Inelastic neutron scattering studies of ethylene-containing square planar platinum complexes

JOSEPH HOWARD, KEITH ROBSON and THOMAS C. WADDINGTON Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, U.K.

(Received 5 March 1982)

Abstract—The low frequency $(0-850 \,\mathrm{cm}^{-1})$ modes of vibration of the complexes trans-PtCl₂(C₂H₄) · L (where L = ND₃, CD₃CN, DCON(CD₃)₂ and C₆D₃ND₂) and cis-PtCl₂(C₂H₄) · (CD₃)₂ SO have been studied by inelastic neutron scattering, i.r. and Raman spectroscopy. In all complexes, motions of the C₂H₄ moiety relative to the platinum atom (including torsional modes) have been assigned and the barrier to rotation of the C₂H₄ ligand about an axis projected from the platinum atom through the centre of the C=C bond determined. The barriers thus calculated have been compared with energies of activation obtained from nuclear magnetic resonance studies of similar complexes.

INTRODUCTION

Both kinetic (NMR) and spectroscopic techniques have been employed to investigate potential barriers and, particularly using the former, much study has been directed towards platinum-olefin complexes [1-4]. Kinetic measurements (as a function of temperature) enable calculation of the energy of activation (E_a) , while spectroscopic studies (at a single temperature) yield information concerning the energy of transitions within the potential well. From the latter, together with a suitable model for the shape of the barrier, may be calculated both a barrier height (V_n) and also the zero point energy $(h\nu)$ by solution of the Mathieu equation [5]. The two quantities may be related thus

$V_n = E_a + h\nu.$

In many cases it has proved difficult to observe torsional frequencies using optical techniques. However, torsional modes involving appreciable proton motion are readily observed using inelastic neutron scattering (INS) spectroscopy[6]. There are, unfortunately, few examples of ethylene-containing complexes studied by NMR whose INS spectra allow relatively easy interpretation. Nonetheless, several successful INS studies have been reported[7–9].

BACKGROUND

The structures of *cis*- and *trans*-PtCl₂(C₂H₄) · L most probably resemble that of *cis*-PtBr₂(C₂H₄) · NH₃[10] and may thus be thought of as being derived from Zeise's salt, K[PtCl₃(C₂H₄)], which contains a square planar ion[11-19]. Rotation of the ethylene ligand within Zeise's salt has been observed using wide-line NMR[20] and has been proved, in variable temperature ¹H and ¹³C NMR studies of [Os(CO)NO(C₂H₄) (PPh₃)₂]PF₆, to take place about an axis perpendicular to the C=C bond[21]. Molecular orbital calculations carried out by WHEELOCK *et al.*[22] have shown, that for divalent *trans*-ethylene platinum complexes, the potential function describing this motion has a minimum when the ethylene ligand is perpendicular to the plane and a metastable minimum when the ethylene ligand lies in the plane.

EXPERIMENTAL

The trans-ethylene complexes, $PtCl_2(C_2H_4) \cdot ND_3$, $PtCl_2(C_2H_4) \cdot CD_3CN$, $PtCl_2(C_2H_4) \cdot DCON(CD_3)_2$, $PtCl_2 \cdot CD_3CN$, $PtCl_2(C_2H_4) \cdot DCON(CD_3)_2$, $PtCl_2 \cdot CD_3CN$ $(C_2H_4) \cdot C_6D_5ND_2$ and $PtCl_2(C_2H_4) \cdot C_6D_5NH_2$, were prepared from Zeise's dimer, [PtCl₂(C₂H₄)]₂, by addition of one equivalent of the appropriate ligand in ethanol using the procedure described by MEESTER et al. for the analogous compounds with hydrogenous ligands [23]. (C₆D₅NH₂ was prepared from C₆D₅ND₂ by shaking $C_6D_5ND_2$ with excess H_2O_2 .) Cis-PtCl₂(C_2H_4) · (CD₃)₂SO was prepared similarly to the method described in the literature by BOUCHER and BOSNICH [24] for cis- $PtCl_2(C_2H_4) \cdot (CH_3)_2SO[24]$. ND₃, DCON(CD₃)₂ and C₆D₅ND₂ were purchased from Merck Sharp and Dohme Ltd., whilst CD₃CN and (CD₃)₂SO were supplied by Ciba-Geigy. In all cases, employment of deuterated ligands was intended to simplify analysis of INS spectra by decreasing the intensity of those hydrogenous modes not associated with the ethylene ligand.

INS spectra of the samples (polycrystalline powders contained in sealed silica cells) were measured employing spectrometers on the Dido and Pluto reactors at AERE Harwell. Neutron energy gain time-of-flight (TOF) spectra were obtained in the case of the perdeuterated trans-ethylene complexes at 243 K using the Dido 6H long wavelength spectrometer [25, 26] and in the case of cis-PtCl₂(C₂H₄) (CD₃)₂SO at 293 K using the Dido 4H5 cold neutron spectrometer [26, 27]. Higher energy transfer neutron energy loss spectra were recorded employing the Pluto beryllium filter detector (BFD) spectrometer [28] (77 K) for trans-PtCl₂(C₂H₄) trans-PtCl₂(C₂H₄) \cdot DCON(CD₃)₂ ·ND1. and cis-PtCl₂(C₂H₄) · (CD₃)₂SO and the Dido BFD spectrometer [29] (16, 77 and 77 K, respectively) for trans-PtCl₂(C₂H₄) · CD₃CN, trans-PtCl₂(C₂H₄) · C₆D₅ND₂ and trans-PtCl₂(C₂H₄) · C₆D₅NH₂.

