

Resonance Raman Spectra of Single Crystals of Mixed-Valence Linear Chain Complexes of Platinum

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Résumé

Les spectres Raman de résonance de monocristaux de rouge de Wolfram, de vert de Reihlen et d'autres complexes mixtes à chaînes linéaires de platine ont été enregistrés dans la région de 4000 à 100 cm^{-1} . Les spectres Raman de résonance montrent une progression ν_1 , où ν_1 est la fréquence de vibration symétrique $\dots \text{Pt}^{\text{II}} \dots \text{X} - \text{Pt}^{\text{IV}} - \text{X}$ des complexes mixtes $[\text{Pt}^{\text{II}}(\text{etn})_4] [\text{Pt}^{\text{IV}}(\text{etn})_4\text{X}_2] \text{X}_4 \cdot 4\text{H}_2\text{O}$ et $[\text{Pt}^{\text{II}}(\text{tn})_2] [\text{Pt}(\text{tn})_2\text{X}_2] (\text{ClO}_4)_4$ (où etn = éthylamine, tn = triméthylamine et $\text{X} = \text{Cl}$, Br , et I). Les spectres des monocristaux pour lesquels $E \parallel Z$ (E , le vecteur champ électrique du laser est parallèle à l'axe Z passant le long de la chaîne $\dots \text{Pt}^{\text{II}} \dots \text{X} - \text{Pt}^{\text{IV}} - \text{X}$) présentent une exaltation de la fréquence ν_1 , alors que les spectres pour lesquels $E \perp Z$ sont caractéristiques de l'effet Raman classique et montrent les vibrations des groupes latéraux dans le plan des complexes de platine. Les intensités des vibrations sont dépendantes de l'orientation des divers groupes par rapport au vecteur champ électrique E .

Abstract

Resonance Raman spectra of single crystals of Wolfram's red, Reihlen's green and similar mixed-valence linear-chain complexes of platinum with nitrogen and halogen ligands around the platinum atom have been recorded in the region 4000-100 cm^{-1} . The resonance Raman spectra show a characteristic intense progression $\nu_1 \nu_1$ where ν_1 is the symmetric, $\dots \text{Pt}^{\text{II}} \dots \text{X} - \text{Pt}^{\text{IV}} - \text{X}$ stretching frequency of the mixed-valence

complexes $[\text{Pt}^{\text{II}}(\text{etn})_4] [\text{Pt}^{\text{IV}}(\text{etn})_4\text{X}_2] \text{X}_4 \cdot 4\text{H}_2\text{O}$ and $[\text{Pt}^{\text{II}}(\text{tn})_2] [\text{Pt}(\text{tn})_2\text{X}_2] (\text{ClO}_4)_4$ (where etn = ethylamine tn = trimethylenediamine and $\text{X} = \text{Cl}$, Br or I). The spectra of the single crystals with $E \parallel Z$ (electric wave-sector, E of the laser light parallel to the Z -axis along the $\dots \text{Pt}^{\text{II}} \dots \text{X} - \text{Pt}^{\text{IV}} - \text{X}$ chain) show resonance enhancement of the ν_1 frequency, whereas the spectra with $E \perp Z$ are characteristic of the classical Raman effect showing the vibrations of the lateral groups in the plane of the platinum complexes. The intensities of the vibrations are dependent on the orientation of the various groups with respect to the electric wave-vector, E .

Introduction

Recently, several papers have been published on resonance Raman spectra of mixed-valence linear-chain compounds as powders (1-5) and single crystals (6-8). These compounds are semiconductors in which the platinum exists in two different valences in the chemical formula forming linear-chains in the crystal with alternate valences, Pt^{II} and Pt^{IV} , where there is a charge transfer between orbitals on adjacent metal atoms through the orbitals of the bridging halogen atom. This transfer of electron charge along the linear-chain is responsible for the intense broad absorption (or reflectance) band and the observation of the characteristic resonance Raman spectra of the symmetric $\dots \text{Pt}^{\text{II}} \dots \text{X} - \text{Pt}^{\text{IV}} - \text{X}$ stretching frequency. The length of these chains in the crystal is not known and it depends on the conditions of crystallization, solvent and nature of compound. The crystal structure data on similar systems (9) show chains of halide-platinum atoms of different length in the crystal. The compounds

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are colored, lustrous, metallic, usually fine needle shaped crystals giving intense resonance Raman spectra, due to the halide-platinum bond along the chain axis. The polarized reflectance and resonance Raman spectra of these mixed-valence crystals are particularly interesting. These optical properties, however, are lost when the crystals are put into solution, where the components of the mixed valence compounds are liberated. The colour of a concentrated solution of a mixed valence compound is deeper than the colour of its components.

It seems that the different valences are trapped in sites in the crystal in such a way as to be able to communicate through an overlap of orbitals of the adjacent metal atoms *via* the halogen bridging atoms. This may be accomplished by an electron charge transfer between the two metals. This electron delocalization is responsible for the resonance Raman spectra. Detailed information can be obtained about the charge transfer in these complexes from studies on single crystals. In the case of single crystals, one can study the optical properties (6) in the direction of the one dimensional chain ($E \parallel Z$) and perpendicular to this direction ($E \perp Z$) and the resonance Raman spectra when the exciting frequency of the source is inside the absorption band. The off-resonance Raman spectra or the normal Raman spectra are observed when $E \perp Z$ or when the exciting frequency is far removed from the intense electronic absorption band in the visible or near-infrared region which is characteristic of these compounds. The resonance and off-resonance Raman spectra provide information both on the electronic excitations and the vibrational transitions in these systems.

Experimental

The spectra were recorded as in our previous papers (7); for details, see the Figure captions. The compounds were prepared following published methods (7, 10). All measurements were performed at room temperature with the 514.5 nm excitation line.

