Far-infrared Single-crystal Study of Potassium Tetrabromoplatinate(II)

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It is shown from far-i.r. reflectance measurements on a single crystal of $K_2[PtBr_4]$ that the internal modes $\nu_2(A_{2u})$,-π(Pt–Br) and $\nu_7(E_u)$,δ(Pt–Br) are almost accidentally degenerate at 128 and 129 cm^{-1} at 295 K and 129 and 133 cm^{-1} at 38 K. The lattice modes are in the order $E_u > A_{2u} > E_u$. The principal values of the low-frequency dielectric constant are estimated to be 7.06 [$\varepsilon(1) = \varepsilon(2)$] and 4.20 [$\varepsilon(3)$].

THE i.r.-active modes of vibration of the $K_2[PtCl_4]$ structure ($P4/mmm \equiv D^1_{4h}$, $Z = 1$)[1] span the representation[2] $2A_{2u} + 4E_u$. Internal modes of the square-planar anion are responsible for one of the A_{2u} (ν_2, an out-of-plane deformation) and two of the E_u modes [ν_6, the in-plane ν(M–X) stretch; and ν_7, an in-plane deformation]. The ν_6 mode is readily identified as it is the highest-frequency band in the spectrum, but the order of ν_2 and ν_7 cannot be determined from either powder or solution data, although the symmetry species can be unambiguously decided by single-crystal spectroscopy in polarised light. This was done for $K_2[PtCl_4]$ by i.r. transmission through a thin crystal slice,[2] the result being the expected order $\nu_7 > \nu_2$. In addition the order of the three i.r.-permitted lattice modes was shown to be $E_u > A_{2u} > E_u$.

In $K_2[PtCl_4]$ the ν_2 and ν_7 internal modes are separated from the highest lattice mode by *ca.* 60 cm^{-1}, but for $K_2[PtBr_4]$ the reduced internal-mode frequencies are low enough for there to be ambiguity about the assignment, especially as i.r. spectra of mulls show one less than the theoretical number of bands. We have resolved this problem by study of a single crystal using i.r. reflectance at near-normal incidence. The compounds $K_2[PtCl_4]$ and $K_2[PtBr_4]$ are isomorphous[3,4] and the same selection rules therefore apply to both.

EXPERIMENTAL

Crystals of $K_2[PtBr_4]$ of size *ca.* $5 \times 3 \times 1$ mm were obtained by slow evaporation of an aqueous solution of the salt containing 10% HBr. Excellent extinctions observed

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under the polarising microscope allowed identification of the indicatrix axes. The *c* axis was parallel to the longest side of the crystal. A crystal was mounted on a copper plate using an epoxy resin in which fine aluminium powder had been *mixed* to improve thermal contact. The copper plate was mounted in a CTI-20 closed-circuit liquid-helium cryostat. Spectra were obtained using a Beckman RIIC FS-720 Fourier spectrometer fitted with an RS-7F reflectance module and an FS–820 step drive; an integrating time of 5.12 s was used at each sample point.

TABLE 1

Far-i.r. vibrational wavenumbers (cm^{-1}) for $K_2[PtBr_4]$

	Single-crystal i.r. reflectance				
	295 K		38 K		
Assignment	LO[a]	TO[b]	LO[a]	TO[b]	$K_2[PtCl_4]$ (ref. 2)
A_{2u} Modes					
ν_{L1} Lattice mode	94	90	96	91	98
ν_2 π(Pt–Br)	156	128	157	129	170
E_u Modes					
ν_{L2} Lattice mode	96	75	97	78	87
ν_{L3} Lattice mode	109	102	113	106	112
ν_7 δ(Pt–Br)	145	129	142	133	194
ν_6 ν(Pt–Br)	246	231	247	236	323

[a] ε' Nodes. [b] ε'' Maxima.