Unlike BFD spectra, which can be obtained in a form

immediately comparable with optical spectra by plotting "detected neutron counts per *n* monitor counts"vs energy, "raw" TOF data require several corrections [30] and formulation in terms of various useful functions [31] (e.g. $P'(\alpha, \beta)$ [6]) before comparison. However, it should be noted that both $P'(\alpha, \beta)$ (TOF data) and "detected counts" (BFD data) are proportional to the amplitude weighted density of states multiplied by the Debye-Waller factor [32]. Transition frequencies in BFD spectra have been calculated from observed band maxima using known correction factors [28].

The intensities of INS bands have been measured using a DuPont curve resolver. Where appropriate measured INS intensities have been compared with those calculated for the hindered translational and rotational modes (Fig. 1) of the coordinated ethylene molecule (Table 1) using methods described previously[6, 7, 33].

Far i.r. measurements (50-400 cm⁻¹) were made at ambient and liquid nitrogen temperatures using a Beckmann-RIIC FS720 Fourier transform spectrophotometer, whilst the mid i.r. (200-850 cm⁻¹) was scanned at room temperature using a Perkin-Elmer 577 spectrophotometer. With the former instrument, samples were run as nujol mulls supported on polyethylene discs, with latter as nujol mulls between CsI plates.

Raman spectra were measured in the range $0-850 \text{ cm}^{-1}$ with a Cary 82 Raman spectrophotometer employing a Spectra-physics model 125 He/Ne laser at 15802 cm⁻¹ (14 mW power at the sample).

RESULTS AND DISCUSSION

Previous INS studies of Zeise's salt and dimer have shown that motions of the ethylene group dominate the spectra as a result of the very large incoherent scattering cross-section of the proton[7, 33]. Coordination of ethylene to hypothetical MX_3^- to form a square planar complex results in the appearance of six new normal modes. Of these, three (τ_x, τ_y) or antisymmetric stretch and τ_z) may be considered as hindered rotations and three $(t_x \text{ or wag}, t_y \text{ or rock and } t_z \text{ or }$ symmetric stretch) as hindered translations of the ethylene ligand (Fig. 1). τ_z , t_x and t_y have been observed in TOF spectra (i.e. below 250 cm^{-1}) of Zeise's dimer [7] (Table 2), the most intense of these, and indeed the most intense band below ~700 cm⁻¹, being τ_z . Of the remaining modes, τ_x (found at ~1180 cm⁻¹ in optical spectra[34] has not been located in INS spectra of Zeise's salt and dimer [33], whilst τ_{y} and t_{z} have been observed in

Table 1. Predicted relative intensities in the INS spectrum of the three rotational and three translational modes of the ethylene ligand relative to the platinum atom

Mode	Predicted Relative Intensity ^a
т _х	6.7
$\tau_y \text{ or } v_{as}(Pt-C_2H_4)$	2,6
τ_z or $C_2^{H_4}$ torsion	3.0
t_x or $Pt-C_2H_4$ wag	1.0
t or Pt-C2H4 rock	1.0
$t_z \text{ or } v_s(Pt-C_2H_4)$	1.0

*Calculated using neutron diffraction data for the ethylene ligand in Zeise's salt[19].

BFD spectra at \sim 490 and \sim 400 cm⁻¹, respectively [33] (Table 2).

Since the method of assigning the bands in each complex is essentially similar, we will only discuss in detail trans-PtCl₂(C₂H₄) \cdot ND₃ and cis- $PtCl_2(C_2H_4) \cdot (CD_3)_2SO$. The other trans complexes will therefore be commented upon only in so far as there are any differences or additional assignments between them and trans- $PtCl_2(C_2H_4) \cdot ND_3$.

(a) Trans-PtCl₂(C₂H₄) \cdot ND₃

INS spectra of $trans-PtCl_2(C_2H_4) \cdot ND_3$ are shown Figs. 2(a) and 3(a) and the frequencies derived from these and optical data are summarized in Tables 2 and 3.

Bearing in mind the resolution of the spectrometer (~40 cm⁻¹[28]), the three intense bands in the BFD spectrum of *trans*-PtCl₂(C₂H₄) · ND₃ below 650 cm⁻¹ must represent the symmetric stretch (t_2), antisymmetric stretch (τ_y) and the C₂H₄ torsion (τ_z) of the ethylene ligand. The 388 and 474 cm⁻¹ BFD bands may be assigned to the symmetric (t_z) and antisymmetric (τ_y) stretches respectively following the assignments of these modes at 386 and 475 cm⁻¹ in i.r. and Raman spectra of the equivalent NH₃ ligand complex[23].



