Low-temperature Far-infrared Spectra of some Tetrachloropalladate(II) and Tetrachloroplatinate(II) Salts

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Far-i.r. spectra of $A_2[PdCl_4]$ and $A_2[PtCl_4]$ (A = K, NH_4, or ND_4) have been investigated at temperatures below 100 K for the first time. Several new bands occur in the 200—360 cm^{-1} region on cooling to *ca.* 20 K. These and other features are discussed with the aid of single-crystal polarised-transmission measurements on $[NH_4]_2[MCl_4]$ (M = Pd or Pt) in the range 60—180 cm^{-1}, which yield evidence for the positions of the translatory modes. A theoretical analysis is given of the space groups to which these solids might transform at low temperatures. Among the structural possibilities considered are out-of-plane distortions of the anions.

AT room temperature $K_2[PdCl_4]$, $K_2[PtCl_4]$, and $[NH_4]_2[PdCl_4]$ crystallise in the tetragonal system with the symmetry of space group $P4/mmm$ ($\equiv D_{4h}^1$), $Z = 1$.[1-4] Accordingly factor-group analysis (f.g.a.) predicts simple vibrational spectra (Table 1) which have been studied often, but never at very low temperatures. In this paper we report that the far-i.r. spectra of the above compounds, as well as those of $[NH_4]_2[PtCl_4]$, $[ND_4]_2[PtCl_4]$, and $[ND_4]_2[PdCl_4]$ (which are reasonably presumed to be isostructural), become rather complex below *ca.* 150 K, and consider reasons for this behaviour. The increasing use of very low sample temperatures in vibrational spectroscopy holds dangers of interpretation which are well illustrated by our observations on these simple and highly symmetric systems in which anomalies are readily recognised. We began this work in the expectation that the ammonium salts would undergo a phase change at low temperatures due to the need to form a structure capable of accommodating this cation at temperatures below those at which it rotates within the lattice, and also because assignment of their far-i.r. spectra had not been settled for the lattice-mode region. The potassium salts were included due to the need for improved analysis of their spectra prior to understanding their behaviour under pressure.[5]

RESULTS

Our new data are shown in Table 2 and in Figures 1 and 2 (polycrystalline samples). Single-crystal absorption spectra of $[NH_4]_2[PdCl_4]$ and $[NH_4]_2[PtCl_4]$ were also obtained in polarised light in the 60—180 cm^{-1} region at temperatures

TABLE 1

Unit-cell-group analysis of $A_2[MCl_4]$ (D_{4h}^1, $Z = 1$) *

D_{4h}	T_A	T	R^-	R^+	N_i	Activities
A_{1g}					1	Raman ($x^2 + y^2$, z^2)
A_{2g}			1	1		
B_{1g}					1	Raman ($x^2 - y^2$)
B_{2g}				1	1	Raman (xy)
E_g			1	2		Raman (xz, yz)
A_{1u}						
A_{2u}	1	1			1	i.r. (z)
B_{1u}					1	
B_{2u}		1				
E_u	1	2			2	i.r. (x, y)

* Internal modes of A (where applicable) have been omitted. The C_2' axis of the D_{4h} factor group coincides with the crystallographic x axis. T_A = acoustic, T = optic-branch translatory, and R^- = rotatory modes of $[MCl_4]^{2-}$; R^+ = rotatory modes of $[NH_4]^+$ (where applicable); and N_i = internal modes of $[MCl_4]^{2-}$.

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[1] R. G. Dickenson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404.

[2] W. Theilacker, *Z. anorg. Chem.*, 1937, **234**, 161.

[3] J. D. Bell, D. Hall, and T. N. Waters, *Acta Cryst.*, 1966, **21**, 440.

[4] R. H. B. Mais, P. G. Owston, and A. M. Wood, *Acta Cryst.*, 1972, **B28**, 393.

[5] D. M. Adams and S. J. Payne, unpublished work.

TABLE 2

Vibrational frequencies (wavenumbers/cm^{-1}) and assignment for $A_2[MCl_4]$. Values are given for ambient temperature with those for *ca.* 20 K in parentheses

