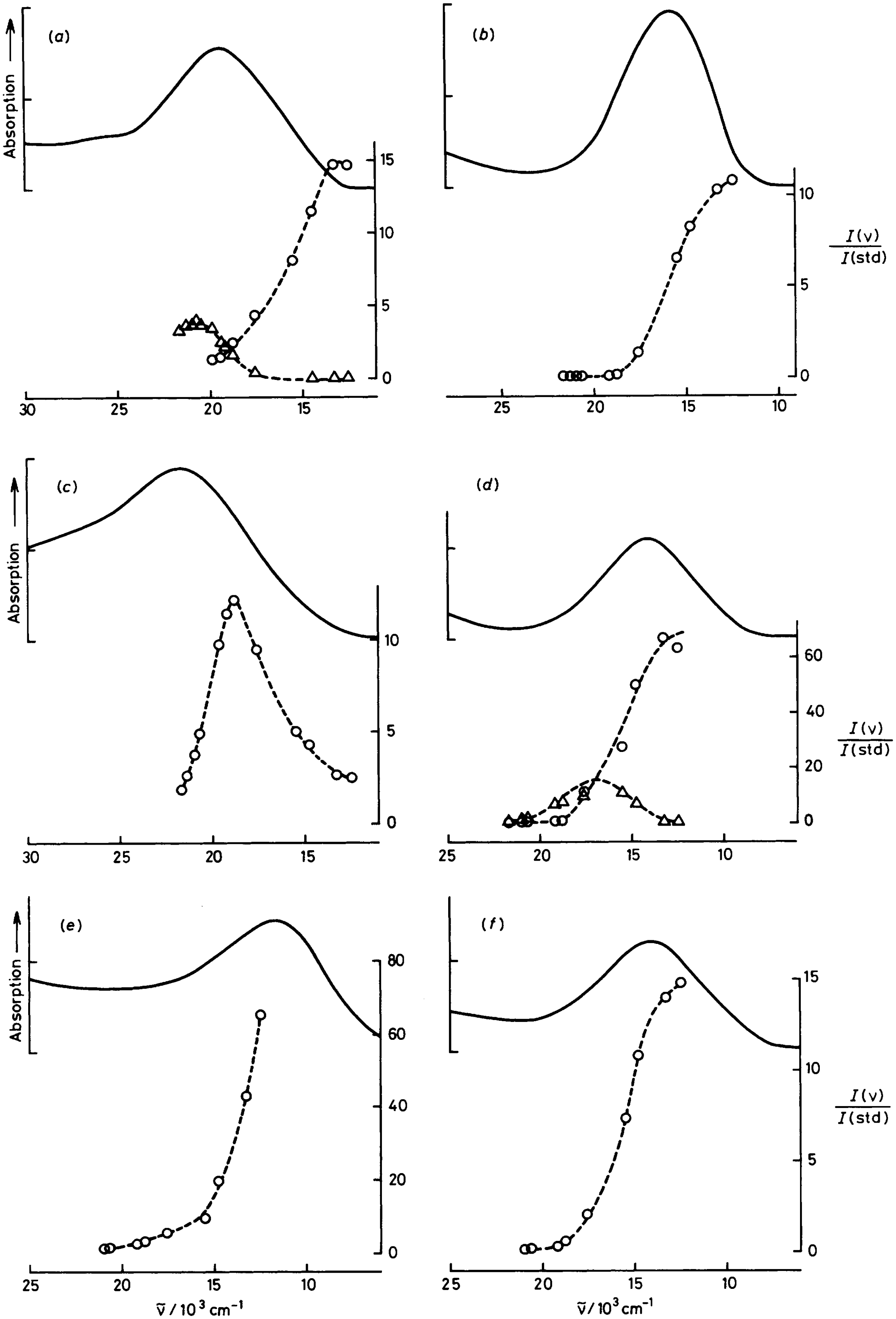

Figure 2. Electronic spectra (alkali halide discs, 295 K) and excitation profiles (*ca.* 80 K, based on relative peak heights) of the ν_1 bands (○) of (*a*) $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2Cl_2]Cl_4$, (*b*) $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2Br_2]Br_4$, (*c*) $[Pt(\textit{cis}\text{-dach})_2][Pt(\textit{cis}\text{-dach})_2Br_2]Br_4$, (*d*) $[Pt\{(-)\text{-dacp}\}_2][Pt\{(-)\text{-dacp}\}_2Br_2]Br_4$, (*e*) $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2I_2]I_4$, and (*f*) $[Pd(dach)_2][Pd(dach)_2Cl_2]Cl_4$. The excitation profiles of the ν_1 bands of $[Pt(\textit{cis}\text{-dach})_2][Pt(\textit{cis}\text{-dach})_2Cl_2]Cl_4$ and $[Pt(\textit{cis}\text{-dacp})_2][Pt(\textit{cis}\text{-dacp})_2Br_2]Br_4$ are also indicated (△) in (*a*) and (*d*) respectively

