55 •

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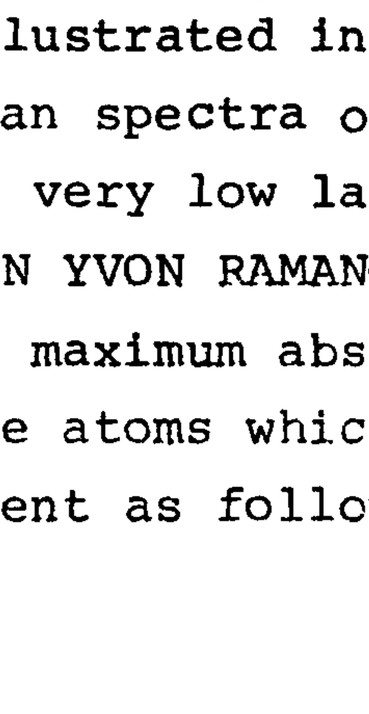
Ref.:

Dear Miss Wakeling,

Resonance Raman Spectra of Platinum Compounds

We would like to report here briefly, the first results we have obtained on the resonance Raman spectra of the platinum compound[1] $Pt(en)Cl_3$ (brown) where (en= $H_2NCH_2CH_2NH_2$). This compound is of interest because of its relation to the problem of the possibility of the existence of Pt(III) and the conductivity and color of platinum compounds[2], in general. The spectra reported here are consistent with the resonance Raman effect and the energy profile of the absorption spectrum of $Pt(en)Cl_3$.

The spectra are illustrated in Figs. 1 and 2. In Fig. 1 are shown the resonance Raman spectra of $Pt(en)Cl_3$ with exciting lines 4579, 5145 and 6328Å at very low laser energies (<20mW). The Raman spectrometer was a JOBIN YVON RAMANOR HG.2S. The line 4579Å falls almost at the region of maximum absorbance and shows resonance effects on the bridging chlorine atoms which probably link different oxidation states of the same element as follows[3]:



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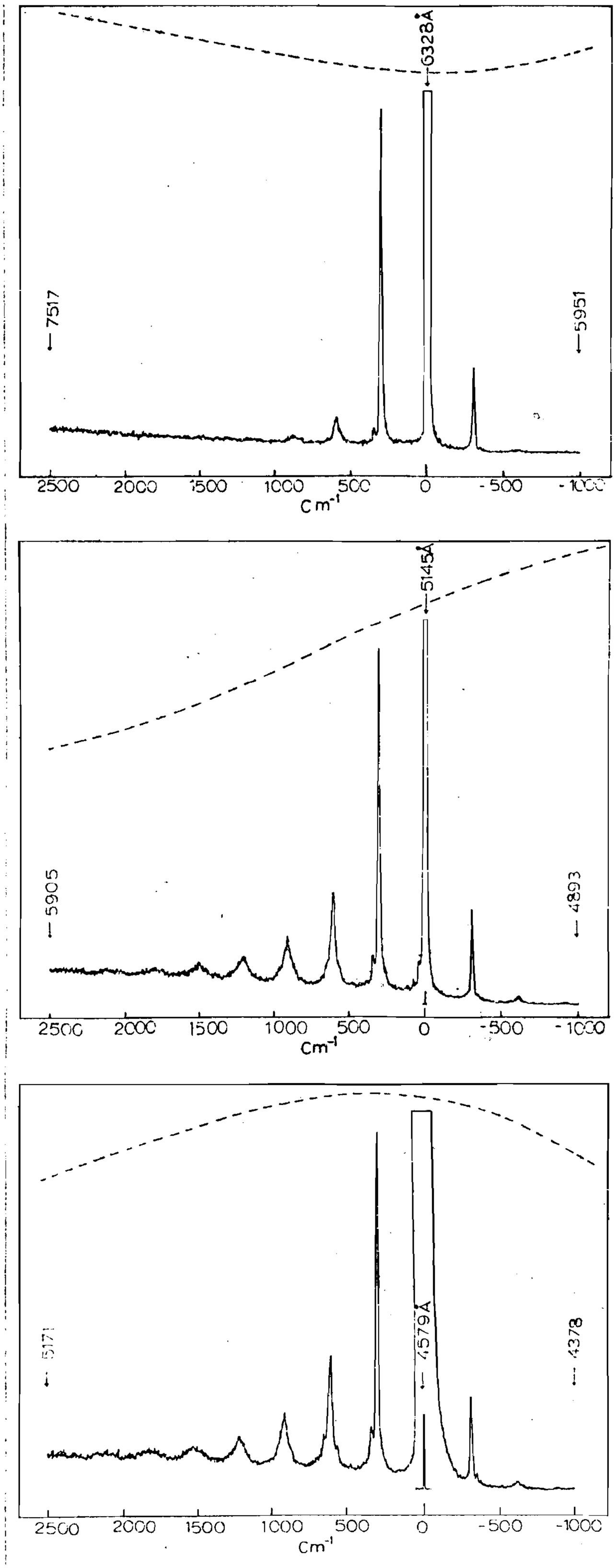
6328Å
7517
5951
2500
2000
1500
1000
500
0
-500
-1000
C m⁻¹
5145Å
5905
4893
2500
2000
1500
1000
500
0
-500
-1000
Cm⁻¹
5171
4579Å
4378
2500
2000
1500
1000
500
0
-500
-1000
Cm⁻¹

