

Effect of high external pressures on the vibrational spectra of Zeise's complexes, $K[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_3]$ and $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_2]_2$

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Abstract

The pressure dependences (dv/dP) of the main IR and Raman bands of Zeise's complexes, $K[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_3]$ and $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_2]_2$, have been determined for the first time for selected pressures up to ~ 33 kbar with the aid of diamond-anvil cells. Neither complex undergoes a pressure-induced structural change throughout the pressure range investigated. The dv/dP values range from -0.13 to 0.79 cm^{-1} kbar^{-1} . The negative values have proved particularly informative in identifying the location of the C=C stretching modes of the Pt–ethylene groups, a topic of considerable disagreement in the literature.

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1. Introduction

Transition-metal alkene complexes are the oldest class of organometallic complexes known and they have been extensively studied for almost two centuries. The most famous example, Zeise's salt $K[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_3]$, was first reported in 1830 [1], and is considered as the prototype for the classic Dewar-Chart-Duncanson model for the bonding in transition-metal alkene complexes [2,3]. Donation of electronic charge from the filled π -orbital of the ethylene C=C bond to an empty orbital on platinum and concomitant π -backbonding from a filled platinum d-orbital to the empty π^* -orbital of the ethylene C=C bond would be expected to lead to a reduction in the C=C bond order and consequently an increase in the C=C bond length. The ethylene moiety should also become non-planar. X-ray [4] and neutron [5,6] diffraction measurements have shown that the

C=C bond distance is indeed increased by 0.038 Å over the value for free ethylene. Platinum–alkene complexes have also been investigated by vibrational spectroscopy, where it would be expected that a weakening of the C=C bond would result in a lowering of the C=C force constant and, therefore, a reduction in the associated vibrational frequency. Since the molecular symmetry of the platinum–alkene complexes is low, however, many of the fundamental vibrational modes will have the same symmetry and there will be extensive vibrational coupling between the C=C stretching and symmetric CH_2 deformation modes. There is no obvious correlation between the frequency shift of the C=C stretching mode, which is weak in the IR spectrum, and the strength of the Pt–alkene bond. Moreover, despite extensive vibrational studies of Zeise's salt [3,7–16], there is still considerable disagreement over the correct assignment of the C=C stretching mode. There is a related platinum–ethylene complex, known as Zeise's dimer $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_2]_2$, which is chlorine-bridged; however, this complex has been less well characterized structurally and spectroscopically [7,9].

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The application of high external pressures to Zeise's salt and the related dimer should lead to reductions in the Pt–C₂H₄ distances in the complexes, thereby increasing the π -backbonding and further weakening the C=C bonds and affording lower $\nu(\text{C}=\text{C})$ frequencies. In this paper, we report the results of the first study of the IR and Raman spectra of the two Zeise's complexes as a function of high external pressures.

2. Experimental section

2.1. Materials

Zeise's salt (purity 99%) and Zeise's dimer (purity 99%) were purchased from Aldrich Chemical Co. and Strem Chemicals Inc., respectively, and were used as received.

2.2. Vibrational spectra

Infrared spectra were recorded on a Nicolet 6000 FT-IR spectrometer equipped with a liquid N₂-cooled, mercury–cadmium–telluride (MCT-B) detector. The pressure measurements were made with the aid of a diamond-anvil cell (DAC; Diamond Optics Inc., Tucson, AZ) fitted with a pair of type-IIA diamonds. The samples were contained in a 400- μm diameter hole drilled in the center of a 200- μm thick, circular, stainless-steel gasket, together with some dry NaNO₂ (0.3–0.5% in NaBr) as the pressure calibrant [17]. The antisymmetric $\nu(\text{N}-\text{O})$ mode of the NO₂⁻ ion was used in this work rather than that of the more commonly used NO₃⁻ ion, because the frequency of the latter proved to be overlapped with some of the important sample bands. The stainless-steel gasket was used to ensure that the pressure gradient over the diamond faces was minimal and so no pressure-transmitting fluid was considered necessary for the pressure range being investigated.