RESULTS AND DISCUSSION

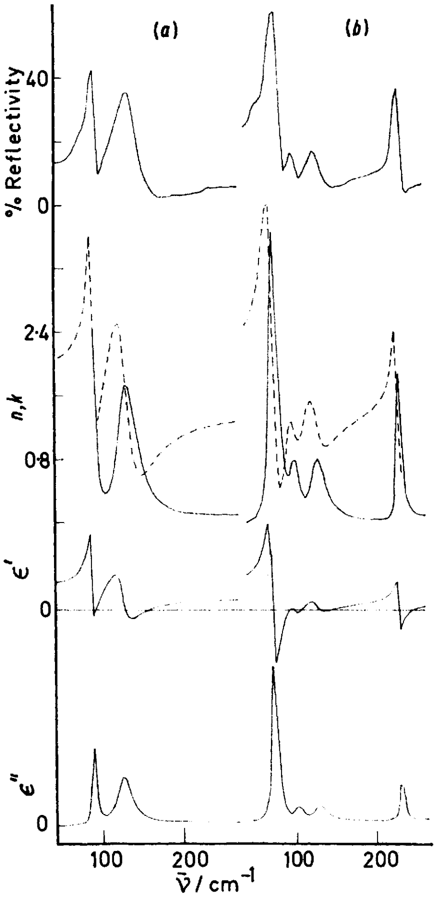
The observed reflectance spectra were analysed by the Kramers–Krönig method to yield the functions *n* (refractive index), *k* (absorption index), and the real (ε') and imaginary (ε'') parts of the complex dielectric constant. These parameters are related by equations (1) and (2). Transverse optical (TO) mode frequencies correspond to maxima of ε'' and longitudinal optical (LO) frequencies to zero values of ε'. Independent analyses by the classical harmonic oscillator method yielded closely similar results. These functions are illustrated in the Figure.

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad (1)$$

$$n^* = n - ik = (\varepsilon^*)^{\frac{1}{2}} \qquad (2)$$

The most important result from these experiments is that ν_7 (E_u) and $\nu_2(A_{2u})$ are coincident within experimental error: they appeared as a single band in mull spectra even at 38 K. That this result is genuine and not due to failure to distinguish properly between orientations is shown by the good extinctions elsewhere in the single-crystal spectra. In contrast to $K_2[PtCl_4]$,[5] no new features developed in the i.r. spectra on cooling to 38 K.

Goggin and Mink [6] found that the i.r. spectrum of a chloroform solution of $[NBu^n_4]_2[PtBr_4]$ showed a band at 105 cm^{-1} with a shoulder at *ca.* 112 cm^{-1}, apart from ν(Pt–Br), ν_6 at 227 cm^{-1}; almost the same frequencies were found for the solid. The assignment ν_2 at 105 and ν_7 at *ca.* 112 cm^{-1} was made. Only one lattice mode was found for this salt, at 88 cm^{-1}. By comparison with this (correct) assignment for ν_2 and ν_7 in the $[NBu^n_4]^+$ salt, the assignment of ν_2 at 102 and ν_7 at 129 cm^{-1} for the first two bands below ν_6, ν(Pt-Br) in $K_2[PtBr_4]$, would have been reasonable. However, our single-crystal experiments show unambiguously that ν_2 and ν_7 are coincident at 128 cm^{-1} and that the lattice modes follow the same order as in $K_2[PtCl_4]$, *viz.* $E_u > A_{2u} > E_u$. However, there must be considerable Fermi resonance between the E_u lattice modes and ν_7 and the A_{2u} ν_{L1} and ν_2, to have raised ν_2 by 23 and ν_7 by *ca.* 14 cm^{-1} above the values for the $[NBu^n_4]^+$ salt.



Observed i.r. reflectance spectrum of $K_2[PtBr_4]$ with the incident electric vector (*a*) parallel to *c* (A_{2u} modes) and (*b*) perpendicular to *c* (E_u modes), and the calculated functions *n*, *k*, ε', and ε'' at 295 K

From the values of ω_i(TO) and ω_i(LO) extracted from the reflectance spectra, the principal components of the radiofrequency dielectric-constant tensor (ε_0) were calculated using the extended Lydanne–Sachs–Teller equation (3), where for A_{2u} modes *n* is the extraordinary ray refractive index (1.5934) [3] and for E_u modes it is the ordinary ray refractive index (1.74).[3] Thus $\varepsilon(1) = \varepsilon(2) = 7.06$ and $\varepsilon(3) = 4.20$. There are no literature values for comparison with these estimates.

$$\varepsilon_0 = (n)^2 \prod_i \left[\frac{\omega_i(\mathrm{LO})}{\omega_i(\mathrm{TO})}\right]^2 \qquad (3)$$

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