Results and Discussion

The polarized resonance Raman spectra of single crystals of halogen-bridged chain compounds of platinum, such as Wolfram's red and Reihlen's green (10a) and the derivatives $[\text{Pt}(\text{tn})_2] [\text{Pt}(\text{tn})_2\text{X}_2] (\text{ClO}_4)_4$ (where tn = trimethylenediamine and $\text{X} = \text{Cl}, \text{Br}, \text{or I}$) have

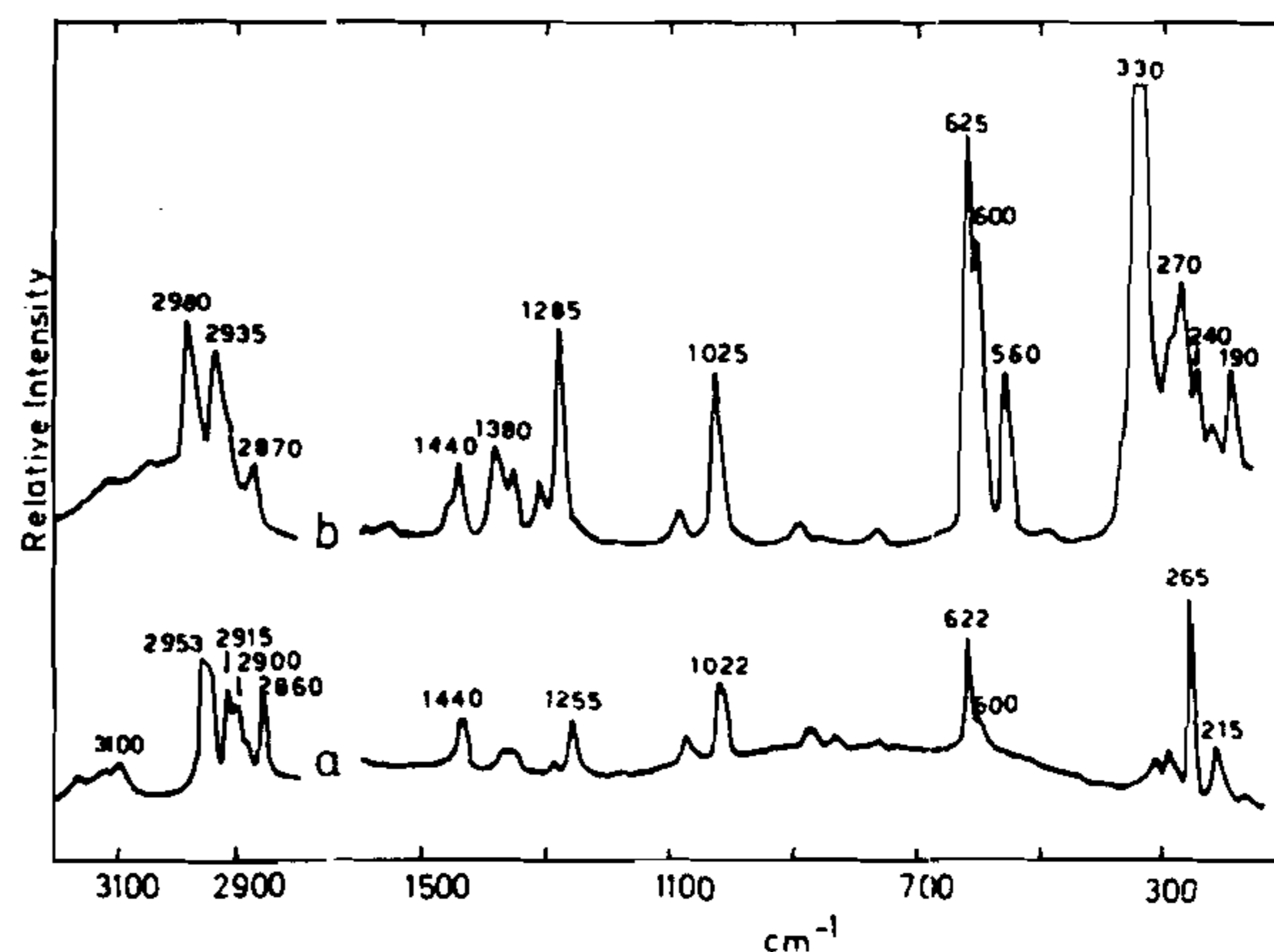


Figure 1. Raman spectra of a) $[\text{Pt}^{\text{II}}(\text{C}_2\text{H}_5\text{NH}_2)_4]\text{Cl}_2$ and b) $[\text{Pt}^{\text{IV}}(\text{C}_2\text{H}_5\text{NH}_2)_4]\text{Cl}_2$.

been recorded and are given in Figures 1-3. The Raman spectra of the powders have been published (11). It is shown here that the spectra with $E \parallel Z$ exhibit intensity enhancement through resonance of the ν_1 symmetric stretching fundamental of $\dots \text{Pt}^{\text{II}} \dots \text{X} - \text{Pt}^{\text{IV}} - \text{X}$ which is accompanied by an overtone progression. In the case of Wolfram's red, single crystals (Figure 2, (X1)) the $\text{Pt}^{\text{IV}} - \text{Cl}$ stretching frequency is observed at 315 cm^{-1} and its overtones at 625, 932, 1240, 1550 cm^{-1} , etc. The spectrum with $E \perp Z$ (X15, vertical scale expansion) exhibits the

