

Polarized Crystal Spectrum of Potassium Tetrachloroplatinite(II) at Liquid Helium Temperature

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As part of an investigation of the electronic structure of square planar platinum(II) complexes, the polarized crystal spectrum of K_2PtCl_4 has been taken at the temperature of liquid helium. The spectrum obtained is shown in Fig. 1 and the oscillator strengths for the separate bands as obtained by Gaussian analysis are shown in Table 1.

Crystal spectra of K_2PtCl_4 taken at room temperature have been reported by Yamada,¹ by Martin and Lenhardt,² and by Day *et al.*³ The room temperature spectrum obtained here as a preparatory

step in the recording of the 5°K spectrum was very similar to that reported by Day *et al.*³ and diverged slightly from that reported by Martin and Lenhardt.²

The essential differences between the spectra previously reported and the spectrum reported here, are the following (ignoring the natural decrease in intensity as expected from the vibronic model⁴).

- (i) The appearance of a band located at 24 000 (*xy*) and 23 940 (*z*) cm^{-1}
- (ii) The appearance of structure in the bands at 20 700 (*z*), 23 940 (*z*) and 26 000 cm^{-1} .

The progression reaching from 23 000 to 28 000 cm^{-1} contains some 19 members separated by 270–290 cm^{-1} , the progression around 23 940 (*z*) cm^{-1} 8 members separated by 275–295 cm^{-1} , and the progression around 20 700 cm^{-1} (*z*), 3 members separated by 260–280 cm^{-1} .

The totally symmetric ground state vibrational frequency α_{1g} is known⁵ to be 335 cm^{-1} , so on account of the widely extended progressions we must identify

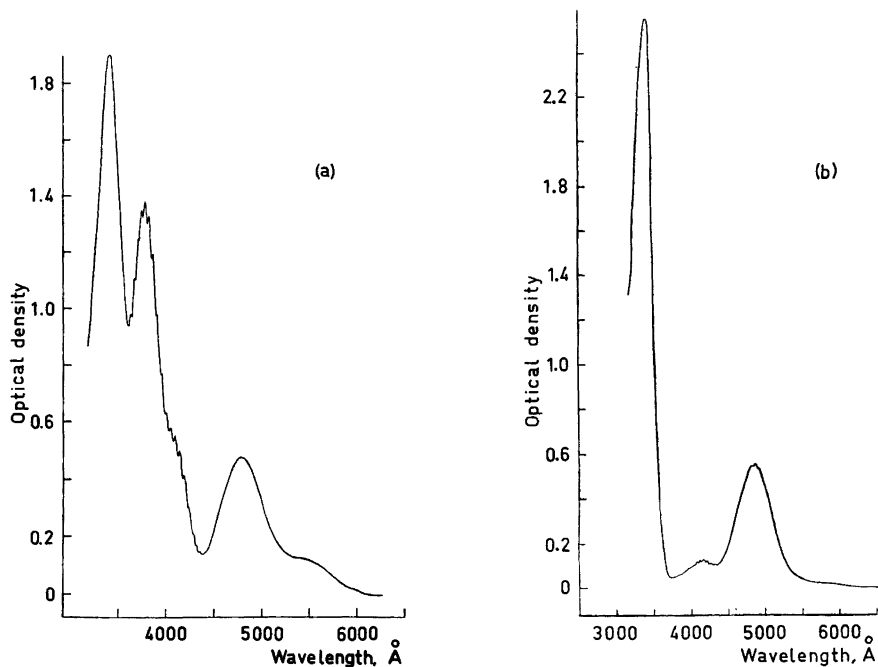


Fig. 1. 5°K crystal spectrum of K_2PtCl_4 polarized *xy* (a) and *z* (b). The *z* axis is coincident with the fourfold axis.

Table 1. Band maxima and oscillator strengths in 5°K spectrum of K_2PtCl_4 .

ν_{\max} cm^{-1}	oscillator-strength $\times 10^4$	polarization
17 190	0.03	<i>z</i>
16 930	0.005	<i>xy</i>
18 100	0.09	<i>xy</i>
20 660	0.77	<i>z</i>
20 810	0.73	<i>xy</i>
23 940	0.13	<i>z</i>
24 000	0.35	<i>xy</i>
26 050	1.6	<i>xy</i>
29 900	4.3	<i>z</i>
29 250	3.6	<i>xy</i>

the structure in all the bands as being the normally expected ⁴ totally symmetric progression.

The solution and crystal spectrum of the compound has been assigned by a number of authors^{1-3,2,3} however, no one so far has succeeded in a conclusive identification of the band at 20 000 cm^{-1} and the band at 29 000 cm^{-1} . A short discussion of an assignment, which seems to be consistent with the now available experimental data is given in the following.

In most previous work the band at 26 000 cm^{-1} has been identified with the ${}^1A_{1g}-{}^1A_{2g}$ transition. The 5°K spectrum strongly supports this regarding polarization, intensity and structure. The band around 18 000 cm^{-1} seen only *xy* has been assigned to the ${}^1A_{1g}-{}^3A_{2g}$ transition previously because of the polarization which is consistent with the symmetry group D_{4h} . However, since the singlet-triplet transition is actually seen, the relevant symmetry group is not the single group D_{4h} but the double group D_{4h}' . In this group ${}^3A_{2g}$ is split into the components Γ_1 and Γ_5 , neither of these by reason of symmetry being polarized only *xy*. The 3E_g , however, has a Γ_2 component which should be polarized only *xy*, and this could be identified with the band at 18 000 cm^{-1} .

