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RESONANCE RAMAN SPECTRA OF $[Pt(tn)_2][PtBr_2(tn)_2]X_4$ (tn = trimethylenediamine, X = ClO_4 and BF_4)

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Resonance Raman spectra of $[Pt(tn)_2][PtBr_2(tn)_2]X_4$ were measured with the excitation lines, 457.9, 488.0, 514.5, 530.9, 568.2, 647.1 and 676.4 nm. The symmetric Br-Pt-Br stretching (ν_1) vibration was strongly enhanced in this region. The excitation profiles of ν_1 and its overtones roughly follow the band contour of its electronic absorption. This is a marked contrast to that of Reihlen's Green, where the excitation profiles of the same vibrations were remarkably different from its electronic spectrum.

Recently, Clark et al. measured the resonance Raman spectra of mixed-valence compounds such as Wolffram's Red, $[PtL_4][PtCl_2L_4]Cl_4\cdot 4H_2O$(L = ethylamine)$^{1)}$ and its bromo analog(Reihlen's Green)$^{2)}$. In both cases, the spectra were dominated by a very intense progression of the ν_1 vibration(symmetric X-Pt-X stretching mode, X = Cl and Br). They found that the excitation profiles of ν_1 and its overtones of these compounds were markedly different from their electronic(diffuse reflectance) spectra. In the case of Reihlen's Green, the excitation profiles gave sharp maxima at ca. 625 nm and exibited no resonance enhancements between ca. 600 and 400 nm, whereas the electronic spectrum showed a broad band between 700 and 400 nm, the band maximum being at ca. 550 nm. The lack of resonance enhancement in the 600-400 nm region was attributed to "destructive interference effect"$^{3)}$.

In this paper, we studied the resonance Raman spectra and excitation profiles of analogous complexes, $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$ and $[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$, where tn is trimethylenediamine. According to X-ray analysis$^{4)}$, the structures of these compounds are similar to those of ethylamine analogs: the octahedral $[PtBr_2(tn)_2]^{2+}$ ion and the square-planar $[Pt(tn)_2]^{2+}$ ion are stacked alternately in chains by forming the Pt(IV)-Br--Pt(II) bridge.

Preparation of the compounds has been reported elsewhere$^{5)}$. The Raman spectra were recorded on a Spex Model 1401 double monochromator combined with a Spectra-Physics Model 164 Ar-ion laser or a Kr-ion laser. Detection was made by using a cooled RCA C31034 photomultiplier in conjunction with a Spex digital photometer system. The intensity of each band was estimated from the peak area (peak height

Table 1 Wavenumbers(cm^{-1}) and assignments of resonance Raman bands of $[Pt(tn)_2][PtBr_2(tn)_2]X_4$

X	ν_1					$2\nu_1$				$3\nu_1$	$4\nu_1$	$5\nu_1$
ClO_4 (in K_2SO_4)	178.8	213	284	315 (sh)	328	358	391 (sh)	424 (sh)	508 (sh)	539	708	886
BF_4 (in K_2SO_4)	180.7	213	283	313 (sh)	328	361	395 (sh)	427 (sh)	502 (sh)	541	716	877
ClO_4 (in KBr)	184.5	221			336	370	401			552	733	912

times half-band width). To plot an excitation profile, the intensity of the 986 cm^{-1} band of potassium sulfate was used as the internal standard. The corrections for spectrometer sensitivity and the ν^4 law were made for all the bands plotted in the excitation profiles. Frequency calibration was made by using the Ar-ion laser lines. The Raman spectra were measured in K_2SO_4 or KBr pellets which were prepared under the pressure of about 17,000 lbs. During the Raman measurements, the sample was rotated to avoid thermal decomposition at the laser beam focus.

The electronic spectra were measured at room temperature using a Shimazu Multipurpose Spectrophotometer Model MSP-5000. The nujol mull technique was employed.

The resonance Raman spectra of $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$ in a K_2SO_4 pellet obtained by using three excitation lines are shown in Fig. 1. The spectra of the analogous BF_4 salt are very similar to those of the ClO_4 salt, reflecting the red shift of the absorption peak maximum.

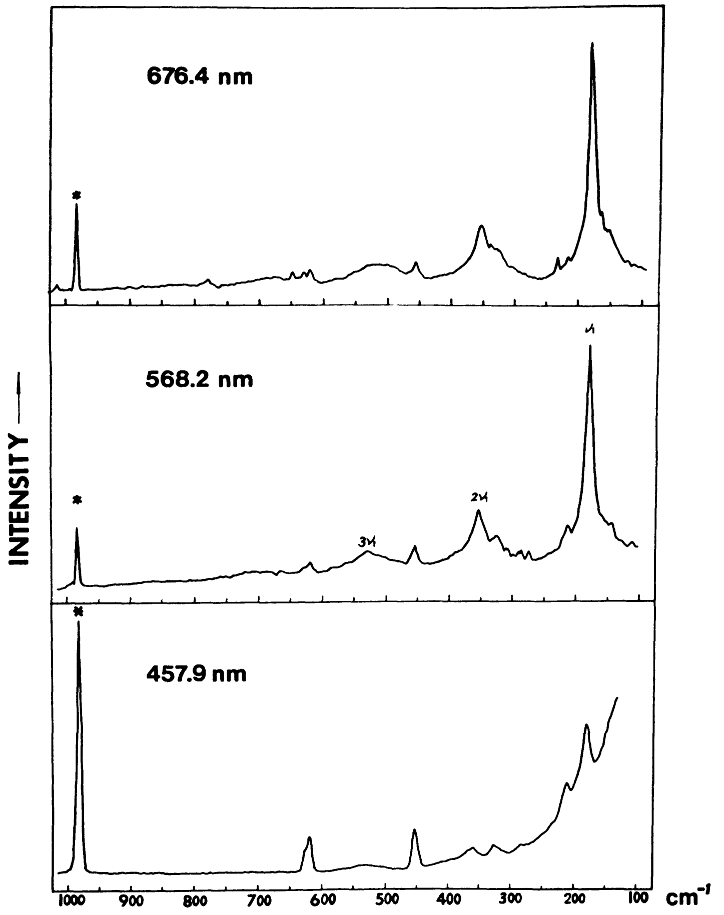

Fig. 1 Resonance Raman spectra of $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$ in K_2SO_4 pellets with three excitation lines. The asterisk indicates the 986 cm^{-1} band of K_2SO_4.