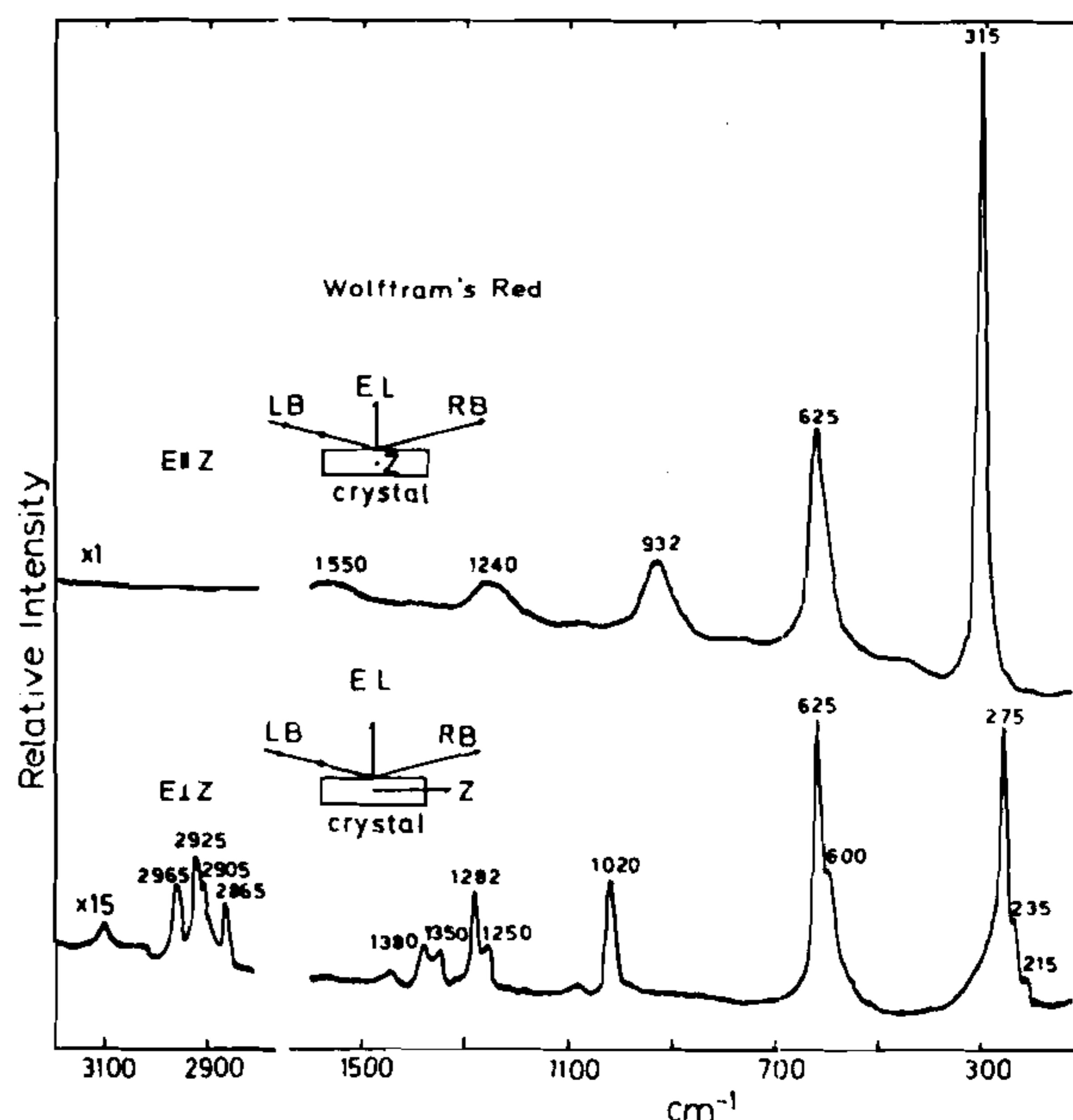


Figure 2. Polarized Raman spectra of a single crystal of Wolfram's red with the electric vector (E) parallel and perpendicular to the chain axis (Z). LB = Laser beam, RB = Reflectance beam, EL = Entrance Lens of monochromator; slits 2 cm^{-1} .

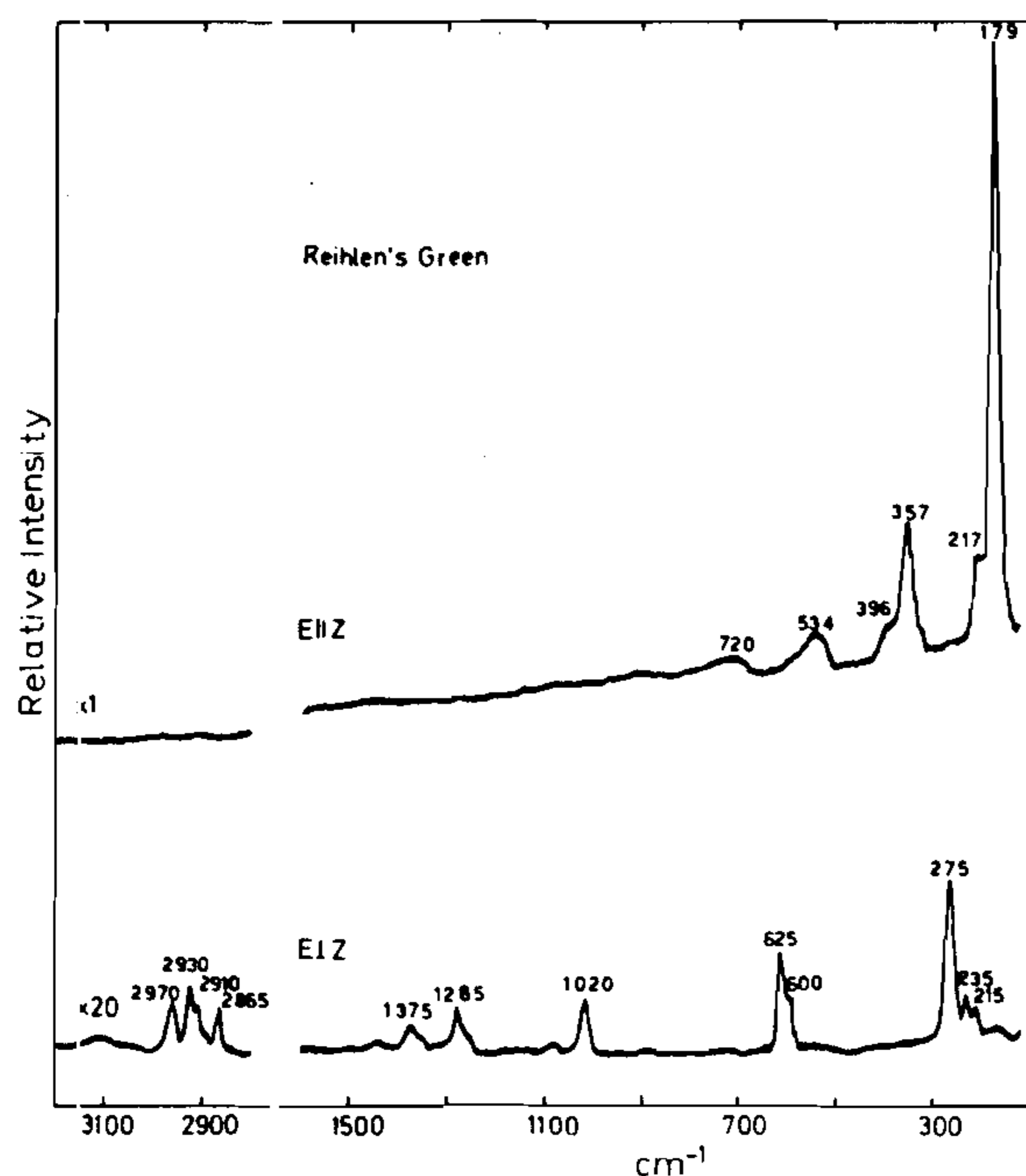


Figure 3. Same as Figure 2 but for Reihlen's green.