Raman spectra were recorded on an Instruments S.A. spectrometer fitted with a Jobin-Yvon Ramanor U-1000, 1.00-m double monochromator equipped with a Nacet optical microscope. The excitation sources used were the 514.521-nm green line from a 5-W Spectra Physics model 164 Ar⁺-ion laser and the 568.188-nm yellow line of a 3-W Coherent Innova 100-K3 Kr⁺-ion laser. Mechanical slit widths of 300 and 500 μm were employed, corresponding to resolutions of 2 and 4 cm⁻¹, respectively. The high-pressure Raman measurements were conducted with the aid of another type of DAC (Diacell Products, Leicester, UK) fitted with a circular, stainless-steel gasket (400- μm thick, 300- μm central hole). A ruby chip was used as the internal pressure calibrant [18]. Again, no pressure-transmitting fluid was deemed necessary for the pressure range being investigated.

3. Results and discussion

No discontinuities or changes in slope were observed in the wavenumber (ν) vs. pressure (P) plots for the main IR and Raman bands of Zeise's salt for pressures up to ~33 kbar (Figs. 1 and 2), indicating the absence of any pressure-induced structural changes. The $d\nu/dP$ values obtained from the IR and Raman data are given in Tables 1 and 2, respectively.

The disagreement in the literature regarding the assignment of the peaks in the 1500–1200 cm⁻¹ region stems chiefly from the extent of mixing of the ethylene C=C stretching mode with the CH₂ scissoring and twisting modes. An intense, polarized peak at 1243 cm⁻¹ in the solution Raman spectrum of Zeise's salt was assigned by Hiraishi [7] to the $\nu(\text{C}=\text{C})$ mode coupled to the CH₂ scissoring mode. In the solid, under pressure, the Raman intensity of this peak decreased dramatically at around 16 kbar and was overlapped by the diamond band at 1353 cm⁻¹. In the corresponding IR spectrum of the solid, the peak appeared at 1253 cm⁻¹, but showed a positive pressure dependence (0.37 cm⁻¹ kbar⁻¹). The weak mode at 1515 cm⁻¹ collapsed in the IR spectrum following the initial application of pressure. Only the 1418 cm⁻¹ peak, displayed a negative pressure dependence and it is considered to be most likely associated with the C=C stretching mode. We reached this conclusion on the basis of earlier work by Adams and Ekejiuba [19] and by us [20–24] on transition-metal carbonyl complexes in which negative pressure dependences for certain $\nu(\text{CO})$ modes could be associated with increased π -backbonding under pressure. Further support for this conclusion comes from the most recent normal-coordinate calculation on Zeise's salt and its perdeuterated analogue [25]. The 1418 cm⁻¹ band is due predominantly to C=C stretching (60%

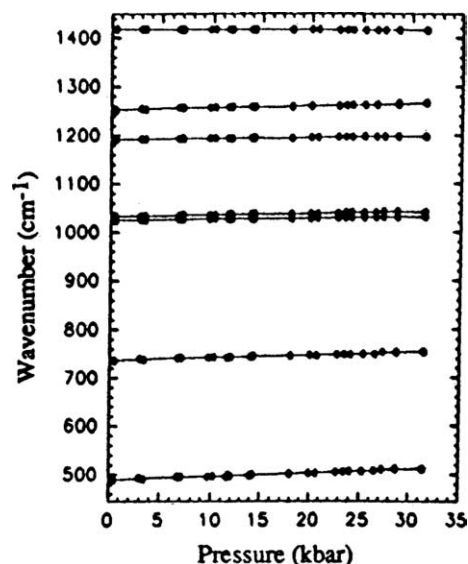


Fig. 1. Pressure dependences of selected IR bands of Zeise's salt.

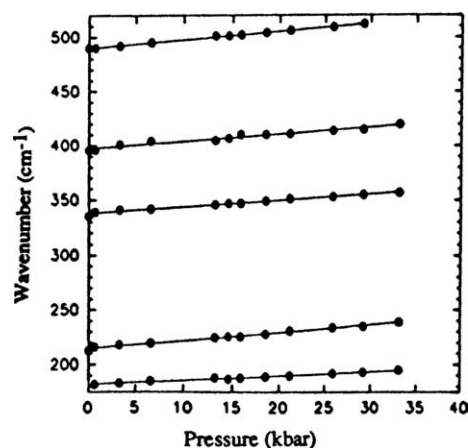


Fig. 2. Pressure dependences of the Raman bands of Zeise's salt.