Table 1. Summary of data on 1,2-diaminocycloalkane complexes

	Colour		Intervalence band	Excitation profile			Progression		$I(2\nu_1)$ [d]
Complex	Crystal [a]	Powder [b]	$\nu_{max.}$ [c]/cm^{-1}	$\nu_{max.}$ [d]/cm^{-1}	ω_1 [d]/cm^{-1}	x_{11} [d]/cm^{-1}	in ν_1 [d]	λ_0/nm	$I(\nu_1)$
(1)	Green	Purple	19 400	13 100	285.5 ± 0.5	-0.85 ± 0.05	$11\nu_1$	647.1	0.69
e			*ca.* 24 000	20 800	310.3 ± 0.3	-0.93 ± 0.03	$9\nu_1$	457.9	0.64
(2)	Gold	Blue	15 900	$\leqslant$12 500	161.4 ± 0.3	-0.35 ± 0.02	$10\nu_1$	752.5	0.66
(3)	Purple	Brown	21 800	18 800	187.2 ± 0.3	0.0 ± 0.03	$8\nu_1$	476.5	0.58
(4)	Gold	Blue	16 500	$\leqslant$12 500	164.8 ± 0.3	-0.33 ± 0.03	$8\nu_1$	752.5	0.69
(5)	Gold	Blue	16 000	$\leqslant$12 500	163.1 ± 0.3	-0.33 ± 0.03	$9\nu_1$	752.5	0.66
(6)	Gold	Blue	14 300	$\leqslant$12 500	163.1 ± 0.3	-0.48 ± 0.03	$9\nu_1$	752.5	0.60
f				17 000	184.5 ± 0.5	-0.2 ± 0.1	$6\nu_1$	476.5	0.30
(7)	Black	Blue	11 700	<12 500 [c]	123.8 ± 0.5	-0.28 ± 0.08	$8\nu_1$	752.5	0.53
(8)	Brown	Blue	14 000	$\leqslant$12 500 [c]	242.7 ± 0.7	-0.66 ± 0.08	$6\nu_1$	752.5	0.54
g			*ca.* 25 000		301.7 ± 0.5	-0.9 ± 0.1	$5\nu_1$	488.0	0.54

[a] By reflected light. [b] By transmission. [c] At *ca.* 295 K. [d] At *ca.* 80 K. [e,f,g] Complexes $[Pt(\textit{cis}\text{-dach})_2][Pt(\textit{cis}\text{-dach})_2Cl_2]Cl_4$, $[Pt(\textit{cis}\text{-dacp})_2]$˜ $[Pt(\textit{cis}\text{-dacp})_2Br_2]Br_4$, and $[Pd(\textit{cis}\text{-dach})_2][Pd(\textit{cis}\text{-dach})_2Cl_2]Cl_4$ respectively, these being deduced to be present in the samples of (1), (6), and (8) obtained from the original preparations.

Table 2. Wavenumbers (cm^{-1}), relative intensities, full-widths at half-maximum ($\Delta\tilde{\nu}_{\frac{1}{2}}$), and assignments of bands in the r.R. spectra *

(*a*) $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2Cl_2]Cl_4$

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	Assignment
132.2			
153.0			
179.1			
196.4			
217.6			δ(N–Pt–N)
281.9	1.00	11.4	$\nu_1(Cl\text{–}Pt^{IV}\text{–}Cl)_{sym}$
360.6			$\nu_2(Cl\text{–}Pt^{IV}\text{–}Cl)_{asym}$
413.6			ν_1 + 132.2
434.8			ν_1 + 153.0
563.1	0.69	21.3	$2\nu_1$
627.5			ν(ring)
715.5			$2\nu_1$ + 153.0
843.5	0.51	31.5	$3\nu_1$
909.7			ν_1 + ν(ring)
990.9			$3\nu_1$ + 153.0
1 121.3	0.37	42	$4\nu_1$
1 187.9			$2\nu_1$ + ν(ring)
1 268.2			$4\nu_1$ + 153.0
1 397.5	0.30	51	$5\nu_1$
1 463			$3\nu_1$ + ν(ring)
1 541			$5\nu_1$ + 153.0
1 673	0.20	59	$6\nu_1$
1 941	0.16	71	$7\nu_1$
2 212	0.12	75	$8\nu_1$
2 480	0.08	80	$9\nu_1$
2 745	*ca.* 0.05	*ca.* 90	$10\nu_1$
3 005	<0.05	>90	$11\nu_1$

(*b*) $[Pt(\textit{cis}\text{-dach})_2][Pt(\textit{cis}\text{-dach})_2Cl_2]Cl_4$

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	Assignment
136.0			
162.4			
196.0			
295			
299.5			
308.6	1.00	11	ν_1
361.4			ν_2
453			ν_1 + (162.4 or 136.0)
504			ν_1 + 196.0
589			ν_1 + 299.5
614.1	0.64	24	$2\nu_1$
669.7			ν_1 + 361.4
882			$2\nu_1$ + 299.5
920.0	0.46	35	$3\nu_1$
972			$2\nu_1$ + 361.4
1 028			ν(C–N)
1 036			
1 061			
1 180			$3\nu_1$ + 299.5
1 223.5	0.28	46	$4\nu_1$
1 278			$3\nu_1$ + 361.4
1 305			
1 343			δ(H–C–H)
1 363			
1 522.8	0.17	55	$5\nu_1$
1 822	0.09	65	$6\nu_1$
2 120	*ca.* 0.05	*ca.* 75	$7\nu_1$
2 420	<0.05	>75	$8\nu_1$
2 710	<0.05	>75	$9\nu_1$
3 007			ν(C–H)
3 066			ν(C–H)
3 299			ν_1 + ν(C–H)
3 362			ν_1 + ν(C–H)

* Obtained as a CsCl disc at *ca.* 80 K with (*a*) 647.1 and (*b*) 457.9 nm excitation lines.

powders are listed in Table 1. The electronic transmission spectra (Figure 2) are characterised by strong bands, assigned to the intervalence $M^{IV} \leftarrow M^{II}$ transition in each case. The band maxima are observed to decrease in wavenumber in the order Cl > Br > I and Pt > Pd. For the different isomers of the dach ligand, for the same metal and halogen, the trend in the electronic band maxima is found to be *cis* > *meso* > *trans* ~ racemate.