normal Raman spectrum. The bands in this spectrum are due to the vibrations of $C_2H_5NH_2$ coordinated to the metal through the nitrogen. In the $3300 - 2850 \text{ cm}^{-1}$ region there are the N-H and C-H stretching frequencies and in the $1400 - 1250 \text{ cm}^{-1}$ region the bending N-H and C-H deformations of $-NH_2$ and CH_3-CH_2- groups (11). The band at 1020 cm^{-1} is attributed to the C-N vibration and that at 625 cm^{-1} with the shoulder at 600 cm^{-1} to a rocking $-NH_2$. The bands at 275 and 235 cm^{-1} are assigned to the N-Pt-N in-plane bending deformations (5a).

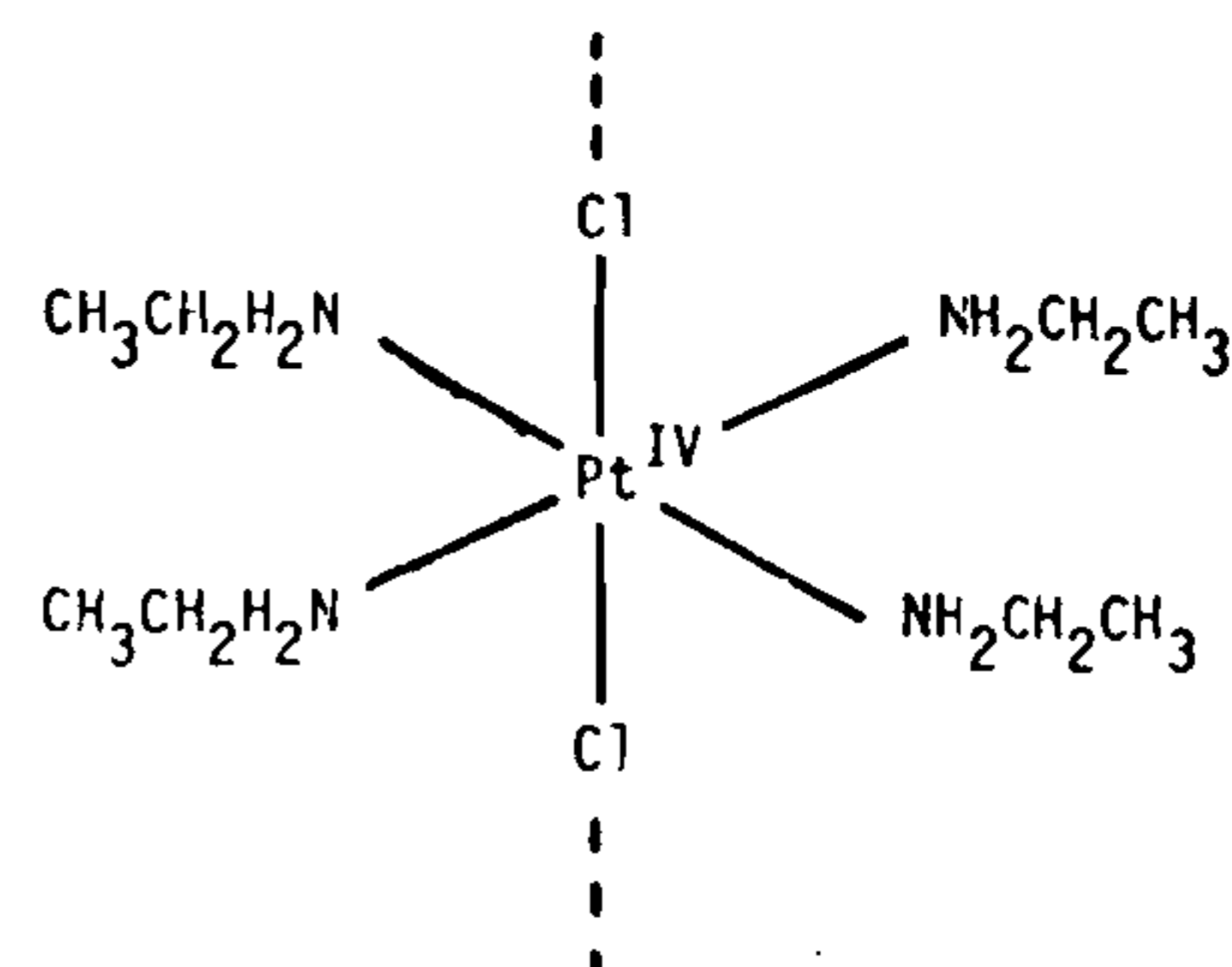
The resonance spectrum of Reihlen's green salt single crystals is shown in Figure 3. The $E||Z$ (X1) spectrum exhibits a progression which originates with the $Pt^{IV} - Br$ stretching fundamental at 179 cm^{-1} with its overtones at $357, 534, 720 \text{ cm}^{-1}$, etc. (5-7). The spectrum with $E\perp Z$ (X20), exhibits the normal Raman effect with the bands of the N-H and C-H stretchings in the $3300 - 2850 \text{ cm}^{-1}$ region, just as in the case of Wolfram's red salt, and the deformations of these groups in the $1400 - 1200 \text{ cm}^{-1}$ region. The spectrum is similar to that obtained for the Wolfram's red with $E\perp Z$, which is expected, and the assignments are given in Table I. It is clear from these spectra that the bands at $215, 235, 275$ and 625 cm^{-1} with the shoulder at 600 cm^{-1} of Wolfram's red are due to vibrations of the lateral groups and not to the vibrations in the chain (combination tones) as has been previously sug-

Table I. Raman Bands (in cm^{-1}) of Platinum-Ethylamine and Platinum-Trimethylenediamine Complexes