Table 1
Pressure dependences of the main IR-active vibrations of Zeise's salt

| ν (cm ⁻¹) | $d\nu/dP$ (cm ⁻¹ kbar ⁻¹) | Assignment [7] | Assignment [8] |
|---------------------------|---|--|--|
| 3093 | 0.68 | | a ₂ , $\nu_{\text{sym}}(\text{C-H})$ |
| 3075 | 0.64 | | b ₂ , $\nu_{\text{asym}}(\text{C-H})$ |
| 3010 | 0.38 | b ₁ , $\nu(\text{CH}_2)$ | a ₁ , $\nu_{\text{sym}}(\text{C-H})$ |
| 1418 | -0.08 | a ₁ , $\delta_{\text{sym}}(\text{CH}_2)$ + $\nu(\text{C=C})$ | a ₁ , $\delta_{\text{sym}}(\text{CH}_2)$ + $\nu(\text{C=C})$ |
| 1252 | 0.37 | a ₁ , $\rho_{\text{twist}}(\text{CH}_2)$ | a ₁ , $\nu(\text{C=C})$ + $\delta_{\text{sym}}(\text{CH}_2)$ |
| 1192 | 0.17 | | b ₂ , $\rho_{\text{twist}}(\text{CH}_2)$ |
| 1033 | 0.27 | b ₁ , $\rho_{\text{wag}}(\text{CH}_2)$ | b ₁ , $\rho_{\text{wag}}(\text{CH}_2)$ |
| 1025 | 0.16 | b ₂ , $\rho_{\text{wag}}(\text{CH}_2)$ | |
| 736 | 0.54 | a ₁ , $\rho_{\text{twist}}(\text{CH}_2)$ | b ₁ , $\nu(\text{CH}_2)$ |
| 490 | 0.72 | | b ₁ , $\nu_{\text{asym}}(\text{Pt-C}_2\text{H}_4)$ |

Table 2
Pressure dependences of the strongest Raman-active vibrations of Zeise's salt

| ν (cm ⁻¹) | $d\nu/dP$ (cm ⁻¹ kbar ⁻¹) | Assignment |
|---------------------------|--|---|
| 490 | 0.76 | $\nu_{\text{sym}}(\text{Pt-C}_2\text{H}_4)$ [7,8] |
| 396 | 0.66 | $\nu_{\text{asym}}(\text{Pt-C}_2\text{H}_4)$ [8] |
| 336 | 0.59 | $\nu_{\text{sym}}(\text{Pt-Cl}_2)$ [7,8] |
| 294 | 0.56 | $\nu_{\text{asym}}(\text{Pt-Cl}_2)$ [7,8] |
| 213 | 0.72 | Skeletal def. [7] |
| 182 | 0.39 | Lattice vibration |

R + 2% $\alpha\beta$), while the band at 1253 cm⁻¹ is associated mainly with CH₂ scissoring (120% $\alpha\beta$ + 13% R), where the internal coordinates concerned are R (C=C bond), α (HCH angle) and $\alpha\beta$ (HCC angle). For the related palladium complex, K[Pd(η^2 -C₂H₄)Cl₃], the corresponding modes are assigned at 1526 cm⁻¹ (C=C stretching) and 1267 cm⁻¹ (CH₂ scissoring); these particular assignments are supported by recent density functional theory calculations and isotopic shift data [26] (see Table 3).

The two Raman bands appearing in the 550–400 cm⁻¹ region have been assigned to Pt–ethylene stretching modes. Both bands display shoulders, which