Fig. 1

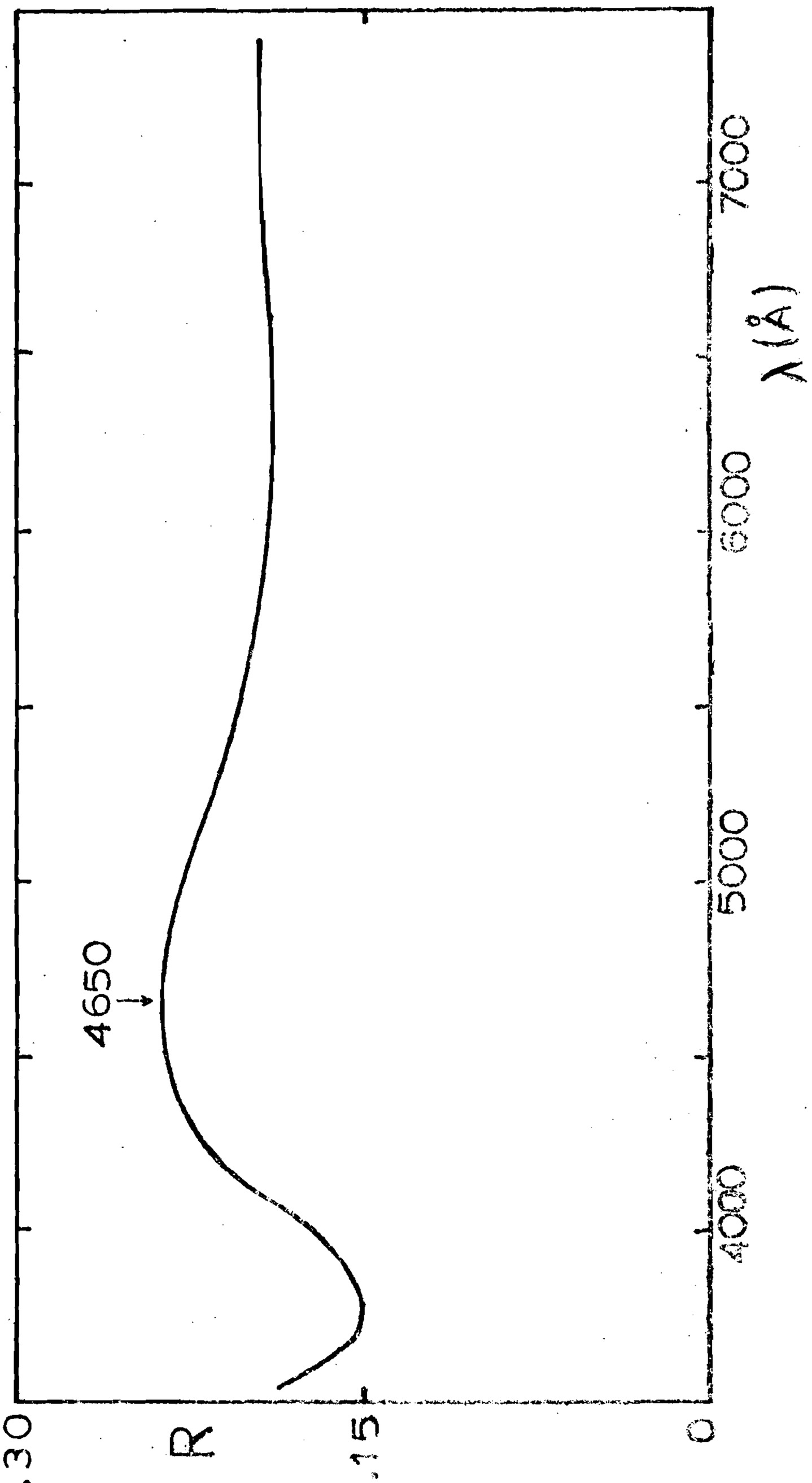

Fig. 2

From the spectra it is shown the resonance effect on the fondamental band at 304 cm^{-1} with the overtones at 608, 910,1210, 1500 cm^{-1}. The bands of the other vibrations of the molecule are ~~very~~ too weak to be seen. The weak satellite bands observed at the fondamental and the first overtone may be the $Pt\begin{matrix}Cl\\Cl\end{matrix}$ unit vibrations at 348 cm^{-1} and the isotope effect of Cl^{37}. The Raman spectrum of $Pt(en)Cl_2$ taken with a sensitivity 50 times higher shows the Pt-Cl vibrations at 306 and 331 cm^{-1} and the Pt-N vibration near 565 cm^{-1}. The resonance Raman effect is most likely due to the charge transfer spectrum through the bridging halogens from Pt(II) to Pt(IV). There is free electron mouvement in this direction which is also shown from its conductivity ($>10^{-11}$ $\Omega^{-1}cm^{-1}$) and its reflectance spectrum (See Fig. 2).

We are now working to take spectra with single crystals of $Pt(en)Cl_3$ in order to distinguish the chain axis from the plane vibrations when we have the electric vector along or perpendicular to the Cl-Pt(IV)-Cl --- Pt(II)---Cl-Rt(IV)-Cl chain. In this chain we have one halogen bridge which links different oxidation states of the same element[4].

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