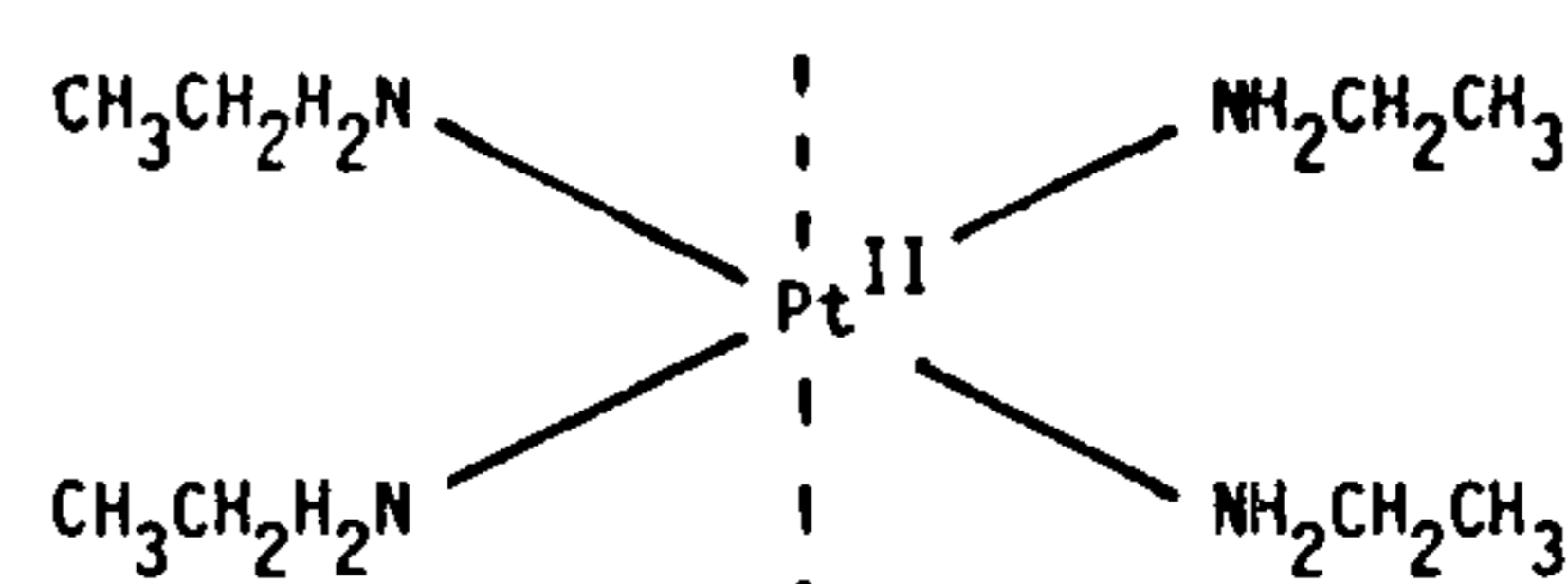
Complex	Reflected Color of Crystals	Single Crystal Maxima of Reflectance Spectra (nm)	Assignments (cm^{-1})	
			ν_{Pt-X}	$\nu_{C-H}, \delta_{N-Pt-N}$
$[Pt^{II}(C_2H_5NH_2)_4]Cl_2$	white	—	600	265
$[Pt^{IV}(C_2H_5NH_2)_4Cl_2]Cl_2$	yellowish	—	330	560 270
$[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}(C_2H_5NH_2)_4Cl_2]Cl_4 \cdot 4H_2O$ (Wolfram's red)	red-greenish	470	315	600 275
$[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}(C_2H_5NH_2)_4Br_2]Br_4 \cdot 4H_2O$ (Reihlen's green)	green	565	179	600 275
$[Pt^{II}(tn)_2][Pt^{IV}(tn)_2Cl_2](ClO_4)_4$	greenish-redish	465	308	515, 475 225
$[Pt^{II}(tn)_2][Pt^{IV}(tn)_2Br_2](ClO_4)_4$	green	575	171	520, 475 240
$[Pt^{II}(tn)_2][Pt^{IV}(tn)_2I_2](ClO_4)_4$	golden	~1000	127	515, 475 225

gested (11b). The Raman spectra of the polycrystalline powders of (a) $[Pt^{II}(C_2H_5NH_2)_4]Cl_2$ and (b) $[Pt^{IV}(C_2H_5NH_2)_4Cl_2]Cl_2$ are shown in Figure 1 and the classical Raman bands in the regions previously discussed are observed. The assignments are given in the Table I. It is interesting to notice in these normal Raman spectra that the bands of the lateral groups ($CH_3CH_2NH_2-$) of the tetravalent metal compound are more intense than those of the divalent one (see Figure 1). This may be due to orientational effects (12) of the groups in the crystal or to polarizability changes due to charge differences between the divalent metal (Pt^{2+} , d^8 configuration) and the tetravalent metal (Pt^{4+} , d^6 configuration).

Polarizability (α) changes may also explain the intensity enhancement of the bands of the lateral groups, $etn = NH_2CH_2CH_3$, of the Pt^{4+} compound as follows



These groups may be partially oriented in the oxidation state Pt^{4+} but not in that of Pt^{2+} .



The charge distribution may be responsible for the intensity enhancement of the Raman bands in the case of the tetravalent platinum compound. The total polarizability tensor (α) is related to the induced moment μ by

$$\mu = \alpha E$$

$$\text{and } \frac{\mu_{\text{Pt}^{\text{II}}}}{\mu_{\text{Pt}^{\text{IV}}}} = \frac{(\alpha_{xx}, \alpha_{yy})_{\text{Pt}^{\text{II}}}}{(\alpha_{xx}, \alpha_{yy})_{\text{Pt}^{\text{IV}}}}$$

The induced dipole moment μ of the $\text{Pt}^{\text{IV}} - \text{N}$ bond is different from that of the $\text{Pt}^{\text{II}} - \text{N}$ bond and the polarizabilities (α) differ in the two cases. This difference could explain the higher Raman intensities in the Pt^{IV} complexes.