Fig. 1. The three hindered rotations, τ_x , τ_y (antisymmetric stretch) and τ_{zx} and the three hindered rotations, t_x (wag), t_y (rock) and t_z (symmetric stretch), of the ethylene ligand relative to the platinum atom.

tcl3 ($C_{4}H_{4}$) Tetans- tetans- <th>'tCl₃(C₂H₄)] [[7,33]</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>	'tCl ₃ (C ₂ H ₄)] [[7,33]								
$ \begin{bmatrix} 7, 33 \end{bmatrix} \ \ \ \ \ \ \ \ \ \ \ \ \$	[7, 33]	$[PtCl_2(C_2H_4)]_2$	trans-	trans-	trans-	trans-	trans-	cis-	Assignment
29.0 ± 2.0 3.0 ± 2.0 3.0 ± 2.0 4.0 ± 4.0		[7, 33]	$\operatorname{Ptcl}_2(\operatorname{C_2H}_4).\operatorname{ND}_3$	$Ptcl_2(c_2H_4).cD_3cN$	$\text{Ptcl}_2(c_2^{}\text{H}_4^{}),\text{Dcon}(\text{cD}_3^{})_2^{}$	PtC1 ₂ (C ₂ H ₄).C ₆ D ₅ ND ₂	$\operatorname{Ptcl}_2(c_2H_4).c_6D_5NH_2$	$PtCl_{2}(C_{2}H_{4}).(CD_{3})_{2}SO$	
61.0 ± 3.5 61.0 ± 3.5 61.0 ± 3.5 62.0 ± 3.5 62.0 ± 3.5 62.0 ± 3.5 62.0 ± 4.5 82.0 ± 4.5 82.0 ± 4.5 82.0 ± 4.5 82.0 ± 4.5 85.0 ± 4.5 82.5 ± 4.5 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 95.0 ± 4.0 133.5 ± 7.0 133.5 ± 7.0 133.5 ± 7.0 133.5 ± 7.0 133.5 ± 7.0 133.5 ± 7.0 133.5 ± 7.0 133.5 ± 6.5 134.5 ± 6.5 134.5 ± 6.5 134.5 ± 6.5 134.5 ± 6.5 134.5 ± 6.5 134.5 ± 6.5 134.5 ± 6.5 134.5 ± 6.5 134.5 ± 6.5 134.5 ± 6.5				29.0 ± 2.0	34.0 ± 2.0	33.0 ± 2.0		42.0 ± 2.0	Totto and a
82.0 ± 4.5 85.0 ± 4.5 85.0 ± 4.5 82.5 ± 4.5 92 ± 4.5 96.0 ± 4.0 110 122.0 ± 6.5 127.5 ± 7.0 132.5 ± 7.5 123.5 ± 7.0 133.5 ± 7.0 133.5 ± 6.5 185 170 170.5 ± 10.0 166.5 ± 9.5 175.0 ± 10.0 166.0 ± 9.5 170 ± 8 173.5 ± 6.5 190 218.0 ± 13.0 207.0 ± 12.0 218.0 ± 13.0 207.0 ± 12.0 218.0 ± 13.0 207.5 ± 12.0 133.5 ± 6.5 291 ± 8 291 ± 8 271 ± 8 271 ± 8 271 ± 8 271 ± 8 208.0 ± 11.5 200 400 388 ± 10 291 ± 8 345 ± 10 340 ± 8 349 ± 10 400 400 388 ± 10 394 ± 8 4.17 ± 10 382 ± 8 349 ± 10 400 407 40 474 ± 10 4.75 ± 10 382 ± 8 4.97 ± 8 4.72 ± 10 720 718 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 800 ± 10 810 ± 10 801 ± 8 818 ± 10 801 ± 8 806 ± 10 191 ± 10			61.0 ± 3.5	49.5 ± 3.0	51.0 ± 3.0	60.0 ± 3.5		62.0 ± 2.5	
110 122.0 ± 6.5 127.5 ± 7.0 132.5 ± 7.5 123.5 ± 7.0 133.5 ± 6.5 185 170 170.5 ± 10.0 166.5 ± 9.5 175.0 ± 10.0 166.0 ± 9.5 170 ± 8 172.0 ± 9.0 190 218.0 ± 13.0 207.0 ± 12.0 218.0 ± 13.0 202.5 ± 12.0 208.0 ± 11.5 208.0 ± 11.5 201 291 ± 8 291 ± 8 271 ± 8 275 ± 8 208.0 ± 11.5 201 291 ± 8 345 ± 10 201 ± 8 275 ± 8 208.0 ± 11.5 201 201 201 202.5 ± 12.0 205 ± 12.0 208.0 ± 11.5 208.0 ± 11.5 400 388 ± 10 394 ± 8 345 ± 10 340 ± 8 345 ± 8 349 ± 10 400 400 388 ± 10 394 ± 8 275 ± 8 349 ± 10 400 407 417 ± 10 453 ± 8 457 ± 8 344 ± 8 201 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 201 810 ± 10 830 ± 8 818 ± 10 821 ± 8 237 ± 8 719 ± 10				82.0 ± 4.5	85.0 ± 4.5	82.5 ± 4.5	92 ± 8	96.0 ± 4.0	п (С1-Рt-С1) ⁸
183 170 170: 5 \pm 10.0 166.5 \pm 9.5 173: 0 \pm 10.0 166.0 \pm 9.5 170 \pm 8 172.0 \pm 9.0 190 218.0 \pm 13.0 207.0 \pm 12.0 218.0 \pm 13.0 202.5 \pm 12.0 208.0 \pm 11.5 201 ± 8 291 ± 8 271 ± 8 271 ± 8 275 ± 8 200 400 388 \pm 10 394 ± 8 44.7 \pm 10 340 ± 8 349 ± 8 400 487 474 ± 10 474 ± 10 474 ± 10 473 ± 8 497 ± 8 472 ± 10 720 718 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 840 820 ± 80 818 ± 10 821 ± 8 834 ± 8 719 ± 10 719 ± 10 720 718 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 840 810 ± 10 830 ± 8 818 ± 10 821 ± 8 844 ± 8 806 ± 10		110	122.0 ± 6.5	127.5 ± 7.0	132.5 ± 7.5	123.5 ± 7.0		133.5 ± 6.5	$Pt-C_2H_4$ wag (t_x)
190 218.0 ± 13.0 207.0 ± 12.0 218.0 ± 13.0 202.5 ± 12.0 208.0 ± 11.5 291 ± 8 291 ± 8 291 ± 8 271 ± 8 275 ± 8 208.0 ± 11.5 200 400 388 ± 10 345 ± 10 340 ± 8 345 ± 10 349 ± 10 400 400 388 ± 10 394 ± 8 4,17 ± 10 382 ± 8 349 ± 10 400 487 474 ± 10 4,75 ± 8 505 ± 10 4,83 ± 8 4,97 ± 8 349 ± 10 720 718 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 840 810 ± 10 830 ± 8 818 ± 10 821 ± 8 844 ± 8 806 ± 10	185	170	170.5 ± 10.0	166.5 ± 9.5	175.0 ± 10.0	166.0 ± 9.5	170 ± 8	172.0 ± 9.0	C_2H_4 torsion (τ_z)
291 ± 8 271 ± 8 275 ± 8 400 305 ± 10 340 ± 10 340 ± 10 349 ± 10 400 400 388 ± 10 394 ± 8 417 ± 10 382 ± 8 349 ± 10 400 400 388 ± 10 394 ± 8 417 ± 10 382 ± 8 349 ± 10 400 487 474 ± 10 475 ± 8 505 ± 10 483 ± 8 497 ± 8 472 ± 10 720 718 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 840 820 810 ± 10 830 ± 8 818 ± 10 821 ± 8 844 ± 8 806 ± 10		190	218.0 ± 13.0	207.0 ± 12.0	218.0 ± 13.0	202.5 ± 12.0		208.0 ± 11.5	Pt-C ₂ H4 rock (t _y)
400 400 384 ± 10 345 ± 10 340 ± 8 349 ± 10 400 400 388 ± 10 394 ± 8 417 ± 10 382 ± 8 365 ± 8 384 ± 10 490 487 474 ± 10 475 ± 8 505 ± 10 483 ± 8 497 ± 8 472 ± 10 720 718 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 840 810 ± 10 830 ± 8 818 ± 10 807 ± 8 806 ± 10				291 ± 8		271 ± 8	275 ± 8		Combination band
400 400 384 ± 10 394 ± 8 417 ± 10 382 ± 8 503 ± 10 384 ± 10 490 487 474 ± 10 475 ± 8 505 ± 10 483 ± 8 497 ± 8 472 ± 10 720 718 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 840 820 810 ± 10 830 ± 8 818 ± 10 821 ± 8 834 ± 8 806 ± 10				339 ± 8	345 ± 10	340 ± 8	0 + 370	349 ± 10	۷ ₈ (C1-Pt-C1) ⁸
490 487 474 ± 10 475 ± 8 505 ± 10 483 ± 8 497 ± 8 472 ± 10 720 718 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 840 820 810 ± 10 830 ± 8 818 ± 10 821 ± 8 834 ± 8 806 ± 10	007	007	388 ± 10	394 ± 8	417 ± 10	382 ± 8		384 ± 10	$v_{\mathbf{g}}^{(Pt-C_{\mathbf{Z}}H_{4})(\mathbf{t}_{\mathbf{z}})$
720 718 713 ± 10 724 ± 8 753 ± 10 707 ± 8 737 ± 8 719 ± 10 840 820 810 ± 10 830 ± 8 818 ± 10 821 ± 8 834 ± 8 806 ± 10	067	487	474 ± 10	475 ± 8	505 ± 10	483 ± 8	497 ± 8	472 ± 10	$v_{ag}^{(Pt-C_2H_4)(\tau_y)}$
840 820 810 ± 10 830 ± 8 818 ± 10 821 ± 8 834 ± 8 806 ± 10	720	718	713 ± 10	724 ± 8	753 ± 10	707 ± 8	737 ± 8	719 ± 10	CH ₂ rock
	840	820	810 ± 10	830 ± 8	818 ± 10	821 ± 8	834 ± 8	806 ± 10	CH ₂ rock