The wavenumber of the intervalence band is a measure of the extent of interaction between M^{II} and M^{IV}, which in turn depends (among other factors) on the $M^{II} \cdots M^{IV}$ separation; *i.e.* a decrease in the $M^{II} \cdots M^{IV}$ separation (presumably on account of the metal ions thus being more nearly equivalent) results in a decrease in the intervalence transition energy.[4] The latter also depends on the halogens, decreasing with increasing degree of covalency of the M^{IV}–X bond, as well as on the stereochemistry of the ligand (N–N). As indicated above, the complex with *cis*-N–N results in the highest $M^{IV} \leftarrow M^{II}$ transition energy, this being a consequence of the long $Pt^{II} \cdots Pt^{IV}$ distance which is itself a consequence of steric repulsion between these isomeric forms of the ligand in the complex along the chain direction.

Table 3. Wavenumbers (cm^{-1}), relative intensities, full-widths at half-maximum, and assignments of bands in the r.R. spectra *

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	Assignment
(*a*) $[\mathrm{Pt}\{(-)\text{-dach}\}_2][\mathrm{Pt}\{(-)\text{-dach}\}_2\mathrm{Br}_2]\mathrm{Br}_4$			
65.9			
94.8			
160.7	1.00	10.2	ν_1
194.6			
226			$\nu_1 + 65.9$
255.0			$\nu_1 + 94.8$
321.3	0.66	18.1	$2\nu_1$
356.3			$\nu_1 + 194.6$
415.0			$2\nu_1 + 94.8$
479.4	0.43	26.8	$3\nu_1$
574.3			$3\nu_1 + 94.8$
628			ν(ring)
638.3	0.27	34	$4\nu_1$
733			$4\nu_1 + 94.8$
795.2	0.17	39	$5\nu_1$
890			$5\nu_1 + 94.8$
951.9	0.11	48	$6\nu_1$
1 109.5	0.07	52	$7\nu_1$
1 267	0.05	60	$8\nu_1$
1 417	*ca.* 0.03	*ca.* 70	$9\nu_1$
1 570	<0.03	>70	$10\nu_1$
(*b*) $[\mathrm{Pt}(cis\text{-dach})_2][\mathrm{Pt}(cis\text{-dach})_2\mathrm{Br}_2]\mathrm{Br}_4$			
87.3			
152.4			
187.2	1.00	10.2	ν_1
209.3			
224.0			
242.8			
303.7			
342.5			$\nu_1 + 152.4$
374.9	0.58	22.0	$2\nu_1$
430.3			$\nu_1 + 242.8$
456.8			$\nu_1 + 303.7$
492.5			
562.7	0.37	32.3	$3\nu_1$
611.8			$2\nu_1 + 242.8$
752.5	0.27	49	$4\nu_1$
806.8			$3\nu_1 + 242.8$
939.1	0.15	59	$5\nu_1$
985			$4\nu_1 + 242.8$
1 130.8	0.10	71	$6\nu_1$
1 214			δ(H–C–H)
1 319	0.05	80	$7\nu_1$
1 500	<0.05	>80	$8\nu_1$
(*c*) $[\mathrm{Pt}\{(-)\text{-dach}\}\{(+)\text{-dach}\}][\mathrm{Pt}\{(-)\text{-dach}\}\{(+)\text{-dach}\}\mathrm{Br}_2]\mathrm{Br}_4$			
73.5			
94.4			
151.2			
163.5	1.00	8.3	ν_1
194.5			
210.6			
242.2			
257.7			$\nu_1 + 94.4$
327.6	0.69	16.5	$2\nu_1$
355.9			$\nu_1 + 194.5$
378.9			$\nu_1 + 210.6$
420.0			$2\nu_1 + 94.4$
490.4	0.43	23.6	$3\nu_1$
581			$3\nu_1 + 94.4$
626.8			ν(ring)
652.8	0.27	31	$4\nu_1$
815.4	0.20	42	$5\nu_1$
974.6	0.13	49	$6\nu_1$
1 135	0.07	55	$7\nu_1$
1 295	*ca.* 0.05	*ca.* 60	$8\nu_1$
(*d*) $[\mathrm{Pt}\{(\pm)\text{-dach}\}_2][\mathrm{Pt}\{(\pm)\text{-dach}\}_2\mathrm{Br}_2]\mathrm{Br}_4$			
67.7			
94.5			
161.0	1.00	9.1	ν_1
194.9			
208.7			
255.5			$\nu_1 + 94.5$
322.4	0.66	17.3	$2\nu_1$
355.9			$\nu_1 + 194.9$
370			$\nu_1 + 208.7$
416.1			$2\nu_1 + 94.5$
482.7	0.41	25.2	$3\nu_1$
577.6			$3\nu_1 + 94.5$
642.5	0.27	34	$4\nu_1$
735			$4\nu_1 + 94.5$
799.6	0.16	39	$5\nu_1$
958.6	0.09	43	$6\nu_1$
1 117.3	0.05	47	$7\nu_1$
1 272	<0.05	>50	$8\nu_1$
1 430	<0.05	>50	$9\nu_1$

* Obtained as CsBr discs at *ca.* 80 K with (*a*) 752.5, (*b*) 476.5, (*c*) 752.5, and (*d*) 752.5 nm excitation.