			$[PdCl_4]^{2-}$			$[PtCl_4]^{2-}$		
D_{4h}	Mode	Type	A = NH_4	ND_4	K	NH_4	ND_4	K
I_1	A_{1g}	$\nu(MX)_{sym}$	304 (305)		307 [a]	326 [a]		332 [b]
I_2	B_{1g}	$\delta(MX_4)$			195 [a]	196 [a]		200 [b]
I_3	B_{2g}	$\nu(MX)_{asym}$			274 [a]	306 [a]		308 [b]
I_4	A_{2u}	$\pi(MX_4)$	173 (188)	*ca.* 165 (172)	*ca.* 172 (172)	*ca.* 170 (186)	*ca.* 160 (170)	174 (173)
I_5	B_{1u}	$\pi(MX_4)$						
I_6	E_u	$\nu(MX_4)_{asym}$	332 (338)	333 (337)	335 (342)	322 (326)	324 (324)	325 (328)
I_7	E_u	$\delta(MX_4)$	210 (219)	*ca.* 200 (210)	*ca.* 191 (195)	*ca.* 206 (216)	*ca.* 215 (210)	191 (196)
R_1	A_{2g}	$R_z(MX_4)$						
R_2	E_g	$R_{x,y}(MX_4)$	70 (80)		71 [a]	78 [a]		
T_1	A_{2u}	T_z	*ca.* 125 (*ca.* 129)	*ca.* 115 (*ca.* 120)	*ca.* 108 (113)	*ca.* 117 (*ca.* 119)	*ca.* 104 (*ca.* 109)	*ca.* 100 (*ca.* 102)
T_2	B_{2u}	T_z						
T_3	E_u	$T_{x,y}$	*ca.* 125 (*ca.* 137)	*ca.* 115 (*ca.* 125)	*ca.* 115 (122)	*ca.* 128 (*ca.* 130)	*ca.* 110 (*ca.* 117)	113 (119)
T_4	E_u	$T_{x,y}$	*ca.* 125 (*ca.* 120)	*ca.* 115 (*ca.* 100)	92 (97)	*ca.* 116 (*ca.* 124)	*ca.* 104 (*ca.* 95)	89 (94)
R_3	A_{2g}	$R_z(A)$						
R_4	B_{2g}	$R_z(A)$						
R_5	E_g	$R_{x,y}(A)$						
R_6	E_g	$R_{x,y}(A)$						
	Other bands		308 [c] {(312) (308)	298 (298)	295 {(*ca.* 310) (295)	304 (305)		br {(298) (287) (275) (235) (223)
						282 (284)		
			298 (298)		275 {(277) (270)			
			165 (169)		(240)			
			(92)			(92)	79 (79)	

[a] Ref. 8. [b] Ref. 9. [c] Frequencies for 'other bands' are given at *ca.* 80 K with those for *ca.* 20 K in parentheses.

down to *ca.* 20 K. The new observation is that as the temperature of each of the six compounds was lowered progressively to 20 K new bands gradually appeared, mostly in the 200—360 cm^{-1} region, and shifted to higher frequency. Since all the bands predicted on the basis of the room-temperature structure are already present in the room-temperature spectra, these new bands require an explanation in terms of either a phase transition to a new structure or second-order processes within the old one. A further notable feature is the breadth of the central region of the spectra of the ammonium salts.

ASSIGNMENT AND DISCUSSION

We first note previous spectroscopic work on these compounds. Complete Raman [6,7] and i.r. solution data,[6] and single-crystal Raman studies (at room temperature) of $K_2[PdCl_4]$ and $[NH_4]_2[PtCl_4]$,[8] have established the room-temperature anion and solid-state assignments unambiguously, except for the order of the i.r.-active $I_4(A_{2u})$ $\pi(MCl_4)$ and $I_7(E_u)$ $\delta(MCl_4)$ modes which was settled for $K_2[PtCl_4]$ by a single-crystal i.r. study.[9] In addition there are several reports of Raman [10,11] and i.r.[12-17] work on powder samples of which some i.r. evidence was collected at 'liquid-nitrogen temperature';[13,17] with the exception of a very weak combination band at 358 cm^{-1} for $K_2[PtCl_4]$, and some weak features at *ca.* 280—300 cm^{-1} for $Cs_2[PtCl_4]$ and $Cs_2[PtBr_4]$,[13] only fundamentals were detected. In the single-crystal i.r. study [9] of $K_2[PtCl_4]$ it was also noted that I_4 appears to be in resonance with a combination. The main features of the room-temperature spectra thus assigned for $A_2[MCl_4]$ are: (*i*) $I_6(E_u)$ ν(M–Cl) at *ca.* 320 cm^{-1}; (*ii*) a middle region at *ca.* 150—260 cm^{-1} containing $I_4(A_{2u})$ and $I_7(E_u)$ close together; and (*iii*) three translatory modes ($A_{2u} + 2E_u$) in the region 80—120 cm^{-1}, exactly in accord with f.g.a. predictions.

The Lattice-mode Region.—For the room-temperature structure (D^1_{4h}) f.g.a. predicts three i.r.-active translatory modes, A_{2u} (z-polarised) + $2E_u$ (x- and y-polarised). When the cation is ammonium rotatory modes are possible for it but for D_{4h} these have only Raman activity (Table 1). For $K_2[PtCl_4]$ single-crystal absorption work [9] confirmed the order E_u (112) > A_{2u} (98) > E_u (87 cm^{-1}). Since ammonium is much lighter than potassium it was thought that one or more of these

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[6] P. L. Goggin and J. Mink, *J.C.S. Dalton*, 1974, 1479.