e 2.	Comparison of the INS spectroscopic frequencies (cm ⁻¹) and assignments of the <i>trans</i> - and <i>cis</i> -PtCl ₂ (C_2H_4) · L complexes and Zeise's salt and dimer	
	e 2. (

^{*}Mode description stated is that applicable to *trans*-PtCl₂(C₂H₄) · L complexes. In the case of *cis*-PtCl₂(C₂H₄) · (CD₃)₂SO, π (Cl-Pt-Cl) becomes π (Cl-Pt-L) and ν_{4} (Cl-Pt-Cl) becomes ν (Cl-Pt-L).

 v_{ν} symmetric stretch; v_{ω} , antisymmetric stretch; δ , in-plane bend; π , out-of-plane bend.



Fig. 2. BFD spectra of (a) $trans-PtCl_2(C_2H_4) \cdot ND_3$ (77 K), (b) $trans-PtCl_2(C_2H_4) \cdot CD_3CN$ (16 K), (c) $trans-PtCl_2(C_2H_4) \cdot DCON(CD_3)_2$ (77 K), (d) $trans-PtCl_2(C_2H_4) \cdot C_6D_5ND_2$ (77 K), (e) $trans-PtCl_2(C_2H_4) \cdot C_6D_5NH_2$ (77 K) and (f) $cis-PtCl_2(C_2H_4) \cdot (CD_3)_2SO$ (77 K), \oplus , × and + denote data collected using the Al(111), Al(311) and Al(511) monochromator planes, respectively.