Table 4. Wavenumbers (cm^{-1}), relative intensities, full-widths at half-maximum, and assignments of bands in the r.R. spectra *

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	Assignment
(*a*) $[\mathrm{Pt}\{(-)\text{-dacp}\}_2][\mathrm{Pt}\{(-)\text{-dacp}\}_2\mathrm{Br}_2]\mathrm{Br}_4$			
69.3			
98.3			
162.2	1.00	13.8	ν_1
208.6			
238.0			
259.8			$\nu_1 + 98.3$
323.5	0.60	23.6	$2\nu_1$
370.9			$\nu_1 + 208.6$
421.3			$2\nu_1 + 98.3$
482.6	0.33	32.3	$3\nu_1$
530			$2\nu_1 + 208.6$
585			$3\nu_1 + 98.3$
643.3	0.21	44	$4\nu_1$
744.6			$4\nu_1 + 98.3$
800.3	0.11	50	$5\nu_1$
906			$5\nu_1 + 98.3$
957.0	0.06	57	$6\nu_1$
1 115	0.04	65	$7\nu_1$
1 270	*ca.* 0.02	*ca.* 75	$8\nu_1$
1 430	<0.02	>75	$9\nu_1$
(*b*) $[\mathrm{Pt}(cis\text{-dacp})_2][\mathrm{Pt}(cis\text{-dacp})_2\mathrm{Br}_2]\mathrm{Br}_4$			
105.3			
158.3			
165.7			
183.7	1.00	9.5	ν_1
209.0			
236.8			
333			2×165.7
348			$\nu_1 + 165.7$
368.5	0.30	14.2	$2\nu_1$
392.5			$\nu_1 + 209.0$
422			$\nu_1 + 236.8$
513.6			$\nu_1 + (2 \times 165.7)$
550.3	0.11	16.5	$3\nu_1$
582.0			ν(Pt–N)
615.7			ν(ring)
734.0	0.05	21	$4\nu_1$
765.7			$\nu_1 + \nu$(Pt–N)
798.5			$\nu_1 + \nu$(ring)

Table 4. (*continued*)

920	*ca.* 0.03	*ca.* 30	$5\nu_1$
1 110	<0.03	>30	$6\nu_1$

* Obtained as a CsBr disc at *ca.* 80 K with (*a*) 752.5 and (*b*) 476.5 nm excitation.

Table 5. Wavenumbers (cm^{-1}), relative intensities, full-widths at half-maximum, and assignments of bands in the r.R. spectrum of [Pt{(−)-dach}$_2$][Pt{(−)-dach}$_2$I$_2$]I$_4$ *

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	Assignment
70.9			
94.9			
108.9			
123.2	1.00	12.6	ν_1
178.0			
193.9			ν_1 + 70.9
218.9			2 × 108.9
246.3	0.53	23.6	$2\nu_1$
320.1			$2\nu_1$ + 70.9
367.7	0.26	33	$3\nu_1$
442.1			$3\nu_1$ + 70.9
490.2	0.13	41	$4\nu_1$
616.1	0.08	47	$5\nu_1$
618.9			ν(ring)
736	0.04	55	$6\nu_1$
850	0.02	67	$7\nu_1$
960	*ca.* 0.01	*ca.* 75	$8\nu_1$

* Obtained as a CsI disc at *ca.* 80 K with 752.5 nm excitation.

Table 6. Wavenumbers (cm^{-1}), relative intensities, full-widths at half-maximum, and assignments of bands in the r.R. spectra *

(*a*) [Pd{(±)-dach}$_2$][Pd{(±)-dach}$_2$Cl$_2$]Cl$_4$

$\tilde{\nu}$/cm^{-1}	$I(v_1\nu_1)/I(\nu_1)$	$\Delta\tilde{\nu}_{\frac{1}{2}}$/cm^{-1}	Assignment
153.4			
183.9			
240.8	1.00	26.8	ν_1
359.8			
389.5			
483.5	0.53	50	$2\nu_1$
594			ν(ring)
720.5	0.23	66	$3\nu_1$
953.8	0.11	83	$4\nu_1$
1 194	*ca.* 0.05	*ca.* 100	$5\nu_1$
1 210			δ(H-C-H)
1 305			
1 355			
1 430	<0.03		$6\nu_1$

(*b*) [Pd(*cis*-dach)$_2$][Pd(*cis*-dach)$_2$Cl$_2$]Cl$_4$

189			
242			ν_1(*trans*)
282			
301.9	1.00	13.4	ν_1
372			
451			ν(Pd-N)
596.7	0.54	28	$2\nu_1$
675			
750			ν_1 + ν(Pd-N)
896.6	0.28	40	$3\nu_1$
1 050			$2\nu_1$ + ν(Pd-N)
1 190	*ca.* 0.1	*ca.* 60	$4\nu_1$
1 485	<0.05		$5\nu_1$

* Obtained as a CsCl disc at *ca.* 80 K with (*a*) 752.5 and (*b*) 488.0 nm excitation.

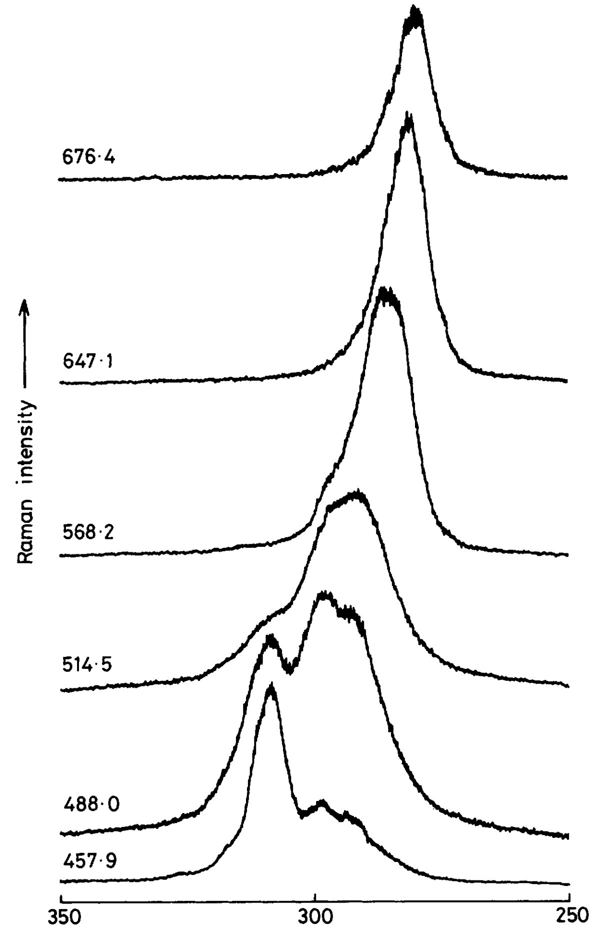

Figure 3. Shape of the ν_1 band of [Pt{(−)-dach}$_2$][Pt{(−)-dach}$_2$-Cl$_2$]Cl$_4$ at *ca.* 10 K with different excitation lines