[7] Y. M. Bosworth and R. J. H. Clark, *Inorg. Chem.*, 1975, **14**, 170.

[8] I. R. Beattie and T. R. Gilson, *Proc. Roy. Soc.*, 1968, **A307**, 407.

[9] D. M. Adams and D. C. Newton, *J. Chem. Soc.* (*A*), 1969, 2998.

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[12] J. R. Durig, R. Layton, D. W. Sink, and B. R. Mitchell, *Spectrochim. Acta*, 1965, **21**, 1367.

[13] J. H. Fertel and C. H. Perry, *J. Phys. and Chem. Solids*, 1965, **26**, 1773.

[14] H. Poulet, P. Delorme, and J. P. Mathieu, *Spectrochim. Acta*, 1964, **20**, 1855.

[15] A. Sabatini, L. Sacconi, and V. Shettino, *Inorg. Chem.*, 1964, **3**, 1775.

[16] J. Hiraishi and T. Shimanouchi, *Spectrochim. Acta*, 1966, **22**, 1483.

[17] C. H. Perry, D. P. Athans, E. F. Young, J. R. Durig, and B. R. Mitchell, *Spectrochim. Acta*, 1967, **A23**, 1137.

translatory modes would be correspondingly higher in frequency and probably be part of the broad middle region of the $[NH_4]_2[MCl_4]$ spectra. Our new single-crystal results show that the lattice modes are much lower than predicted on the basis of mass difference, and are very sensitive to the strength of the hydrogen bonding to ammonium, as shown by the much lower lattice-mode frequency (97 cm^{-1}) reported for $[NH_4]_2[PdBr_4]$.[17]

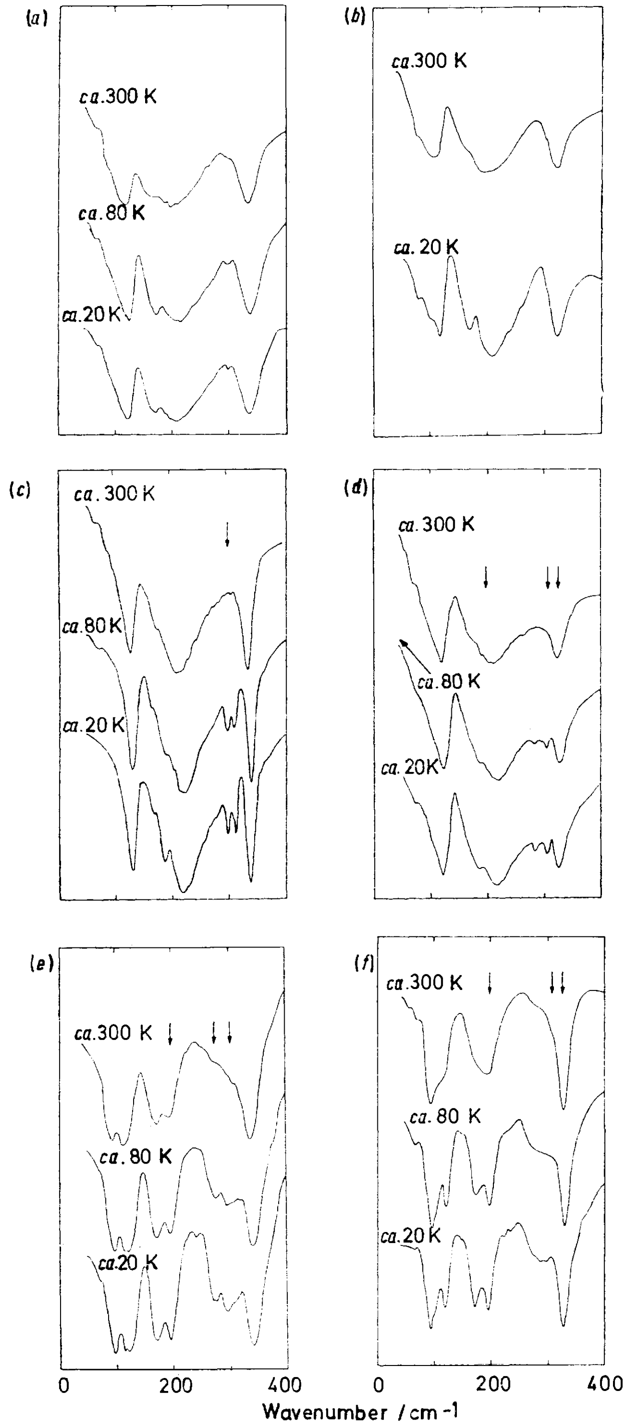

FIGURE 1 Far-i.r. transmission spectra of $A_2[MCl_4]$ powder samples in pressed polyethylene discs. Positions of Raman-active bands are indicated by arrows: (*a*), $[ND_4]_2[PdCl_4]$; (*b*), $[ND_4]_2[PtCl_4]$; (*c*), $[NH_4]_2[PdCl_4]$; (*d*), $[NH_4]_2[PtCl_4]$; (*e*), $K_2[PdCl_4]$; (*f*), $K_2[PtCl_4]$