The Table 1 lists the observed frequencies and band assignments. When the ClO_4 salt was pressed in KBr, its color gradually changed from green(ν_{max}, 16000 cm^{-1}) to brownish orange(ν_{max}, 20,000 cm^{-1}). This change is clearly due to the absorption of water in air by the KBr pellet since it did not occur when the pellet was kept in a desiccator. As is shown in the last row of Table 1, the brownish orange pellet exhibited bands which are shifted to higher frequencies relative to those of the two compounds in K_2SO_4 pellets. As will be discussed later, the vibrational frequencies alone are not enough to elucidate the structural change of the ClO_4 salt in the KBr pellet.

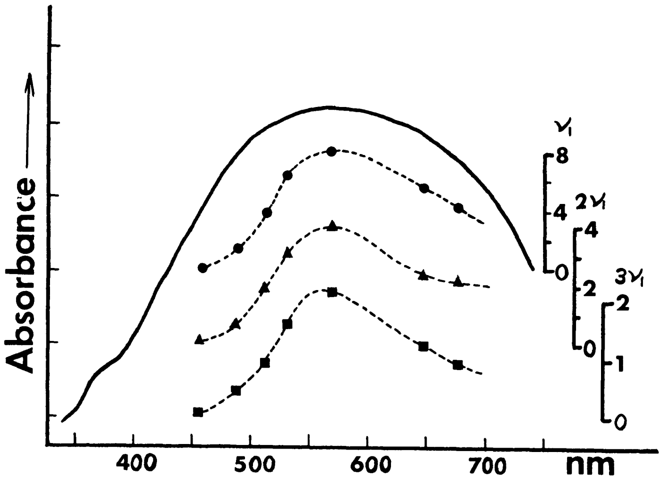

Fig. 2 Excitation profiles of the ν_1, $2\nu_1$, and $3\nu_1$ of the ClO_4 salt in a K_2SO_4 pellet

Similar to the case of Reihlen's Green, the spectra of the $[Pt(tn)_2][PtBr_2(tn)_2]X_4$ type compounds are dominated by the progression of the symmetric Br-Pt-Br stretching (ν_1) mode near 180 cm^{-1}. These frequencies are definitely lower than that of the same mode of $[PtBr_2(tn)_2]Br_2$ (196 cm^{-1}), indicating the weakening of the Pr(IV)-Br bond by the inter-ionic interaction. As is seen in Table 1, the ν_1 frequency is slightly different for each compound. Fig. 2 shows the excitation profiles of ν_1, $2\nu_1$, and $3\nu_1$ of the ClO_4 salt in the K_2SO_4 pellet. It is seen that these excitation profiles resemble the electronic spectrum showing the maximum enhancement near 580 nm.

The origin of the electronic transition in the visible region characteristic of the Pt(II)-Pt(IV) compounds is known to be a charge-transfer from the d_{z^2}(Pt(II)) orbital of the $[Pt(tn)_2]^{2+}$ to the molecular orbital composed of the d_{z^2}(Pt(IV)) and p_z(Br) orbitals of the $[PtBr_2(tn)_2]^{2+}$ ion$^{5),6)}$. This transition is polarized along the Pt(II)····Br—Pt(IV) axis. If we assume a single-state mechanism$^{7)}$, it is easily understood that the Br-Pt-Br stretching (ν_1) mode dominates the resonance Raman spectrum when the exciting line falls in this electronic band. However, the ν_1 frequency of the BF_4 salt(180.7 cm^{-1}) is slightly higher than that of the ClO_4 salt(178.8 cm^{-1}). This frequency trend is consistent with the Pt(IV)-Br distance trend (2.541Å for the BF_4 salt and 2.546Å for ClO_4 salt). However, the difference of Pt-Br distances between these complexes is too small to derive a simple and direct relationship between the ν_1 frequency and the strength of the inter-ionic interaction.

The excitation profiles of the ν_1, $2\nu_1$, and $3\nu_1$ modes of the ClO_4 salt shown in Fig. 2 are markedly different from those of Reihlen's Green by Clark et al.$^{2)}$.

Their excitation profiles show sharp and narrow band-contours with maxima near 625 nm in contrast to its broad electronic absorption with a maximum at 548 nm. Clark et al. suggested a possibility of "destructive interference"$^{3)}$ to account for the lack of resonance enhancement in the 600--400 nm region of the electronic spectrum of Reihlen's Green. On the other hand, our results on $[Pt(tn)_2]$-$[PtBr_2(tn)_2](ClO_4)_4$ show that the excitation profiles roughly follow the band contour of its electronic absorption. Thus, it does not seem necessary to invoke "destructive interference" in our case. At present, it is rather difficult to understand the marked difference in the excitation profiles between our compound and Reihlen's Green. The only difference to be noted between them is that in our compound the Pt(IV) is symmetrically bonded with two bromine atoms whereas in Reihlen's Green the two Pt(IV)-Br distances are not the same. More detailed investigations on the nature of the electronic transitions of these interionic chain compounds is necessary to account for the origin of these differences.

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