The third BFD band (171 cm^{-1}) , which is the most intense feature in the spectrum, consequently must represent the C₂H₄ torsion, its frequency and relative intensity being in agreement with those found for this mode in INS studies of Zeise's salt and dimer [7, 33] (Tables 1 and 2).

The band assigned to the C_2H_4 torsion displays two distinct shoulders in the TOF spectra. That to higher frequency (218.0 cm⁻¹ TOF/203 cm⁻¹ BFD) may be assigned to the Pt- C_2H_4 rock (t_y) located in i.r.[34, 35], Raman[34] and INS[7, 33] investigations of Zeise's dimer in the region 190-201 cm⁻¹ and in optical studies only of Zeise's salt between 210 and 219 cm⁻¹[34, 36]. The lower frequency shoulder (122.0 cm⁻¹ TOF) similarly may be assigned to the remaining platinum-ethylene translational mode, the Pt- C_2H_4 wag (t_x), in accordance with reported frequencies in the i.r. spectrum of Zeise's salt (121 cm⁻¹)[36] and in the INS spectrum of Zeise's dimer (110 cm⁻¹)[7, 33].

Of the remaining unassigned INS bands, those at 713 and 810 cm⁻¹ may, by analogy with Zeise's



Fig. 3. TOF spectra of (a) $trans-PtCl_2(C_2H_4) \cdot ND_3$, (b) $trans-PtCl_2(C_2H_4) \cdot CD_3CN$, (c) $trans-PtCl_2(C_2H_4) \cdot DCON(CD_3)_2$, (d) $trans-PtCl_2(C_2H_4) \cdot C_6D_3NH_2$ and (e) $cis-PtCl_2(C_2H_4) \cdot (CD_3)_2SO$. Spectra (a)-(d) recorded at 243 K, spectrum (e) at 293 K. Scattering angles: (a), (c), (d) = 54°, (b) = 36° and (e) = 66°.

salt and dimer [33, 34] (Table 2), be assigned to CH_2 rocking modes of the ethylene ligand. In view of the prior assignment of all predicted low frequency vibrations of the ethylene ligand relative to the platinum atom, the 44 cm⁻¹ BFD/61 cm⁻¹ TOF band must represent a lattice mode.

i.r. and Raman spectra of trans-The $PtCl_2(C_2H_4) \cdot ND_3$ are essentially in agreement with those reported $(100-500 \text{ cm}^{-1})$ by MEESTER et al. [23] for the equivalent NH₃ ligand complex. We may thus assign the symmetric and antisymmetric chlorine stretches [v_s (Cl-Pt-Cl) and v_{as} (Cl-Pt-Cl)] to bands at 330 cm^{-1} (Raman) and 337 cm^{-1} (i.r.), respectively. Lower frequency i.r. and Raman bands are, however, more difficult to identify as they result from bending modes of the square planar skeleton, the activities and possible splittings of which are problematical in the absence of accurate structural data. Assignment of this region of the spectrum must therefore be tentative. Vibrations at 161 and 183 cm⁻¹ in the i.r. spectrum of Zeise's salt have been assigned to $\delta(Cl-Pt Cl_{trans}$) + (Cl-Pt-C₂H₄) and to $\delta(Cl-Pt-Cl),$ respectively [36], and we shall employ the

I.r.	Raman		INS	Assignment
		BFD	TOF	
	48 s	44 ± 10	61.0 ± 3.5	Lattice mode
			122.0 ± 6.5	$Pt-C_2H_4$ wag (t)
		171 ± 10	170.5 ± 100	C_2H_4 torsion (τ_z)
186 s				δ(Cl-Pt-Cl)
220 s	205 m	203 ± 10	218.0 ± 13.0	$Pt-C_2H_4$ rock (t_y)
330 sh	330 s			v _s (Cl-Pt-Cl)
337 s	344 sh			v _{as} (Cl-Pt-Cl)
346 sh				
378 w	377 w	388 ± 10		$v_{s}(Pt-C_{2}H_{4})(t_{z})$
	415 vw			
	436 sh			v(Pt-L)
467 w	462 sh	474 ± 10		$v_{as}(Pt-C_2H_4)(\tau_y)$
	481 w			
720 m]		
735 sh		713 ± 10		CH ₂ rock
		810 ± 10		CH ₂ rock

Table 3. The INS and optical spectroscopic frequencies (cm^{-1}) and assignments of *trans*-PtCl₂(C₂H₄) \cdot ND₃

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; ν_s , symmetric stretch; ν_{as} , antisymmetric stretch; δ , in-plane bend; π , out-of-plane bend.

equivalent assignments [i.e. δ (Cl-Pt-L) + (Cl-Pt- C_2H_4) and δ (Cl-Pt-Cl), respectively] for the 166 cm^{-1} (Raman) band of trans-(i.r.)/155 obvious $PtCl_2(C_2H_4) \cdot NH_3[23]$, which has no in optical spectra of transanalogue $PtCl_2(C_2H_4) \cdot NH_3$, and the 185 cm⁻¹ i.r. band of trans-PtCl₂(C_2H_4) · NH₃[23], which is insensitive to deuteration.

