Single-crystal Raman Spectrum of Potassium Trichloroammineplatinum(II) Monohydrate

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An assignment for the vibrational spectrum of the anion in $K[PtCl_3(NH_3)],H_2O$ is deduced from single-crystal Raman measurements. Evidence from Raman spectra of powder samples of $K[PtCl_3(ND_3)],D_2O$ and of both the protiated and deuteriated anhydrous materials (Cossa's salt) is also discussed.

MANY investigations of the i.r. and (to a lesser extent) Raman spectra of substituted platinum and palladium(II) complexes have been reported. The broad lines along which interpretations have been made are almost certainly correct but it is not possible, without knowledge of symmetry species, to prove detailed assignments. This is especially true of a complex such as $K[PtCl_3(NH_3)],H_2O$ in which five bending modes all crowd into a narrow frequency interval. As this is one of the simpler platinum(II) complexes we have investigated its Raman spectrum in some detail by single-crystal methods.

Selection Rules.—If each anion is treated as a penta-atomic system (*i.e.*, hydrogen atoms of ammonia neglected) the symmetry is C_{2v} and $\Gamma_{\text{vib.}} = 4a_1 + 2b_1 + 3b_2$, all being Raman-active. The crystal has symmetry $Cmc2_1 = C_{2v}^{12}$ with two formula units in the primitive cell.[1] The anions lie in the yz-plane with the N–Pt–Cl′ axis parallel with the crystal y-axis. Accordingly we transform the C_{2v} molecular axis from z to y giving $\Gamma_{\text{vib.}} = 4a_1 + 2a_2 + 3b_2$ and indicate which axis applies by referring to $C_{2v}(z)$ or $C_{2v}(y)$ as appropriate when discussing molecular (*i.e.*, the anion) modes.

Correlation coupling between the two anions in the cell leads to the scheme, shown in Table 1 together with the factor-group analysis. Modes due to the mole of water of crystallisation have been entirely neglected. Although the i.r. spectrum in the region 350—600 cm^{-1} is dominated by external modes of water, none was evident in the Raman spectra. Dehydration to give Cossa's salt affected the spectra (see below), but no transition actually associated with water was observed.

TABLE 1

Factor-group analysis and correlation scheme for $K[PtCl_3(NH_3)],H_2O$

C_{2v}^{12}	N_T	T_A	T	R	N_i	Pt–N	Pt–Cl′	Pt–Cl
A_1	12	1	3	1	7	1	1	2
A_2	6	0	2	2	2	0	0	0
B_1	6	1	1	2	2	0	0	0
B_2	12	1	3	1	7	1	1	2

N_T = total number of modes in cell ($3N$); T_A = acoustic modes; T = translatory lattice modes; R = rotatory lattice modes; N_i = internal modes (*two* anions); Pt–N, Pt–Cl′, and Pt–Cl = bond stretch representations in internal co-ordinates.

Correlation scheme

$$\begin{tikzcd}
\text{Anion} & \text{Site} \arrow[r, phantom, "\times 2"] & \text{Crystal} \\
C_{2v}(y) & C_s(yz) \arrow[r] & C_{2v}^{12} \\
4a_1 \arrow[r, no head] & 7A' \arrow[r] & 7A_1 + 7B_2 \\
3b_2 \arrow[ur, no head] & & \\
2a_2 \arrow[r, no head] & 2A'' \arrow[r] & 2A_2 + 2B_1
\end{tikzcd}$$

EXPERIMENTAL

$K[PtCl_3(NH_3)],H_2O$ was prepared from K_2PtCl_4 by the method of Elleman and his co-workers.[2] Single crystals *ca.* 4 × 2 × 1 mm^3 were grown by slow evaporation of an aqueous solution. Axes were located by *X*-ray diffraction methods. Morphology of the crystal was as shown in Figure 1. (100) and (010) Faces were developed by grinding, but it proved impossible to grind an (001) face of sufficient optical quality to yield meaningful $z(\rho\sigma)x$ and $z(\rho\sigma)y$ spectra (Figure 2). Attempts to obtain $x(yy)x$ spectra by 180° scattering were also unsuccessful. Single-crystal Raman measurements were therefore restricted to $y(\rho\sigma)x$ experiments.