Resonance Raman Spectra.—Raman spectra were recorded for each complex with a variety of excitation lines (457.9—799.3 nm) at *ca.* 80 K. The spectra are dominated in each case by a long overtone progression, $v_1\nu_1$, where ν_1 is the totally symmetric axial metal–halogen stretching mode (Tables 2—6). Surprisingly, the wavenumbers of ν_1 and its overtones (but not those of the ligand modes) appear to be dependent on the exciting lines used, decreasing reversibly (Pt–Cl by 15 cm^{-1}, Pt–Br by 26 cm^{-1}, Pd–Cl by 59 cm^{-1}) with decreasing excitation energy (457.9—799.3 nm). However, on closer examination of the ν_1 band at *ca.* 10 K and at a spectral resolution of 1—1.5 cm^{-1}, it was realised that the contour of this band contained several components (Figures 3—5). This observation was made only for complexes containing the *trans* ligand. The *cis* ligand gives rise to a complex with the highest value for ν_1, a result which indicates that the Pt$^{\text{IV}}$(N–N)$_2$X$_2$ moiety is in this case most near (of the mixed-valence complexes studied) to behaving like a free moiety, and thus with most nearly ' terminal ' (and therefore short) Pt$^{\text{IV}}$–X bonds.

The most probable interpretation, therefore, of the change in ν_1 band structure with change in $\tilde{\nu}_0$ is that the complexes, where prepared from the unresolved ligand, are in fact mixtures of conformational isomers: [M$^{\text{II}}$(*trans*-N–N)$_2$][M$^{\text{IV}}$-(*trans*-N–N)$_2$X$_2$]X$_4$ [Figure 1(*a*)—(*c*)], [M$^{\text{II}}$(*cis*-N–N)$_2$]-[M$^{\text{IV}}$(*trans*-N–N)$_2$X$_2$]X$_4$ [Figure 1(*d*)], [M$^{\text{II}}$(*trans*-N–N)]-[M$^{\text{IV}}$(*cis*-N–N)(*trans*-N–N)X$_2$]X$_4$ [Figure 1(*e*)], [M$^{\text{II}}$(*trans*-N–N)$_2$][M$^{\text{IV}}$(*cis*-N–N)$_2$X$_2$]X$_4$, [M$^{\text{II}}$(*cis*-N–N)(*trans*-N–N)]-[M$^{\text{IV}}$(*cis*-N–N)(*trans*-N–N)X$_2$]X$_4$ [Figure 1(*f*)], [M$^{\text{II}}$(*cis*-

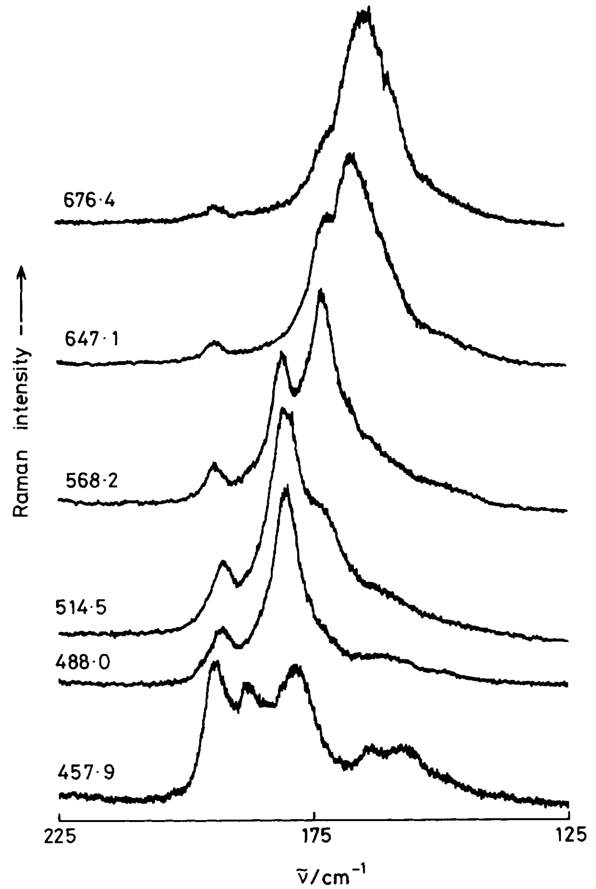

Figure 4. Shape of the ν_1 band of $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2Br_2]Br_4$ at *ca.* 10 K with different excitation lines