MEESTER et al. [23] assigned an i.r. band of trans-PtCl₂(C₂H₄) · NH₃ at 475 cm⁻¹ to ν (Pt-L). Although the spectra of the complexes with deuterated and hydrogenous ligands are very similar in this region, an additional shoulder is present in the Raman spectrum of trans-PtCl₂(C₂H₄) · ND₃ at 436 cm⁻¹. The deuteration shift between the 475 and 436 cm⁻¹ frequencies is 0.92, which is in good agreement with that calculated for ν (Pt-L) (0.93).

(b) Trans-PtCl₂(C₂H₄) \cdot CD₃CN

INS spectra of *trans*-PtCl₂(C₂H₄) \cdot CD₃CN are shown in Figs. 2(b) and 3(b) and the frequencies derived from these are summarized in Table 2.

The INS spectra of trans-PtCl₂(C₂H₄) · CD₃CN may be assigned analogously to trans-PtCl₂(C₂H₄) · ND₃ with the exception of bands at 339 and 82.0 cm⁻¹. The former band we assign to ν_s (Cl-Pt-Cl), its appearance in the BFD spectrum resulting from proton motion associated with this mode of the framework. As expected the INS band associated with ν_s (Cl-Pt-Cl) becomes more intense as the mass of the ligand trans to the ethylene group is increased (Fig. 2). The 82.0 cm⁻¹ band most probably represents π (Cl-Pt-Cl), assigned in Zeise's salt at 92 cm⁻¹[36].

Comparison of the optical spectra of *trans*-PtCl₂(C₂H₄) · CH₃CN and *trans*-PtCl₂(C₂H₄) · CD₃CN shows the i.r. band at 243 cm⁻¹ in the former complex, assigned to ν (Pt-L) by MEESTER *et al.*[23], to move to 229 cm⁻¹ in the CD₃CN ligand complex. This represents a deuteration shift of 0.98, compared with the calculated value of 0.97.

(c) Trans-PtCl₂(C₂H₄) \cdot DCON(CD₃)₂

INS spectra of trans-PtCl₂(C₂H₄) · DCON(CD₃)₂ are shown in Figs. 2(c) and 3(c) and the frequencies and assignments derived from these are summarized in Table 2.

(d) Trans-PtCl₂(C₂H₄) \cdot C₆D₅ND₂

INS spectra of trans-PtCl₂(C₂H₄) \cdot C₆D₅ND₂ are shown in Figs. 2(d) and 3(d) and the frequencies derived from these are summarized in Table 2.

Comparison with the INS assignments for *trans*-PtCl₂(C₂H₄) \cdot ND₃ allows straightforward assignment of the INS spectra of *trans*-PtCl₂(C₂H₄) \cdot C₆D₅ND₂ with the exception of the 271 cm⁻¹ BFD band. It was shown by ¹H NMR that, as a result of manipulation during its preparation, proton exchange (~3.6 atom% H) had taken place at the aniline group nitrogen atom. In order to check whether the 271 cm⁻¹ BFD band could be attributed to motion of the aniline ligand, made visible in the INS spectrum as a result of proton substitution, the BFD spectrum of trans- $PtCl_2(C_2H_4) \cdot C_6D_5NH_2$ was measured (Fig. 2e). However, there was no significant increase in the intensity of the band relative to that assigned to the C₂H₄ torsion (τ_z) on going from trans- (271 cm^{-1}) $PtCl_2(C_2H_4) \cdot C_6D_5ND_2$ to trans- $PtCl_2(C_2H_4) \cdot C_6D_5NH_2$ (275 cm⁻¹). Since the 271 cm⁻¹ band of trans-PtCl₂(C₂H₄) \cdot C₆D₅ND₂ is too intense to result from a $C_6D_5ND_2$ mode, it may represent a combination band (probably 123.5+ 166.0 cm^{-1}) or result from order contamination. It is known that for the Dido BFD spectrometer there is considerable order contamination when using the Al(111) monochromator plane (<Consequently 400 cm^{-1}). at any desired wavelength (λ) , a proportion of neutrons of wavelength $\lambda/2$ will be incident on the sample. Since neutron energy is inversely proportional to λ^2 , there arises the possibility of observing transitions of true energy 4E (wavelength $\lambda/2$) apparently at an energy E (wavelength λ). Bands due to order contamination are necessarily of low relative intensity.

Bands at 346 and 433 cm⁻¹ in the i.r. spectrum of trans-PtCl₂(C₂H₄) · C₆H₅NH₂ have both been assigned by MEESTER et al. to ν (Pt-L)[23]. Whilst no analogue of the 346 cm⁻¹ band is observed in the i.r. spectrum of trans-PtCl₂(C₂H₄) · C₆D₅ND₂, the 433 cm⁻¹ band appears to shift to 407 cm⁻¹. This isotopic shift (0.94) compares with a calculated shift for ν (Pt-L) of 0.97. The BFD spectrum of trans-PtCl₂(C₂H₄) · C₆D₅ND₂ displays increased intensity between 320 and 450 (corrected) cm⁻¹. This indicates that ν (Pt-L) is probably present amongst other vibrations whose intensities are enhanced by proton substitution.

(e) Cis-PtCl₂(C₂H₄) \cdot (CD₃)₂SO

INS spectra of cis-PtCl₂(C₂H₄) · (CD₃)₂SO are shown in Figs. 2(f) and 3(e) and the frequencies derived from these and optical data are summarized in Tables 2 and 4.