The statement by Chatt *et al.*⁶ that neither the band at 29 000 cm^{-1} nor the band at 20 000 cm^{-1} is split under lower symmetry suggests that the 29 000 cm^{-1} band is ${}^1B_{1g}$ and the 20 000 cm^{-1} band the Γ_3 component of 3E_g . The ${}^1A_{1g}-{}^1E_g$ transition then should be located at a

somewhat higher energy and could be identified with the shoulder at 36 500 cm^{-1} reported by Day *et al.*³ in the reflectance spectrum and the shoulder at 37 900 cm^{-1} reported by Chatt *et al.*⁶ in the solution spectrum. This shoulder is not seen in the solution spectrum of related complexes of lower symmetry probably because it is hidden under the very intense charge transfer band located at 46 000 cm^{-1} in the solution spectra of these compounds. The ${}^3B_{1g}$ is split under the double group into the components Γ_4 and Γ_5 of which Γ_4 is expected to have almost zero intensity since no Γ_4 component of the singlet states exists.

The Γ_5 component is able to interact with the Γ_5 components of ${}^3A_{2g}$ and 3E_g , giving rise to three bands all borrowing intensity from the ${}^1A_{1g}-{}^1E_g$ transition. It is stated by Day *et al.*³ that this transition is polarized more strongly *xy* than *z*, which is consistent with our spectrum if the band at 24 000 cm^{-1} is identified with the Γ_5 component at higher energy. The two other Γ_5 states are then assumed to contribute to the bands at 18 000 cm^{-1} and 20 000 cm^{-1} , consistent both with the fact that these bands show a somewhat greater intensity than expected from the coupled singlet states, and with the blurring out of structure in the 20 000 cm^{-1} (*xy*) band. The very weak band at 17 000 cm^{-1} is then assigned the Γ_1 components of ${}^3A_{2g}$ and 3E_g .

The present model seems to account for most of the experimental data and agrees with the molecular orbital scheme described by Gray and Ballhausen.⁸

Two things still seem rather mysterious, the great difference between the *xy* and *z* maxima in the band at 29 000 cm^{-1} , and the complete absence of any structure in this band. The difference cannot be explained from the difference in frequency of the exciting vibrations, since these all have ground state frequencies of the order of 100–300 cm^{-1} ,^{9,10} but it might be that a deeper insight into the nature of the vibronic model and especially its influence on the potential surface could provide an explanation.

It must be said again that the assignment given here is strongly tentative. A conclusive identification should, however, be possible on the basis of a low temperature crystal spectrum of a related compound as $Pt(NH_3)_2Cl_2$. Attempts in this direction are in progress.

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The Reactions of Lignin during Sulphate Cooking

IX.* Interaction between Thiol Groups and Intermediary Epoxide Structures

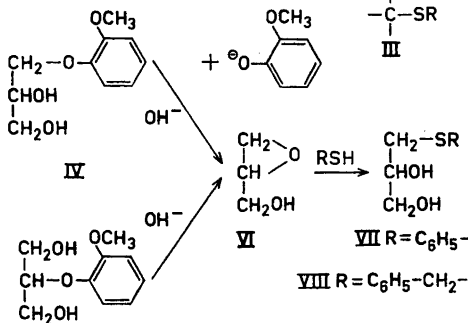
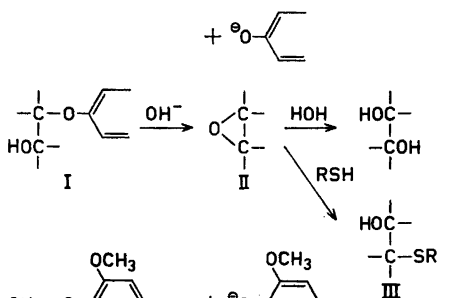
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During sulphate cooking sulfhydryl groups are introduced into lignin. Of the possible pathways of introduction, the addition of sulphide ions present in the cooking liquor to methylene quinone structures formed during the cooking procedure

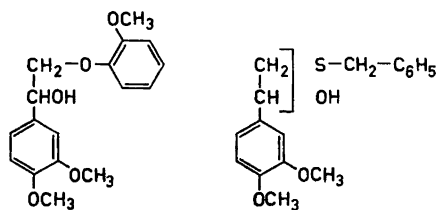
appears to be the most important one.¹ The resulting benzylthiol groups were shown in model studies to enhance the alkaline splitting of neighbouring ($=\beta$) arylether bonds by intramolecular nucleophilic displacement with formation of 1,2-epoxide structures.¹

In the present communication we wish to report on model experiments illustrating another type of reaction in which thiol groups may be involved during sulphate cooking.

The alkaline splitting of β -hydroxyalkyl-arylether bonds (I) was previously shown to proceed via 1,2-epoxide structures (II).^{2,3} It could be anticipated that these structures will be attacked by the strongly nucleophilic thiol groups to yield β -hydroxyalkylsulphides (III). When the



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* Part VIII, see Ref. 1.