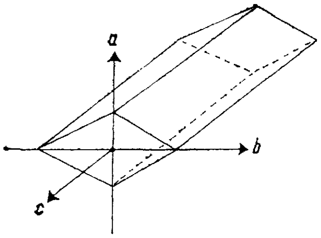

FIGURE 1 Morphology of $K[PtCl_3(NH_3)],H_2O$

The deuteriated complex was prepared by dissolving $K[PtCl_3(NH_3)],H_2O$ in D_2O (99%) followed by evaporation to dryness, the resulting solid being heated overnight at 60 °C. Repetition of this procedure three times resulted in essentially complete conversion into $K[PtCl_3(ND_3)]$. $K[PtCl_3(ND_3)],D_2O$ was prepared by recrystallising the anhydrous complex from D_2O.

Raman spectra were obtained by use of a Coderg PH1 spectrometer with 632·8 nm excitation (*ca.* 15 mW at the sample). Low-temperature spectra were obtained with a Cryocirc cryostat. Frequencies are accurate to ±1·5 cm^{-1}.

RESULTS AND DISCUSSION

The data are summarised in Tables 2—4. It is convenient to consider the spectrum in three regions.

(*a*) *Above* 280 *cm*$^{-1}$.—Modes involving stretching of Pt–N and Pt–Cl bonds are found above 280 cm^{-1}. Pt–N vibrations are readily distinguished by their large shift upon substitution of ND_3 for NH_3, *viz.*, ν(Pt–N) is lowered by 41 cm^{-1} from 536 cm^{-1} in $K[PtCl_3(NH_3)],H_2O$. No i.r. value is available for comparison as external modes of water obscure this region.[3] However, our Raman value

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[1] Y. P. Jeannin and D. R. Russell, *Inorg. Chem.*, 1970, **9**, 778.

[2] T. S. Elleman, J. W. Reishus, and D. S. Martin, *J. Amer. Chem. Soc.*, 1958, **80**, 536.

[3] J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, 1968, **24**, *A*, 819.

for ν(Pt–N) in the *anhydrous* protiated salt, 532 cm^{-1}, compares with the i.r. value of 528 cm^{-1} due to Hiraishi *et al.*[3] and may represent the splitting due to the correlation field, although the difference is barely greater than experimental error.

ν(Pt–Cl) modes generate two bands, 334 and 319 cm^{-1}, both having strong (*zz*) components. They are to be compared with the single polarised line at 325 cm^{-1} in this region, as reported by Denning and Ware for aqueous solutions.[4] We consider that the two bands are the two a_1 ν(Pt–Cl) modes of the anion and that effectively no correlation interaction has occurred: we note the absence of B_2 modes with significant intensity in this region. Studies[5] of the variation of ν(Pt–Cl) with *trans*-influence of the neutral ligand, L, leave little doubt that the 319 cm^{-1} band is primarily ν(Pt–Cl′) where Cl′ represents the unique chlorine. Its proximity to ν(PtCl$_2$)*s* at 334 cm^{-1} correlates with the known equivalence of their bond lengths.[1]

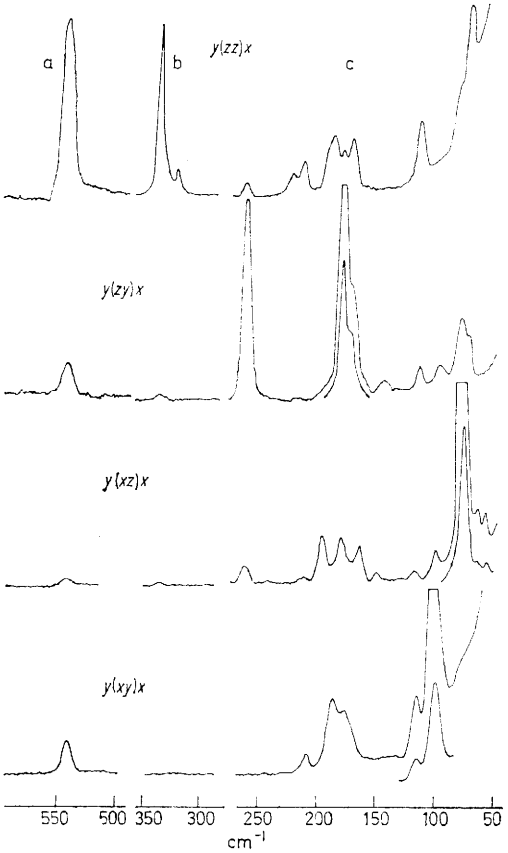

FIGURE 2 Single-crystal Raman spectra of K[PtCl$_3$(NH$_3$)],H$_2$O at *ca.* 100 K. (a) 2 cm^{-1} Spectral slit width, PM 1000 V; inset, PM 960 V. (b) As in (a) but PM 880 V. (c) 4 cm^{-1} Spectral slit width, PM 1000 V