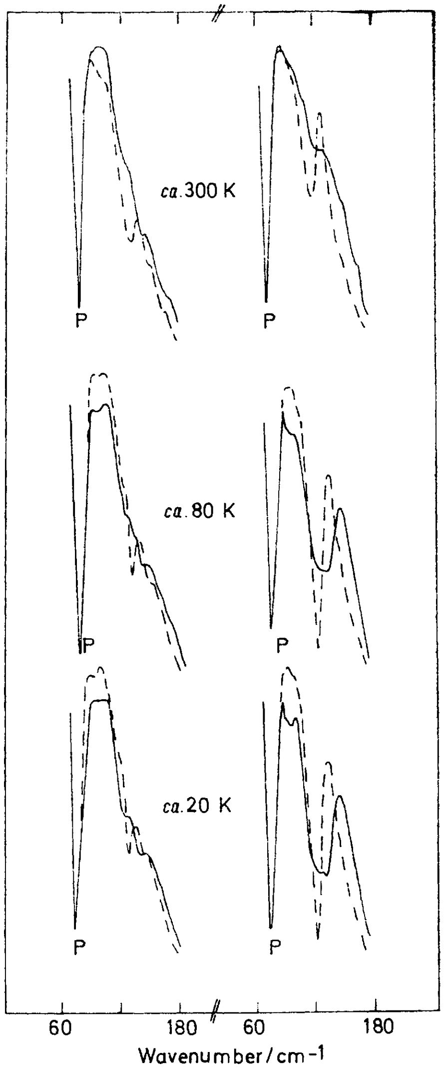

FIGURE 2 Far-i.r. transmission spectra of $[NH_4]_2[PdCl_4]$ (at left) and $[NH_4]_2[PtCl_4]$ as needles mounted in epoxy resin on polyethylene: $E\perp c$ (solid line); $E\parallel c$ (broken line). P = band due to polyethylene

The above order of symmetry species is retained in the salts we have studied. In $[NH_4]_2[PdCl_4]$ the three bands are so close that in powder samples they appear as one (with slight asymmetry) even at 20 K. The A_{2u} mode (120 cm^{-1}) and one of the E_u modes are virtually coincident in $[NH_4]_2[PtCl_4]$, again a result which could only be achieved by single-crystal methods. For both salts the lattice modes shift by nearly the calculated amount on replacement of $[NH_4]^+$ by $[ND_4]^+$. Location of all three translatory modes near 120 cm^{-1} shows that no contribution of this origin need be sought in the broad middle region.

At all temperatures at which we have studied these spectra the same number of bands seem to be present, showing only steady sharpening with decrease of temperature. From this we tentatively conclude that the primitive cell remains unimolecular throughout; there is, however, the possibility that accidental degeneracy could invalidate this conclusion.

The Middle Region (*ca.* 150—260 cm^{-1}).—This is known to contain only two fundamentals, I_4 and I_7, which are close to each other. Single-crystal work on $K_2[PtCl_4]$ showed that I_4 was broad and hence probably in resonance with a combination. Since second-order processes are allowed by virtue of anharmonicity they have negative temperature dependences.[18] Our new observation that by 20 K the middle regions of the i.r. spectra of $K_2[PdCl_4]$ and $K_2[PtCl_4]$ have sharpened substantially therefore supports the supposed origin of the breadth of I_4.

As is clear from Figure 1 the middle region for the ammonium salts is much broader than for $A = K^+$ and remains so even at 20 K although, by that temperature, a prominent shoulder has developed at *ca.* 187 cm^{-1} and shifts to *ca.* 172 cm^{-1} on deuteriation; we assign this shoulder to I_4 (A_{2u}). The deuteriation shift is reasonable as hydrogen bonding is a good medium for coupling internal and lattice modes. The fundamental $I_7(E_u)$ is presumed to account for most of the intensity of the central maximum, assisted by combinations such as the following which yield values in the 180—220 cm^{-1} region: (A_{2u}) $I_1 - T_1$; (E_u) $I_1 - T_3$, $I_1 - T_4$, $R_1 + T_3$, $R_1 + T_4$, $I_3 - T_4$, $R_2 + T_1$, $R_2 + I_5$, and $R_2 + T_2$. The difference modes are unlikely to contribute significantly at low temperature as they are more temperature sensitive than positive combinations. Attempts to confirm the middle region assignment by single-crystal methods were frustrated by difficulties in obtaining sufficient transmission through thin crystal slices.