The polarized resonance Raman spectra of single crystals of the derivatives $[\text{Pt}(\text{tn})_2]$ $[\text{Pt}(\text{tn})_2\text{X}_2]$ $(\text{ClO}_4)_4$ ($\text{X} = \text{Cl}, \text{Br}$) are shown in Figures 4a, 4b and 5 in both orientations ($E \parallel Z$ and $E \perp Z$). The spectra again exhibit the strong

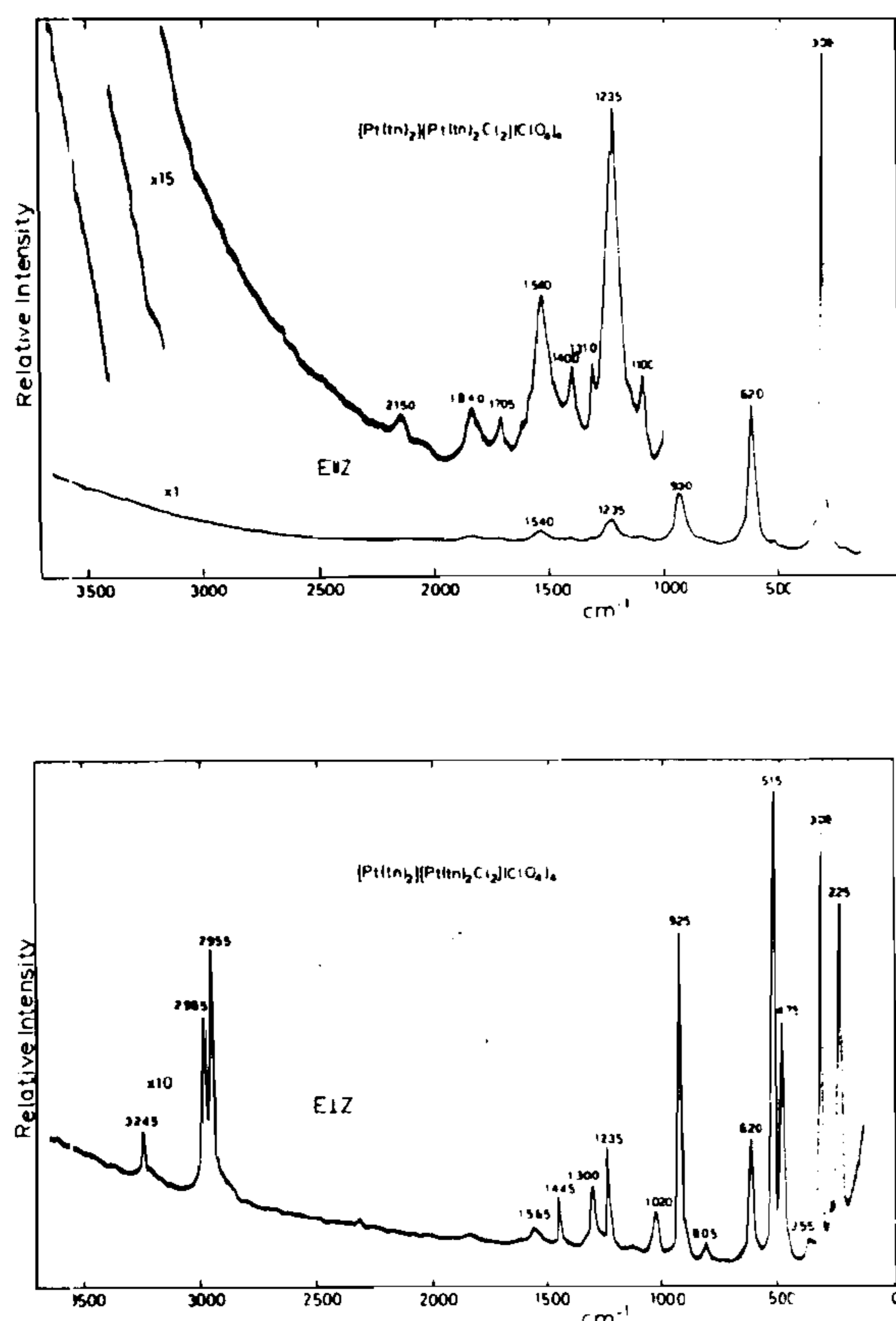


Figure 4. Polarized Raman spectra of a single crystal of $[\text{Pt}^{\text{II}}(\text{tn})_2]$ $[\text{Pt}(\text{tn})_2\text{Cl}_2]$ $(\text{ClO}_4)_4$ with $E \parallel Z$ (a) and $E \perp Z$ (b). Slits 2 cm^{-1} .

ν_1 fundamental of $\text{Pt}^{\text{IV}} - \text{X}$ frequency and its progression when taken with the E vector parallel to the Z -axis, i.e., along the linear-chain of $\dots \text{Pt}^{\text{IV}} \dots \text{X} - \text{Pt}^{\text{IV}} - \text{Pt}^{\text{IV}} \dots$. The $\text{Pt}-\text{Cl}$ progression is shown in Figure 4a ($X \parallel Z$) with the fundamental frequency at 308 cm^{-1} and the overtones at 620, 930, 1235, 1540, etc. The scale expanded spectrum shows weak bands at 1100, 1310, 1400 and 1705 cm^{-1} which may be combinations and are not shown in the spectrum with $E \perp Z$. The $E \perp Z$ excitation gives rise to the classical off-resonance Raman spectrum due to the vibrations of the lateral tn groups. However, the strong fundamental at 308 cm^{-1} with its overtone at 620 cm^{-1} is still visible in the spectrum here due to the fact that the crystals were not well aligned with the E vector. It is also interesting that the strong 925 cm^{-1} band in the spectrum of $E \perp Z$ due to the anion ClO_4 is not observed at all in the spectra of $E \parallel Z$; the lateral group platinum-nitrogen vibrations give rise to the bands at 225, 475 and 515 cm^{-1} and the $\text{C}-\text{H}$ vibrations appear around 2900 cm^{-1} .