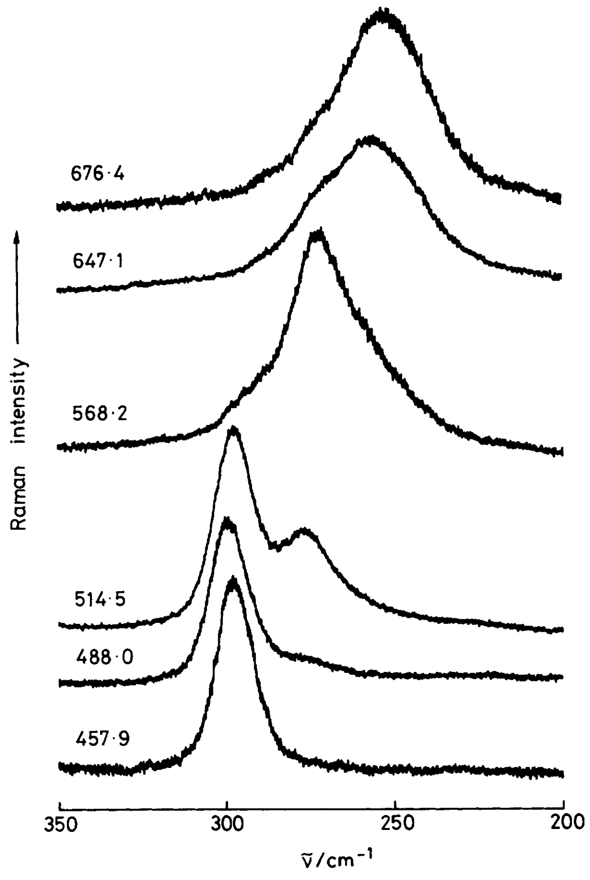

Figure 5. Shape of the ν_1 band of $[Pd(\text{dach})_2][Pd(\text{dach})_2Cl_2]Cl_4$ at *ca.* 10 K with different excitation lines

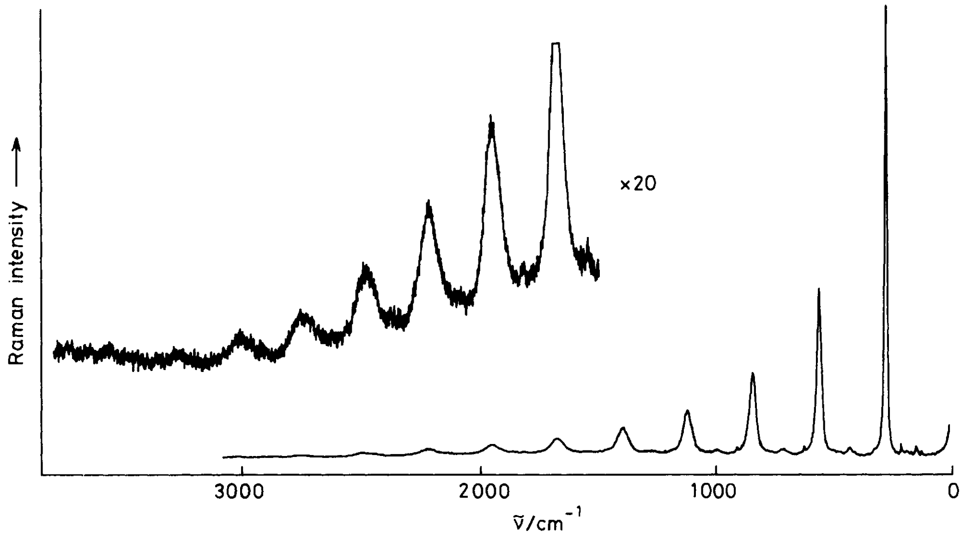

Figure 6. Resonance Raman spectrum of $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2Cl_2]Cl_4$ at *ca.* 80 K with 647.1 nm excitation

$N\text{-}N)_2][M^{IV}(cis\text{-}N\text{-}N)_2X_2]X_4$ [Figure 1(*g*) and (*h*)], each with its own ν_1 value and optimum excitation wavenumber for maximum resonance enhancement. The situation is further complicated by the possibility of the occurrence of different forms of, for example, the last of the complexes above. A further observation is that, when exciting the r.R. spectrum of the *trans* complexes with exciting lines of wavenumber intermediate between that of the electronic band maxima of the all-*trans* and all-*cis* forms, combination bands appear involving both ν_1(all-*trans*) and ν_1(all-*cis*): *e.g.* $2\nu_1$(*trans*) at