The Region above ca. 260 cm^{-1}.—In the single-crystal spectra of $[NH_4]_2[PdCl_4]$ and $[NH_4]_2[PtCl_4]$ the ν(M–Cl) bands showed the expected polarisation behaviour (*i.e.* present in x-polarised spectra), but the new low-temperature bands showed mixed dichroic properties. Their precise origin cannot be defined without much further experimental work, but our current evidence may be consistently interpreted by postulating that on cooling below 150 K all the compounds studied (including the potassium salts) undergo a second-order phase change with lowering of symmetry. The key observation which suggests this is that the new bands gain intensity on cooling; two-phonon processes in the parent D_{4h}^1 structure should lose intensity as the temperature is lowered.

For the ammonium salts decrease of temperature will increase the barrier to cation rotation and decrease the energy available for surmounting it; for the D_{4h}^1 structure such rotatory modes are restricted to the Raman spectra (Table 1); their activities in possible lower-symmetry structures are considered below. Clearly, no such mechanism is possible in the potassium salts, which also show new low-temperature bands. Accordingly we are encouraged to seek a consistent interpretation covering the whole set of compounds (K^+ and $[NH_4]^+$ salts), whilst recognising that different causes may be involved for the two types. Although the temperature dependence of the new bands strongly suggests that they are not due to two-phonon modes in the parent structure, we first show that there is a second reason for rejecting this explanation, *viz.* the paucity of allowed combinations of appropriate energy.

$K_2[PdCl_4]$ *and* $K_2[PtCl_4]$.—In D_{4h} no zone-centre overtones are allowed (since $u \times u = g \times g = g$) but the following symmetry combinations can in principle result in i.r. activity (*i.e.* yield A_{2u} or E_u in the symmetric direct product): (A_{2u}) $A_{1g} \times A_{2u}$, $A_{2g} \times A_{1u}$, $B_{1g} \times B_{2u}$, $B_{2g} \times B_{1u}$; and (E_u) $E_g \times$ (A_{1u}, A_{2u}, B_{1u}, or B_{2u}) and $E_u \times$ (A_{1g}, A_{2g}, B_{1g}, or B_{2g}). It is to be noted that the product $E_g \times E_u$ does not contain A_{2u} since this is in the antisymmetric part and is not associated with i.r. activity. Inserting known frequencies (Table 2) we find that the following are the only binary combinations for $K_2[PdCl_4]$, ($K_2[PtCl_4]$), capable of giving wavenumbers in the 250—330 cm^{-1} region: (A_{2u}) $I_2 + T_2 \approx 305(300)$; ($E_u$) $I_2 + T_3 = 310(313)$, $I_2 + T_4 = 287(289)$, and $I_7 + R_1 \approx 262(276)$, cm^{-1}. The mode T_2 is inactive [estimated as 110(100) cm^{-1}] and hence unlikely to generate appreciable i.r. activity in combination with a Raman-active mode; R_1 is also inactive [estimated as 71(80) cm^{-1}]. This leaves only two reasonable combinations, I_2 plus T_3 or T_4: these are insufficient to account for the number of new low-temperature band maxima, and their breadth, unless a major contribution comes from other critical points in the Brillouin zone. It is important to recall that although i.r. photons have wavevector $\boldsymbol{K} \approx 0$ they can interact with lattice phonons from throughout the zone in second-order processes: conservation of momentum requires $\sum_i \boldsymbol{k}_i \approx 0$, where $\boldsymbol{k}_i$ is a phonon wavevector, and this is satisfied by either a zone-centre combination where both $\boldsymbol{k}_i \approx 0$ (such as we have considered above), or because of the creation and annihilation of pairs of phonons with equal and opposite (but non-zero) $\boldsymbol{k}_i$ from critical points throughout the zone. In the absence of knowledge of the dispersion behaviour of these solids (which would repay study by inelastic neutron scattering) we have been restricted to a consideration of zone-centre processes.

The above arguments all suggest that the new low-temperature bands in $K_2[PdCl_4]$ and $K_2[PtCl_4]$ cannot be adequately explained on the basis of the parent D_{4h}^1 structure. Accordingly we consider the possibility of a phase transition. Following Lifshitz's principle we seek new structures which have the symmetry of sub-groups of D_{4h}. Among other possibilities we have considered explicitly structures in which: (*a*) the anions are rotated about the z, x, or x' (at 45° to x and y) axes; (*b*) the cations and anions are shifted relative to each other; and (*c*) the square-planar anions are permanently distorted in the form of one of the out-of-plane modes

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[18] P. M. A. Sherwood, 'Vibrational Spectroscopy of Solids,' Cambridge, 1972.