The spectra of the bromo and iodo derivatives shown in Figures 5 and 6 with the $\text{Pt}^{\text{IV}} - \text{Br}$ and $\text{Pt}^{\text{IV}} - \text{I}$ fundamentals at 171 cm^{-1} and 127 cm^{-1} together with their overtones show the same trend. It was observed that the partial orientation effects were more evident if excitation was far

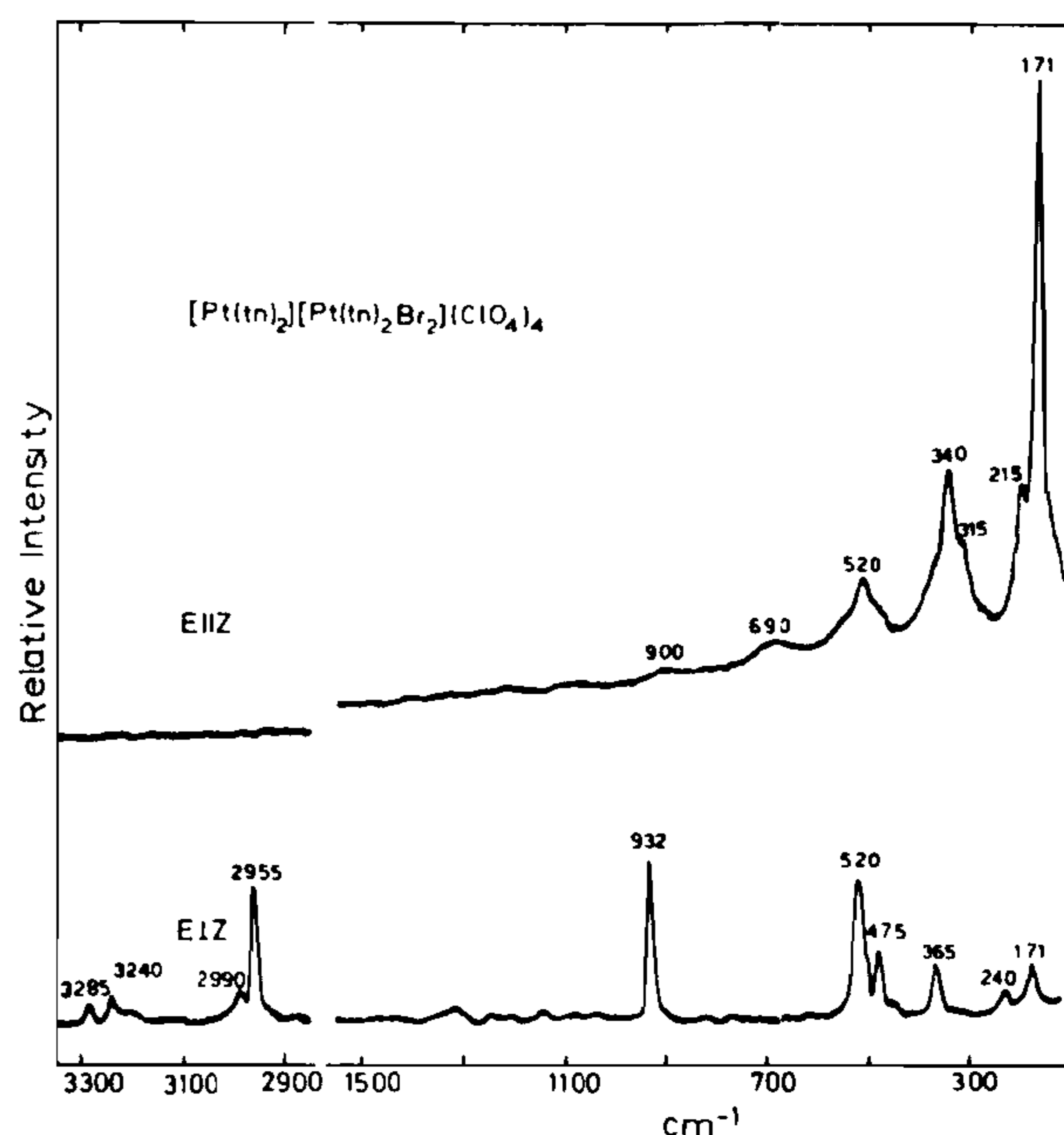


Figure 5. Same as Figure 2 but for $[\text{Pt}^{\text{II}}(\text{tn})_2]$ $[\text{Pt}^{\text{IV}}(\text{tn})_2\text{Br}_2]$ $(\text{ClO}_4)_4$.