A weak band found at 363 cm^{-1} is most probably an overtone [$2 \times 183 = 366$ (A_1)]. It is too high to be a Pt–Cl stretch as such values are only exhibited by binuclear complexes.[6]

Dehydration to Cossa's salt causes very little change in the structure apart from a slight volume contraction of the unit cell.[7] However, closer proximity of the two anions in each primitive cell is clearly reflected in intensity and frequency changes in the ν(Pt–Cl) region (Table 5), and related shifts of both frequency and intensity are evident throughout the rest of the low-frequency spectrum. Owing to the well known difficulty of growing crystals of Cossa's salt[7] we have only obtained Raman spectra of powder samples and cannot confirm the symmetry species. Nevertheless, we believe that the ν(Pt–Cl) assignment of Table 4 is reasonable.

(*b*) *Below* 140 *cm*$^{-1}$. No π(Pt–Cl) mode has ever been detected as low as 111 cm^{-1}: we can therefore confidently consider the bands found in the low-frequency spectrum of the title compound as due principally to lattice modes, although there must be interaction with internal modes of the same symmetries. Nine of the 15 predicted modes were observed, those of lowest frequency being of B_1 species: as two rotatory modes are required, it is likely that these bands principally represent anion rotation.

(*c*) *Region* 140—300 *cm*$^{-1}$.—The band at 252 cm^{-1} is clearly due to a mode involving motion of the nitrogen atom as it shifts to 226 cm^{-1} upon deuteriation. It is of B_2 symmetry and originates in the anion ν_8 mode.

It remains to account for the four bending modes [$a_1 + 2a_2 + b_2$ in $C_{2v}(y)$] which crowd into the 140—190 cm^{-1} region. Assignment of these is the principal reason for undertaking a single-crystal study of this material. In K$_2$PtCl$_4$ this region (which contains both in-plane and out-of-plane deformations) is also complicated by Fermi resonance with combinations,[8] and the same could well be true here.

Crystal A_2 and B_1 spectra are considered together because they both arise from correlation doubling of out-of-plane anion modes of $a_2[C_{2v}(y)]$ symmetry, two being expected. These are assigned at 190 and 174 cm^{-1} (values for liquid-nitrogen temperature B_1 spectra). Since they are not expected above corresponding in-plane deformations, it is likely that the higher band is largely associated with π(Pt–N) motion and the lower one with π(Pt–Cl). The B_1 spectra show a weak feature at *ca.* 160 cm^{-1}, not present in A_2: if this were taken as a fundamental it would be difficult to account for one of the higher bands in B_1/A_2. We consider its origin to be the lattice mode combination $B_1(53) + A_1(109) = B_1(162$ cm$^{-1})$. All of the B_1 modes are distinctly weak because they derive their intensity by correlation coupling of anion a_2 modes.

A_1 and B_2 spectra are considered together since they arise from coupling of in-plane anion a_1 and b_2 deformation modes: one from each species remains to be

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[4] R. G. Denning and M. J. Ware, *Spectrochim. Acta*, 1968, **24**, *A*, 1785.

[5] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

[6] D. M. Adams and P. J. Chandler, *J. Chem. Soc.* (*A*), 1969, 588.

[7] G. A. Kukina and G. B. Bokii, *J. Struct. Chem.*, 1965, **6**, 214.