Table 3
Pressure dependences of the main IR-active vibrations of Zeise's dimer

| ν (cm ⁻¹) | $d\nu/dP$ (cm ⁻¹ kbar ⁻¹) | Assignment |
|---------------------------|--|---|
| 3096w | 0.68 | |
| 3084vw | 0.68 | |
| 3071vw | 0.68 | } ν (C–H) str. |
| 3009w | 0.46 | |
| 2981w | 0.62 | |
| 1514w | 0.23 | ν (C=C) str. + δ (CH ₂) sciss. |
| 1507w | 0.32 | δ (CH ₂) sciss. |
| 1427vs | 0.05 | δ (CH ₂) sciss. + ν (C=C) str. |
| 1413s | -0.13 | δ (CH ₂) sciss. |
| 1239mw | 0.48 | δ (CH ₂) rock. |
| 1234w | 0.27 | ν (C=C) str. |
| 1179mw | 0.33 | δ (CH ₂) rock. |
| 1030vs | 0.03 | δ (CH ₂) wag. |
| 1026vs | 0.79 | |
| 1020vs | 0.00 | |
| 817w | 0.26 | (CH ₂) rock. |
| 814w | 0.14 | |
| 725mw | 0.72 | δ (CH ₂) twist. |
| 721mw | 0.43 | |
| ?w,sh | 0.41 | |
| 490mw | 0.19 | } $\nu_{\text{asym}}(\text{Pt-C})$ str. |

can be attributed to factor group splitting of the Pt–ethylene stretching modes into a_g and b_g components, associated with the P_1/c (C_{2h}⁵) space group of the crystal [4–6], which disappear as the bands broaden with increasing pressure. The pressure dependences are quite large and are similar to those observed for ν (metal-C) modes in transition-metal carbonyl complexes [21,23], affording additional evidence for an increase in π -backbonding due to pressure-induced shortening of the Pt–ethylene bond.

The CH₂ deformation modes are strongly coupled to the C=C stretching vibration. The symmetric CH₂ twist has been assigned previously [9,16] to the IR band at 736 cm⁻¹, and is at lower energy than are the CH₂ wagging and rocking modes, since it is more dependent on the decrease in the C=C bond strength. This 736 cm⁻¹ band exhibits the largest pressure dependence (0.54 cm⁻¹ kbar⁻¹) of all the bands in the IR spectrum. At ~14 kbar, the CH₂ rocking mode appears as a weak, broad band at 840 cm⁻¹, which increases in intensity at the expense of the CH₂ twist due to increased coupling between these modes under pressure. The antisymmetric CH₂ twist was not observed in either the Raman or the IR spectra.

The ν (Pt–Cl) modes are almost coincident in the Raman spectrum and both bands have similar pressure dependences, but do not separate with increasing pressure. It might be expected that the *trans*-chlorine would show some effects of the increased π -backbonding. These low-energy modes are particularly susceptible, however, to intermolecular forces and crystal packing

effects. Therefore, the *trans* influence may play only a secondary role in determining the pressure dependences of the $\nu(\text{Pt}-\text{Cl})$ modes.

Unfortunately, in the case of Zeise's dimer, $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_2]_2$, the pressure dependences of the Raman bands could not be determined because of the intense fluorescence background and sample decomposition upon the prolonged laser irradiation necessary for the pressure measurements. The IR and Raman spectra of the dimer, at ambient pressure, resemble quite closely those of Zeise's salt itself, except for doubling of many bands. The high-energy components of the more clearly resolved doublets exhibit larger pressure dependences than do the low-energy ones. Doublets are observed in the anticipated C=C stretching region ($1500\text{--}1250\text{ cm}^{-1}$) region at 1514/1502, 1427/1413, and 1239/1234 cm^{-1} . The C=C stretching mode in Zeise's dimer is coupled to the CH_2 deformations in much the same way as is that in Zeise's salt. Only the 1413 cm^{-1} band exhibits a negative pressure dependence suggesting a large contribution from the C=C stretching mode, although the other component of the doublet shows only a slight positive pressure dependence. The weak mode at $\sim 1500\text{ cm}^{-1}$, which could not be observed in the IR pressure study of Zeise's salt, is clearly present in the case of the dimer. The shoulder on the low-energy side becomes better defined at higher pressures and the relative intensity pattern gradually changes from the higher energy component being the stronger to the lower energy component becoming the stronger. Such behavior is suggestive of Fermi resonance, but an attempt to fit the band positions according to the method of Sherman and Lewis [27] was unsuccessful. The pressure dependences for the vibrations of Zeise's dimer are similar to those observed for Zeise's salt.

4. Conclusion

It appears that the application of high external pressures may indeed be a useful way of establishing the presence of π -backbonding in organometallic complexes, since the vibrations most involved with π -backbonding tend to exhibit negative pressure dependences.

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