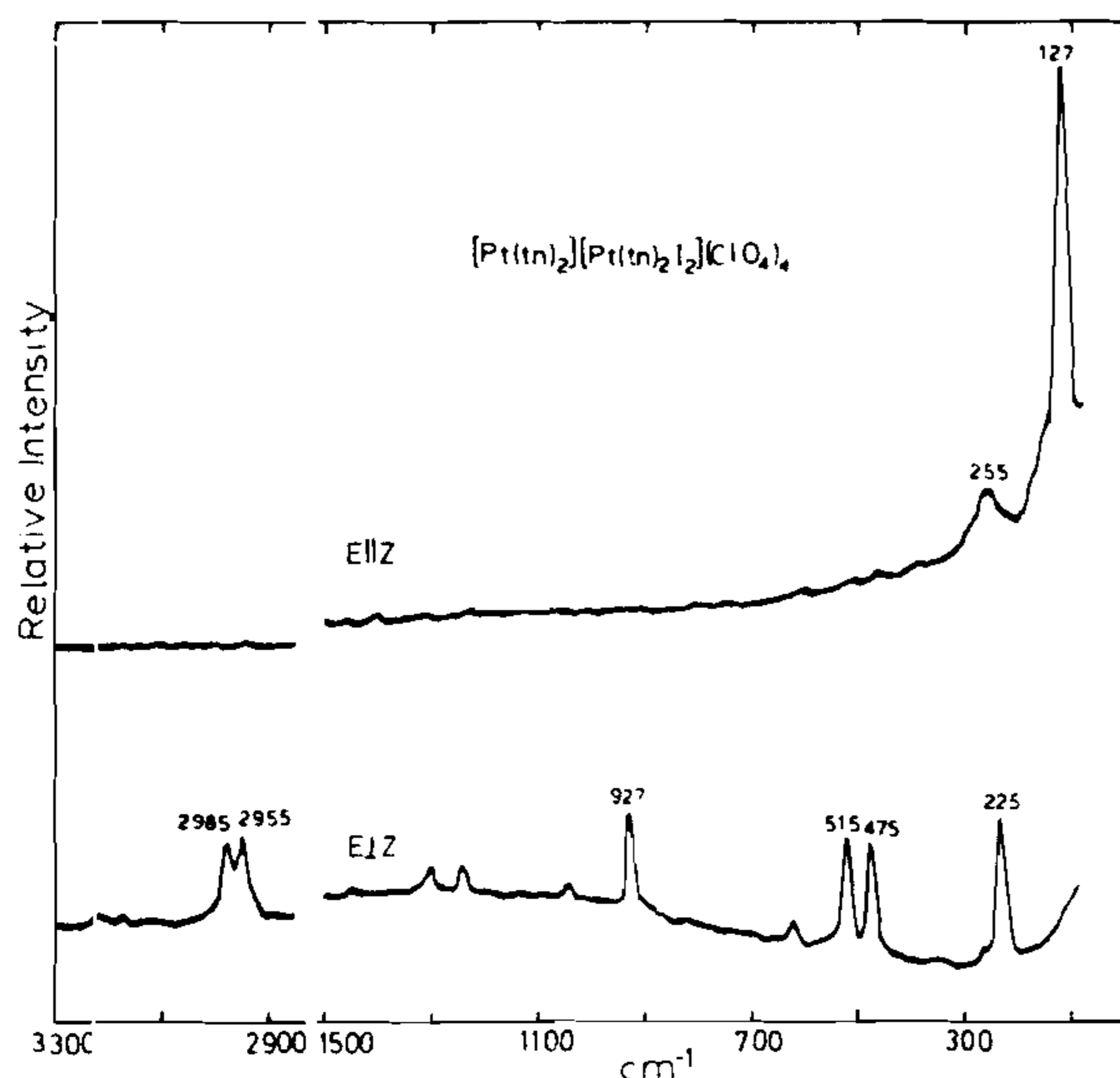


Figure 6. Same as Figure 2 but for $[\text{Pt}^{\text{II}}(\text{tn})_2][\text{Pt}^{\text{IV}}(\text{tn})_2\text{Cl}_2](\text{ClO}_4)_4$.

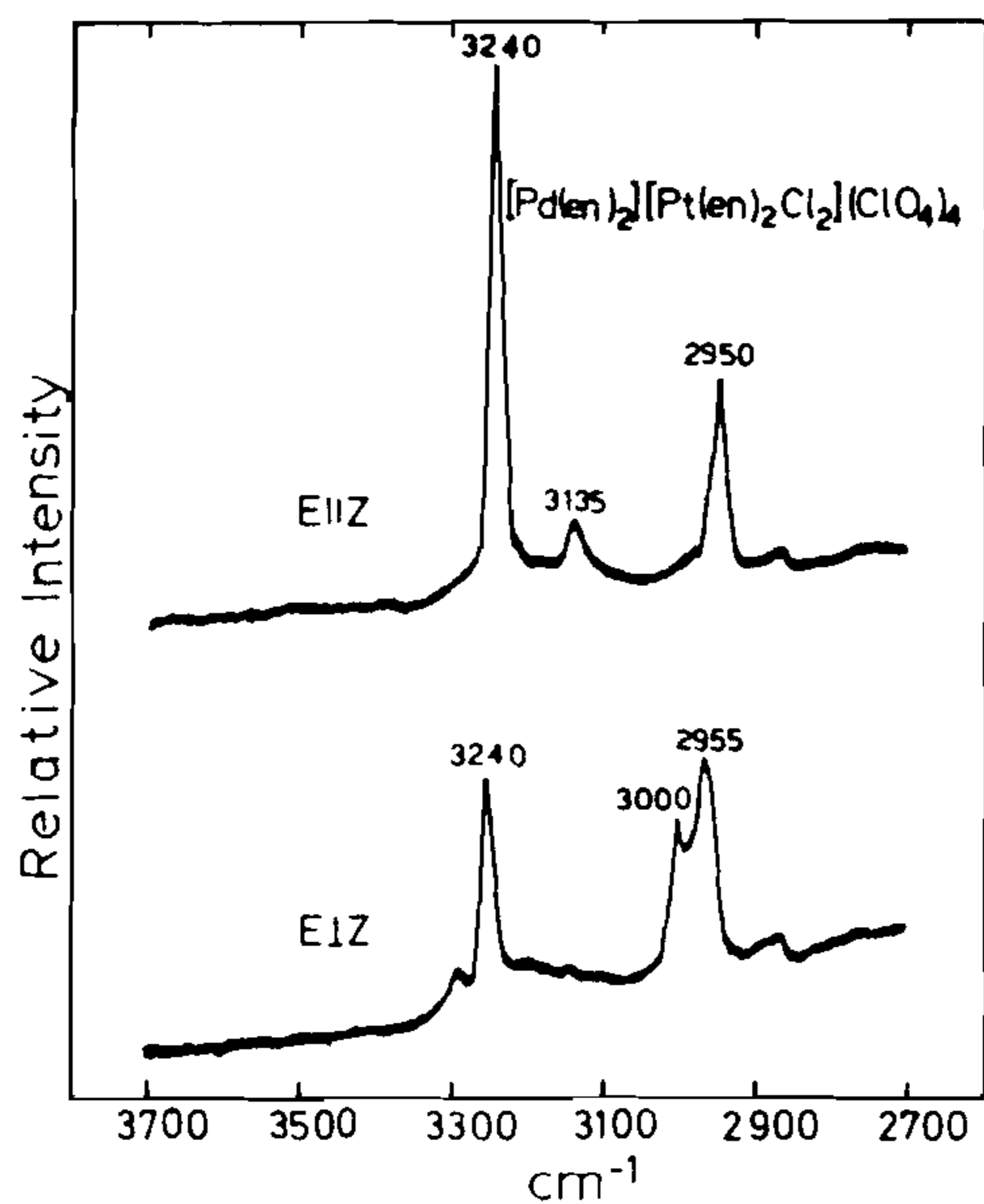


Figure 7. High frequency polarized Raman spectra of $[\text{Pd}^{\text{II}}(\text{en})_2][\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$. Slits 2 cm^{-1} .

away from the resonance region. For example, $[\text{Pd}^{\text{II}}(\text{en})_2][\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$ (en = ethylenediamine), gives yellow crystals (7) and the absorption maximum occurs in the uv region. The high frequency polarized Raman spectra shown in Figure 7 were obtained with the 514.5 nm excitation line. One can see that there is an alternation in the intensity of the bands due to partial orientation of the ethylenediamine-groups.

The polarized resonance Raman spectra of these platinum (II) — platinum (IV) mixed complexes display interesting intensity enhancements due to coupling phenomena between the two platinum atoms in the two and four valences. These are due to a charge transfer $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$ via the halide bridge and to the orientation phenomena of the various groups in the single crystals aligned with the electric wave-vector of the laser light.

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