The INS spectra of cis-PtCl₂(C₂H₄) · (CD₂)₂SO

I.r	. Raman		INS	Assignment
		BFD	TOF	
	18 vs)
	44 s	41 ± 10	42.0 ± 2.0	Lattice modes
57 1	wi 60 s	1	62.0 ± 2.5	
	77 w	J		J
107 1	w 106 w		96.0 ± 4.0	π(Cl-Pt-L)
130	w	1		
141 r	n 144 w	124 ± 10	133.5 ± 6.5	$Pt-C_2H_4$ wag (t_x)
152 1	a a a a a a a a a a a a a a a a a a a	J		
168	sh 168 s			$\delta(C1-Pt-C1_{trans}) + \delta(L-Pt-C_2H_4)$
179 r	n			δ(Cl-Pt-L)
		171 ± 10	172.0 ± 9.0	C_2H_4 torsion (τ_2)
200	sh 201 m)		
207 r	n	201 ± 10	208.0 ± 11.5	$Pt-C_2H_4$ rock (t_v)
217 r	m 221 m	J		,
258	s 262 m			
280 r	n			
318 \$	s 321 m			v(Pt-Cl)
338 #	s 339 vs	349 ± 10		v(Pt-C1)
349 :	sh			
380 v	√ 384 m	384 ± 10		$v_{s}(Pt-C_{2}H_{4})(t_{z})$
408 r	n 411 m			v(Pt-S)
468 1	ə 472 ₩	472 ± 10		$v_{as}^{(Pt-C_2H_4)(\tau_y)}$
628	sh 640 m			v _s (C-S)
635 v	v 650 sh			v _{as} (C-S)
713 v	v 716 w	719 ± 10		CH2 rock
773 :	3			CD_ reck
785 :	sh			J3
809 8	sh	$\frac{1}{806 \pm 10}$		CH. rock
828 \$	8	J		2

Table 4. The INS and optical spectroscopic frequencies (cm^{-1}) and assignments of cis-PtCl₂(C₂H₄) · (CD₃)₂SO

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; ν_s , symmetric stretch; ν_{as} , antisymmetric stretch; δ , in-plane bend; π , out-of-plane bend.

Complex	ũ(m ⁻¹)	High Barrier Approximation ^a (k. mol ⁻¹)	ν ₀ (kJ mol ⁻¹)	$v^{*}(=25 v_{o}/16 in kJ mol^{-1})$; V _m *(=9 V ₀ /16 in kJ mol ⁻¹)
trans-PtCl ₂ ($c_{2}H_{4}$).ND ₃	170.5 ± 10.0	104 ± 13	20.8	32.5	11.7
$trans-PtCl_2(C_2H_4).CD_3CN$	166.5 ± 9.5	99 ± 12	19.8	30.9	11.1
$\texttt{trans-PtCl}_2(\texttt{C}_2\texttt{H}_4).\texttt{DCON}(\texttt{CD}_3)_2$	175.0 ± 10.0	109 ± 13	21.8	34.1	12.3
$trans-PtCl_2(C_2H_4).C_6D_5ND_2$	166.0 ± 9.5	98 ± 12	19.6	30.6	11.0
c1s-PEC12(C2H4).(CD3)250	172.0 ± 9.0	105 ± 11	21.0	32.8	11.8
Pt(acac)(C ₂ H ₄) complexes (average) ^b			25.4	39.7	14.3
$[\operatorname{Ptcl}_2(\operatorname{C}_2H_4)]_2$	170 ± 5	106	21.2	31.1	11.9
$K[Ptcl_{3}(c_{2}H_{4})].H_{2}0$	185 ± 5	118	23.6	36.9	13.3
cs[PtCl ₃ (C ₂ H ₄)]	190 ± 5	125	25.0	39.0	14.1
$[Pdcl_2(c_2H_4)]_2$	155 ± 5	87.8	17.6	27.4	6.9

build of the second and the second a

closely resemble those of the trans- $PtCl_2(C_2H_4) \cdot L$ complexes and assignment has been carried out accordingly.

The i.r. and Raman spectra of cis- $PtCl_2(C_2H_4) \cdot (CD_3)_2SO$ have been compared with for (CD₃)₂SO[37], reported i.r. data cis- $PtCl_2((CH_3)_2SO_2)$ [38] and cis-PtCl₂. $(C_2H_4) \cdot (CH_3)_2SO$ [38, 39]. By reference to the assignments made for the latter compounds, several bands in the optical spectra of cis- $PtCl_2(C_2H_4) \cdot (CD_3)_2SO$ have been identified. For example, bands at 318 (i.r.)/321 cm⁻¹ (Raman) and at 338 (i.r.)/339 cm^{-1} (Raman) in the optical spectra of cis-PtCl₂(C₂H₄) · (CD₃)₂SO correlate with those found at 309 and 333 cm⁻¹ in cis-PtCl₂((CH₃)₂SO)₂ and at 311 and 338 cm⁻¹ in cis- $PtCl_2(C_2H_4) \cdot (CH_3)_2SO$, and which have been assigned to v(Pt-Cl)[38, 39]. The 408 (i.r.)/411 cm^{-1} (Raman) band of cis-PtCl₂(C₂H₄) · (CD₃)₂SO may be tentatively assigned to $\nu(Pt-S)$ following KUKUSHKIN et al. [38] who report two frequencies for this mode in cis-PtCl₂((CH₃)₂SO)₂ (428 and 448 cm⁻¹), and one in cis-PtCl₂(C₂H₄) · (CH₃)₂SO $(443 \text{ cm}^{-1})[38, 39]$. Bands at 628 (i.r.)/640 cm⁻¹ (Raman) and at 635 (i.r.)/650 cm^{-1} (Raman) in the optical spectra of cis-PtCl₂(C₂H₄) · (CD₃)₂SO may be attributed to v_s (C-S) and v_{as} (C-S), respectively by comparison with the frequencies assigned to these modes in (CD₃)₂SO vapour (611 and 619 cm⁻¹)[37]. To higher frequency bands at 773 and $785 \,\mathrm{cm}^{-1}$ in the i.r. spectrum of *cis*- $PtCl_2(C_2H_4) \cdot (CD_3)_2SO$ may be correlated with CD₃ rocking modes [37].