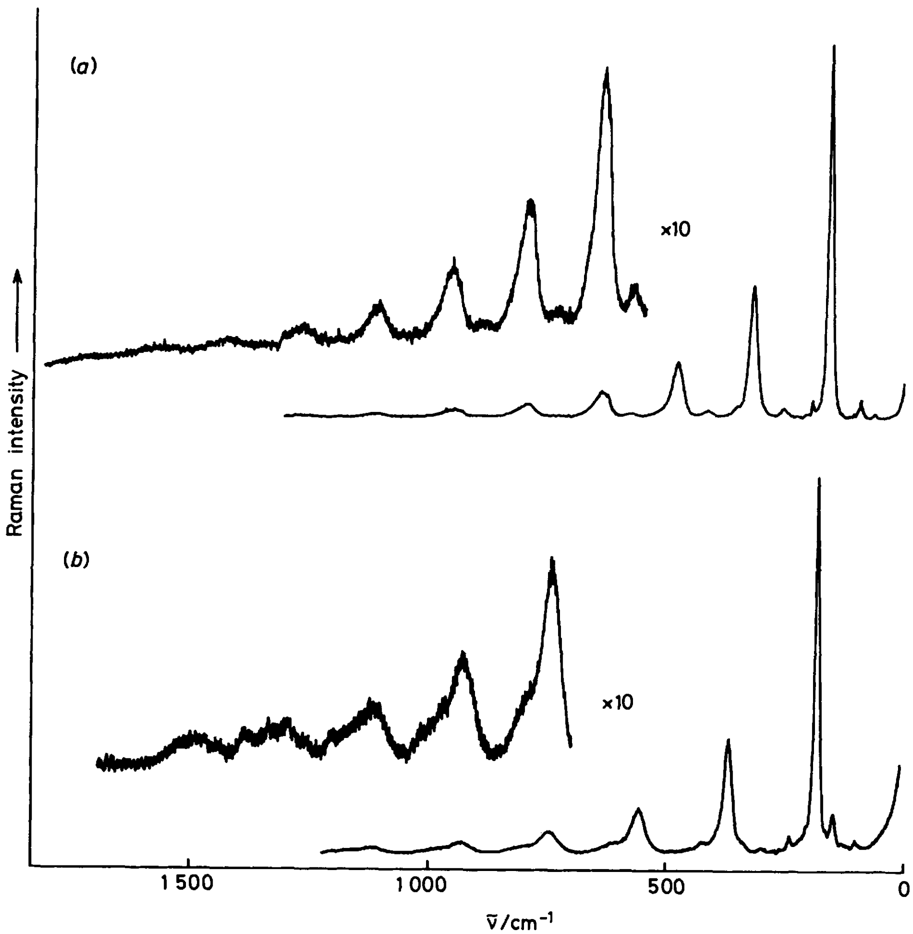

Figure 7. Resonance Raman spectra of (*a*) [Pt{(−)-dach}$_2$][Pt{(−)-dach}$_2$Br$_2$]Br$_4$ at *ca.* 80 K with 752.5 nm excitation, and (*b*) [Pt(*cis*-dach)$_2$][Pt(*cis*-dach)$_2$Br$_2$]Br$_4$ at *ca.* 80 K with 476.5 nm excitation

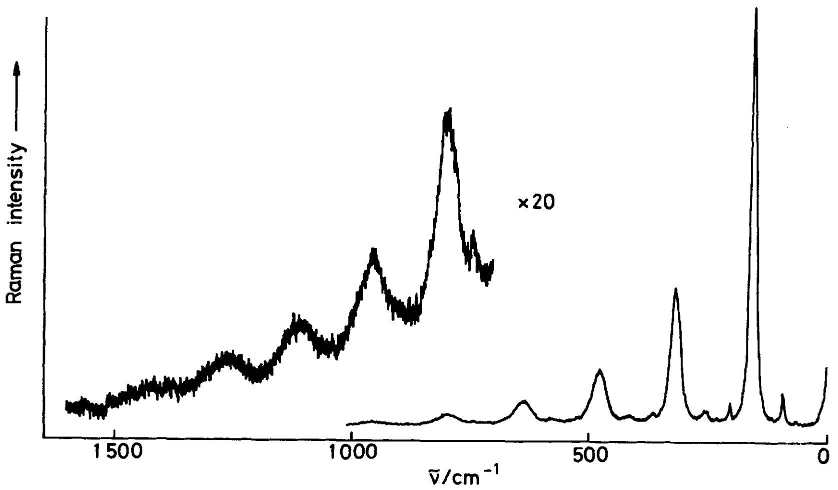

Figure 8. Resonance Raman spectrum of [Pt{(−)-dacp}$_2$][Pt{(−)-dacp}$_2$Br$_2$]Br$_4$ at *ca.* 80 K with 752.5 nm excitation

333 cm^{-1}, ν_1(*cis*) + ν_1(*trans*) at 348 cm^{-1}, and 2ν_1(*cis*) at 368.5 cm^{-1} for [Pt{(−)-dacp}$_2$][Pt{(−)-dacp}$_2$Br$_2$]Br$_4$ with 476.5 nm excitation (Table 4). This suggests that all-*trans* sections and all-*cis* sections may exist within a single chain.

By comparison of the results for the chloro-complexes of palladium and platinum with 1,2-diaminocyclohexane, it is evident that the wavenumber of ν_1 is much more sensitive to the configuration of the ligand for Pd than for Pt, presumably on account of the smaller size of palladium ions.

The observed long overtone progressions in ν_1 (Figures

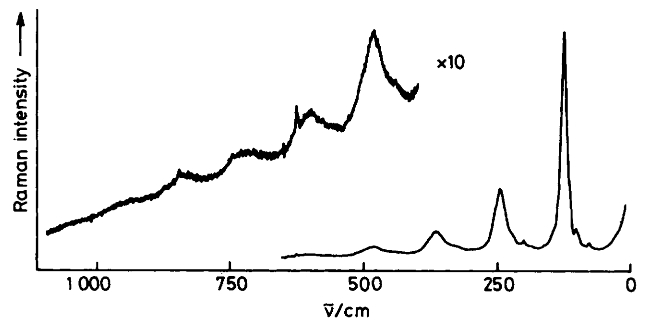

Figure 9. Resonance Raman spectrum of $[Pt\{(-)\text{-dach}\}_2][Pt\{(-)\text{-dach}\}_2I_2]I_4$ at *ca.* 80 K with 799.3 nm excitation

6—10) permit the calculation by standard procedures,[18,19] of approximate values for the harmonic wavenumbers (ω_1) and anharmonicity constants (x_{11}) for each conformer of each complex studied. The results, which are included in Table 1, indicate that ω_1 decreases in the order Cl > Br > I, Pt > Pd, *cis* > *meso* > racemate > *trans*, and *cis*-dach > *cis*-dacp. The x_{11} values are all small (0.0—0.9 cm^{-1}) and all the x_{11}/ω_1 values lie in the range 0—0.003. These are quite typical values for x_{11} for the ν_1 mode of linear-chain complexes.[1]

We had originally supposed that x_{11} for the chloro-complex (1) might be unusually high, due to the fact that this complex has the shortest known $Pt^{II}\cdots Pt^{IV}$ distance (5.158 Å) for a linear-chain complex, and therefore the one for which the chlorine atom is most near to being placed centrally between the platinum atoms (Pt^{IV}–Cl = 2.324 Å, Pt^{II}–Cl = 2.834 Å).[9] However, this appears not to be the case, presumably because the chlorine, even in this complex, is still much closer (by >0.5 Å) to the platinum(IV) than to the platinum(II).