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

TABLE 2

Single-crystal Raman spectra of $K[PtCl_3(NH_3)],H_2O$ at *ca.* 100 K (relative intensities in arbitrary units)

$\Delta\nu/cm^{-1}$	$y(zz)x(A_1)$	$y(zy)x(B_2)$	$y(xz)x(B_1)$	$y(xy)x(A_2)$	Assignment
37			5 [a]		
53			12		
61			10		
71	35	6 [a]	220	8 [a]	
75	10 [a]	25			
96		9	10	120	
111	25	10	5	21	
144		3	3		
160			16		
166	23	30 [a]			
174	17	130	20	24	ν_6,ν_9
183	27			29	ν_4 [b]
191			20		ν_5
208	14			8	
218	6				
256	5	95	8		ν_8
319	100	12		6	ν_3
334	630	28	15	6	ν_2
363	5				
539	41	6	2	9	ν_1
801		2	8		
825	5	10		1	

[a] Shoulder. [b] See text for discussion of Fermi interactions.

TABLE 3

Single-crystal Raman spectra of $K[PtCl_3(NH_3)],H_2O$ at ambient temperature (relative intensities in arbitrary units)

$\Delta\nu/cm^{-1}$	$y(zz)x(A_1)$	$y(zy)x(B_2)$	$y(xz)x(B_1)$	$y(xy)x(A_2)$	Assignment
37	5 [a]		9		
49			9 [a]	12 [a]	
64	15	9	198		
72	3 [a]	9			
87		3	6 [a]	66	
106	9	3	2	6	
142			3		
158			6		
165	30				ν_4 [b]
167				21	ν_6
172		69	9		ν_9
183	5 [a]		8	3	ν_5
201	2				
252	2	36	3	1	ν_8
318	75	3 [a]	3 [a]	6	ν_3
331	400	6	5	3	ν_2
360	3				
536	15	2	1	4	ν_1

[a] Shoulder. [b] See text for discussion of Fermi interactions.

TABLE 4

Raman frequencies/cm^{-1} of powder samples at ambient temperature

$K[PtCl_3(NH_3)],H_2O$	$K[PtCl_3(ND_3)],D_2O$	$K[PtCl_3(NH_3)]$	$K[PtCl_3(ND_3)]$
62sh	61s		
85w	83m		
	104w		
169s	171s	170s	170sh
180sh	181ms	183s	182s
		197m	197s
253wm	226m	249wm	220wm
319sh	317m	295vs	297s
332s	331vs	331s	329vs
536wm	495m	532m	491wm

assigned. There are in fact *three* bands, the two spectra being taken together. On cooling to liquid-nitrogen temperature the most striking change is a rise in intensity of a band in the A_1 spectrum ($183 \mathrm{cm}^{-1}$), present at room temperature as a clear but unresolved high-frequency shoulder on the $168 \mathrm{~cm}^{-1}$ band. The $174 \mathrm{~cm}^{-1}$ band is unquestionably of B_2 symmetry and arises in the anion ν_9 mode. The most reasonable interpretation of the A_1 spectrum is that ν_4 is in Fermi resonance with an overtone of a lattice mode and that upon cooling the upward shift of ν_4 reverses the order of contributions to the Fermi doublet.

TABLE 5

Assignment and approximate description of anion modes in $K[PtCl_3(NH_3)],H_2O$, $C_{2v}(z)$

		Ambient	*ca.* 100 K			Ambient	*ca.* 100 K
a_1	ν_1 ν(Pt–N)	536	539	b_1	ν_5 π(NPtCl)	183	191
	ν_2 ν(Pt–Cl) *s*	332	334		ν_6 π(ClPtCl)	167	174
	ν_3 ν(Pt–Cl′)	318	319	b_2	ν_7 ν(Pt–Cl) [a]	324 [b]	—
	ν_4 δ(ClPtCl)	165 [a]	183 [a]		ν_8 δ(NPtCl)	252	256
					ν_9 δ(ClPtCl)	172	174

[a] Both values displaced by Fermi resonance; see text. [b] Refs. 3, 4.

Other Bands.—Weak bands found at 208 and $218 \mathrm{~cm}^{-1}$ are unlikely to be anion fundamentals, although one or both could be NH_3 torsions. We note that Sheppard *et al.* estimated the barrier to NH_3 rotation in solid $PdCl_2(NH_3)_2$ as $225 \mathrm{~cm}^{-1}$.[9]

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[9] R. C. Leech, D. B. Powell, and N. Sheppard, *Spectrochim. Acta*, 1965, **21**, 559.