TABLE 3

Possible new space groups for $A_2[MCl_4]$ and their selection rules

(a) New space group and number

		Nature of change from D_{4h}^1
C_{2h}^1	10	rotation of $[MX_4]^{2-}$ about x'
C_{2h}^3	12	rotation of $[MX_4]^{2-}$ about x
C_{4h}^1	83	rotation of $[MX_4]^{2-}$ about z
C_{4v}^1	99	A_{2u} out-of-plane distortion of $[MX_4]^{2-}$
D_{2d}^1	111	B_{1u} out-of-plane distortion of $[MX_4]^{2-}$
D_{2d}^5	115	movement of K^+ relative to $[MX_4]^{2-}$
D_4^1	89	orientation of $[NH_4]^+$
D_{2d}^1	111	orientation of $[NH_4]^+$

(b) Correlations from D_{4h}

		$C_2' \longrightarrow C_2'$				C_2'	C_2''
	D_{4h}^1	D_{2d}	C_{4v}	D_4	C_{4h}	C_{2h}	C_{2h}
I_i	A_{1g}	A_1	$A_1(z)$	A_1	A_g	A_g[a]	A_g[a]
	B_{1g}	B_1	B_1	B_1	B_g	A_g	B_g
	B_{2g}	$B_2(z)$	B_2	B_2	B_g	B_g	A_g
	$A_{2u}(z)$	$B_2(z)$	$A_1(z)$	$A_2(z)$	$A_u(z)$	B_u	B_u
	B_{1u}	A_1	B_2	B_1	B_u	A_u	B_u
	$2E_u(x,y)$	$2E(x,y)$	$2E(x,y)$	$2E(x,y)$	$2E_u(x,y)$	$2(A_u + B_u)$	$2(A_u + B_u)$
R_i^-	A_{2g}	A_2	A_2	$A_2(z)$	A_g	B_g	B_g
	E_g	$E(x,y)$	$E(x,y)$	$E(x,y)$	E_g	$A_g + B_g$	$A_g + B_g$
T_i	$A_{2u}(z)$	$B_2(z)$	$A_1(z)$	$A_2(z)$	$A_u(z)$	B_u	B_u
	B_{2u}	A_2	B_1	B_2	B_u	B_u	A_u
	$2E_u(x,y)$	$2E(x,y)$	$2E(x,y)$	$2E(x,y)$	$2E_u(x,y)$	$2(A_u + B_u)$	$2(A_u + B_u)$
R_i^+	A_{2g}	A_2	A_2	$A_2(z)$	A_g	B_g	B_g
	B_{2g}	$B_2(z)$	B_2	B_2	B_g	B_g	A_g
	$2E_g$	$2E(x,y)$	$2E(x,y)$	$2E(x,y)$	E_g	$2(A_g + B_g)$	$2(A_g + B_g)$
T[b]	3	3	3	3	3	6	6
R^-[b]	0	1	1	2	0	0	0
R^+[b]	0	3	2	3	0	0	0
ν(MX)[b]	1	2	2	1	1	2	2

[a] All g modes are Raman and all u modes are i.r. active. [b] Numbers of i.r.-active modes are given: symbols defined as in Table 1.

$I_4(A_{2u})$ or $I_5(B_{1u})$. Although square-planar geometry is the norm for Pd^{II} and Pt^{II} it is not invariable. Thus, *cis*-$[PtCl_2(PMe_3)_2]$ is distorted towards tetrahedral, probably for steric reasons.[19] All these geometrical possibilities are illustrated in Figure 3 and lead to the space groups and selection rules of Table 3.

Ammonium Salts.—Arguments similar to those used for the potassium salts apply. Comparison of the allowed zone-centre combinations with the low-temperature spectra shows only modest agreement, as for the potassium salts. Thus for $[NH_4]_2[PdCl_4]$ ($[NH_4]_2[PtCl_4]$) we obtain the combinations: (A_{2u}) $I_2 + T_2 \approx 323(314)$; ($E_u$) $I_2 + T_3 = 320(324)$, $I_2 + T_4 = 320(312)$, $I_4 + R_2 = 280(284)$, and $I_7 + R_1 \approx 281(284)$ cm^{-1}, where inactive T_2 was taken as 128(118) and R_1 as 71(78) cm^{-1}. In addition, combinations involving rotatory modes of ammonium must be considered. Taking 250 cm^{-1} as a reasonable value no new combinations come within the right frequency range. Although this would account for the number of bands the temperature dependence is not explained.