Conclusion

A summary of the key properties of all the complexes studied is given in Table 1. The complexes are all strongly coloured [platinum chlorides are green, bromides are gold (except for that of *cis*-dach, which is purple), and the iodide is black], highly dichroic, usually forming as needles. All show very intense r.R. spectra which are dominated by the $v_1\nu_1$ progression, which is at most observed to reach as far as the eleventh harmonic. The anharmonicity constant x_{11} is small, being <0.9 cm^{-1} in all cases. The key conclusions are (*a*)—(*c*) below.

(*a*) Of all linear-chain chlorine-bridged complexes of the type studied, the (−)-dach complex has the shortest $Pt^{II}\cdots Pt^{IV}$ distance (5.158 Å), the lowest $Pt^{IV}\leftarrow Pt^{II}$ intervalence band maximum (19 400 cm^{-1}) and excitation profile maximum ($EP_{max.}$ 13 100 cm^{-1}), though both are approximately equal to that for $\{[Pt(en)_2][Pt(en)_2Cl_2]\}_3[CuCl_4]_4$ (en = ethylenediamine),[4] and the lowest value for ω_1 (285.5 cm^{-1}). This is persuasive evidence that all these quantities are related to one another.

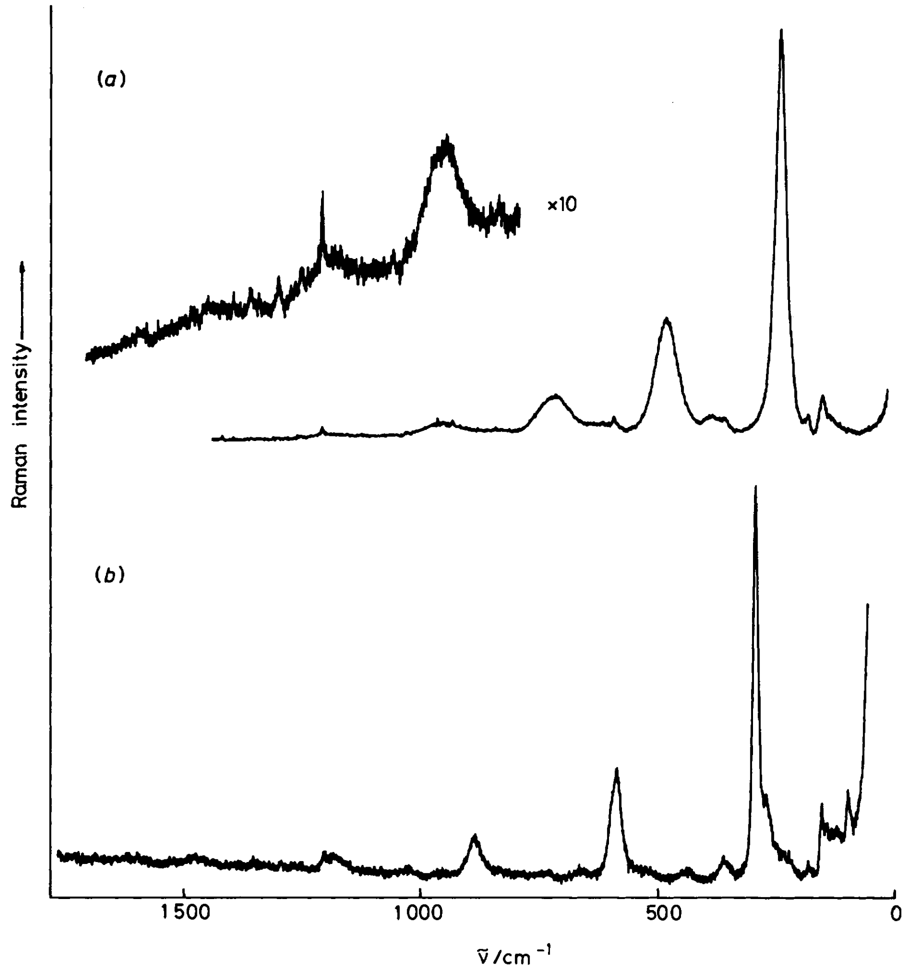

Figure 10. Resonance Raman spectrum of $[Pd(dach)_2][Pd(dach)_2Cl_2]Cl_4$ at *ca.* 80 K, (*a*) with 752.5 nm excitation and (*b*)with 488.0 nm excitation

(*b*) The trends in $\nu_{max.}$, $EP_{max.}$, and ν_1 are all in the order Cl > Br > I, Pt > Pd, *cis* > *meso* > racemate > *trans*, and *cis*-dach > *cis*-dacp. These results indicate that, as expected, the $Pt^{II} \cdots Pt^{IV}$ distance is affected by steric factors associated with the amine ligands, but that this distance itself is not the only factor which affects the extent of interaction between the platinum atoms. Clearly the overlap integrals between suitable orbitals on the metal atom and the bridging ligand are also important, and this factor is at a maximum (among bridging ligands) for iodine, and higher for palladium than for platinum.

(*c*) The different configurations of dach seem all capable of forming linear-chain complexes, all with slightly different $\nu_{max.}$ and ν_1 values; a mixture of isomers with the mixed-valence complexes is thus normally obtained. A consequence of this is that there is an apparent variation of ν_1 with excitation wavenumber. At high resolution, however, the separate ν_1 bands can be resolved, and it is clear that the observations are a consequence of exciting ν_1 of different isomers more effectively at different excitation wavenumbers.

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