Phase transitions are to be expected in the ammonium salts by analogy with the known complicated structural behaviour of $[NH_4]X$ (X = Cl, Br, or I) and many other ammonium salts. When $[NH_4]^+$ loses some or all of its rotational freedom as the temperature of $[NH_4]_2[MCl_4]$ (M = Pd or Pt) is lowered a new structure must be formed which is compatible in symmetry with $[NH_4]^+$. We have considered possible periodic hydrogen-bonded arrays for the $K_2[PtCl_4]$ structure. If the cell remains unimolecular only two are possible; they are shown in Figure 3 and their selection rules in Table 3. We note that the D_{2d}^1 structure is obtained both by consideration of a hydrogen-bonding scheme and by a B_{1u}-type distortion of $[MX_4]^{2-}$ and can therefore form the basis of a unified explanation for the whole set of results. This also provides an explanation for the observed trend in band intensities at low temperatures: $[NH_4]_2[PdCl_4] > K_2[PdCl_4] > [NH_4]_2[PtCl_4] > K_2[PtCl_4]$. We postulate that the resistance of square-planar Pd^{II} to out-of-plane deformation is intermediate between those of Ni^{II} and Pt^{II}. The deformation can also be reinforced in $[NH_4]^+$ salts as shown, and its extent is presumed to be proportional to the intensity of the new bands.

Selection Rules for the New Structures.—The new low-temperature features in $K_2[PdCl_4]$ cannot be due to transformation to a space group having a factor group in which D_{4h} Raman-allowed ν(M–Cl) modes become i.r. active. As Table 3 shows I_1 can become i.r. active in C_{4v} only, and I_3 only in D_{2d}, and hence these factor groups cannot account even for the number of new features let alone their frequencies. The same argument applies to $K_2[PtCl_4]$ with even more force as I_1 and I_3 are known to have frequencies well removed from the new features (Figure 1). Equivalent arguments apply for the ammonium salts.

For the ammonium salts space groups isomorphous with D_4, C_{4v}, and D_{2d} all allow two or three cation rotatory modes to become i.r. active; the problem is whether it is reasonable for such modes to be as high as 310 cm^{-1}

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[19] G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 725.

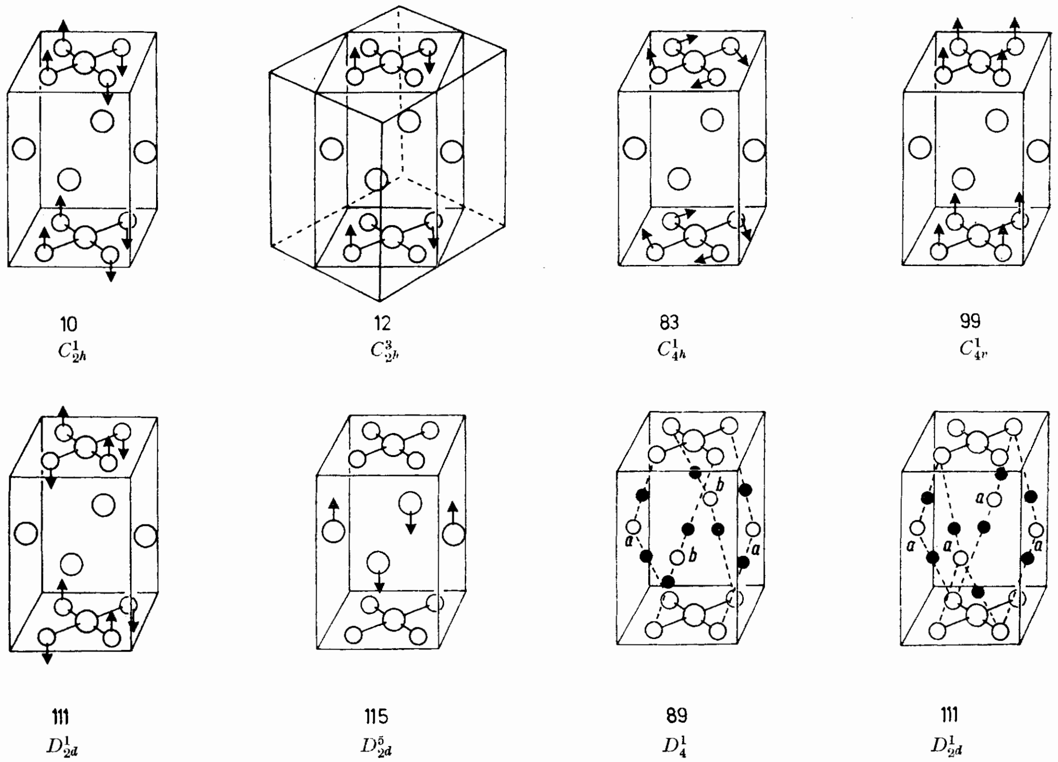

FIGURE 3 Possible structures, and their space-group numbers, with Z(primitive) = 1 to which the room-temperature D^1_{4h} structure may transform in the manner indicated: ● = H. The orientations of the $[NH_4]^+$ ions at *a* and *b* are different

($K_2[PdCl_4]$). For comparison we note $R([NH_4]^+)$ assignments at 264 cm^{-1} in $[NH_4][ReO_4]$ (Raman spectrum),[20] and in the i.r. spectrum at 276 cm^{-1} for α-$[NH_4][HgCl_3]$, shifting to 205 cm^{-1} in the deuteriate.[21] Unfortunately evidence from our $[ND_4]^+$ salts is ambiguous: one band remains at 298 cm^{-1} (palladium), and both appear to vanish in the platinum salt although the breadth of ν(Pt–Cl) is such that another contribution centred near 310 cm^{-1} could be imagined. On present evidence we cannot exclude the possibility that the new bands in the ammonium salts are due to cation rotation, but we incline to the view that both they and the similar features of the potassium salts share a common origin.

It appears that the most realistic origin is second-order processes in the new low-temperature structure(s). Their intensity suggests that they are combinations involving modes which already have i.r. activity. In the D^1_{2d} structure overtones are not i.r. active (except for $E \times E = B_2$), but all modes can attain i.r. activity (*i.e.* B_2 or E) in combinations since $E \times (A_1, A_2, B_1,$ or $B_2) = E$ and $A_1 \times B_2 = A_2 \times B_1 = B_2$. Consequently many combinations of modes in the lattice and ' middle ' regions are permissible. Typically; we have $I_4 + T_4 =$ 308 and $I_7 + R_2 = 299$ for $[NH_4]_2[PdCl_4]$, and $I_4 + T_1 = 305$ and $I_4 + T_4 = 310$ cm^{-1} for $[NH_4]_2[PtCl_4]$. Although a similar scheme could be constructed on the basis of C^1_{4v} we consider D^1_{2d} symmetry as the most probable on the basis of the above evidence. Finally we note that the possibility of a phase change to a bimolecular primitive cell has not been eliminated. Some structurally acceptable possibilities are: $C^3_{2h}(12)$, $D^3_{2h}(49)$, $D^7_{2h}(53)$, $D^2_{4h}(124)$, and $D^{10}_{4h}(132)$. However, since these are all centrosymmetric groups the two-phonon rules are restrictive.

EXPERIMENTAL

Crystals of $[NH_4]_2[PdCl_4]$ and $[NH_4]_2[PtCl_4]$ were grown by slow evaporation of aqueous solutions. Purity was checked by analysis (Found: H, 3.05; Cl, 48.75; N, 9.80. Calc. for $[NH_4]_2[PdCl_4]$: H, 2.85; Cl, 49.9; N, 9.85%) and otherwise by spectroscopy. Tetradeuterioammonium salts were obtained by two successive recrystallisations from D_2O over silica gel.

Rotation and Weissenberg *X*-ray photographs confirmed the crystal morphology of $[NH_4]_2[PdCl_4]$ which, typically, formed needles elongated along *c*. These crystals transmitted green light when examined in light polarised along *c*, but were otherwise dark brown. The morphology of crystalline $[NH_4]_2[PtCl_4]$ was similar to that of $[NH_4]_2$-$[PdCl_4]$ but transmitted red polarised light in all orientations. Low-temperature spectra were obtained using a C.T.I. closed-circuit cryostat giving temperatures in the range *ca.* 20—300 K; values quoted throughout this paper were estimated at the sample which was taken to be *ca.* 5 K above the cold station temperature where the thermocouple was mounted. I.r. spectra were obtained with a Beckman-RIIC FS-720 Fourier spectrometer. A wire-grid polariser was used for work with single crystals. Raman spectra were obtained using 514.5 nm excitation and a Coderg T800 triple-monochromator instrument. Because

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[20] R. A. Johnson, M. T. Rogers, and G. E. Leroi, *J. Chem. Phys.*, 1972, **56**, 789.

[21] R. M. Barr and M. Goldstein, *J.C.S. Dalton*, 1974, 1180.

of the optical properties of $[NH_4]_2[PdCl_4]$ described above, green light can only be transmitted polarised along *c*; hence only the $x(zz)y$ 90° experiment (yielding A_{1g}) was possible, although a weak E_g feature was also detected in breakthrough.

We thank the Danish Natural Science Research Council for a grant to R. W. B. whilst on leave from The Technical University of Denmark.

[5/1121 *Received, 9th June,* 1975]