Assignment of the low frequency optical spectra of *cis*-PtCl₂(C₂H₄) · (CD₃)₂SO is difficult, especially in the absence of low frequency data for the analogous (CH₃)₂SO ligand complex. However, by analogy with the assignments for the *trans*-PtCl₂(C₂H₄) · L complexes, bands at 107 (i.r.)/106 (Raman), 168 (i.r. and Raman) and 179 (i.r.) cm⁻¹ may be assigned to π (Cl-Pt-L) δ (Cl-Pt-Cl_{trans}) + (L-Pt-C₂H₄) and to δ (Cl-Pt-L), respectively.

BARRIER CALCULATION

Following GHOSH *et al.*[7], we have considered the potential function for ethylene rotation about an axis projected from the platinum atom through the centre of the C=C bond (Fig. 1) to be of the form form

$$V(\theta) = \frac{V_0}{2} [(1 - \cos 2\theta) + (1 - \cos 4\theta)].$$
(1)

This expression has a ground state minimum at $\theta = 0^{\circ}$ and a metastable minimum at $\theta = 90^{\circ}$ with a well depth, V_{m}^{*} , of 9 $V_{0}/16$. The maximum occurs at $\theta = 0.5 \cos^{-1} (-1/4) = 52.25^{\circ}$, with a potential energy, V^{*} , of $25 V_{0}/16$, which compares reasonably with the theoretical computation of WHEELOCK *et al.*[22] which placed θ_{max} at $67.5 \pm 11.25^{\circ}$. Applying the simple harmonic oscillator

(SHO) approximation (cos $\theta = 1 - \theta^2/2$) to equation (1) yields

$$V_0 = \frac{kI\bar{\nu}^2}{20}$$

where $\bar{\nu}$ is the torsional frequency (cm⁻¹), *I* is the moment of inertia (a.m.u. Å²) of the ethylene ligand about the *z* axis (Fig. 1) and, if $k = 7.096 \times 10^{-4}$, V_0 is in kJ mol⁻¹.

Table 5 shows the values of V_0 , V_m^* and V^* obtained by GHOSH *et al.*[7] for the complexes investigated in their work, together with the reference value they calculated from NMR data. It will be seen that the V_0 values for the *trans*-PtCl₂(C₂H₄) · L complexes (Table 5) compare well with those reported by GHOSH *et al.*, particularly good agreement being found with the value for [PtCl₂(C₂H₄)]₂. Generally, there seems to be an indication that τ_z occurs at higher energies in the salts (K[PtCl₃(C₂H₄) · H₂O] and Cs[PtCl₃(C₂H₄)]) than in the neutral complexes. This might be explained as the result of crystal field interactions having a greater effect upon the torsional frequencies of the salts.

It is interesting to compare our values for V^* and V_m^* with those reported in the theoretical work on *trans*-PtCl₂(C₂H₄) · NH₃[22]. In this work, V^* lies in the range 30.6-34.1 kJ mol⁻¹ and V_m^* between 11.0 and 12.3 kJ mol⁻¹ as opposed to theoretical predictions[22] of 116 ± 8.4 kJ mol⁻¹ for the former and 9.6 ± 8.4 kJ mol⁻¹ for the latter. Better agreement between calculated and predicted values for V^* may be obtained using the High Barrier Approximation ($V_0 = kI\bar{\nu}^2/4$)[40], however, this model does not predict the existence of a metastable minimum.

Acknowledgements—We would like to thank the SERC for the award of a research studentship to one of us (K.R.) and AERE Harwell and SERC for the provision of neutron beam facilities.

REFERENCES

- C. E. HOLLOWAY, G. HULLEY, B. F. G. JOHNSON and J. LEWIS, J. Chem. Soc. A 53 (1969).
- [2] C. E. HOLLOWAY, G. HULLEY, B. F. G. JOHNSON and J. LEWIS, J. Chem. Soc. A 1653 (1970).
- [3] J. ASHLEY-SMITH, Z. DOUEK, B. F. G. JOHNSON and J. LEWIS, J. Chem. Soc. Dalton 1776 (1972).
- [4] J. ASHLEY-SMITH, Z. DOUEK, B. F. G. JOHNSON and J. LEWIS, J. Chem. Soc. Dalton 128 (1974).
- [5] D. G. LISTER, J. N. MACDONALD and N. L. OWEN, Internal Rotation and Inversion, p. 111. Academic Press, London (1978).
- [6] J. HOWARD and T. C. WADDINGTON, in Recent Advances in Infrared and Raman Spectroscopy, Vol. 7, (edited by R. E. HESTER and R. J. H. CLARK). Heyden, London (1980).
- [7] R. E. GHOSH, T. C. WADDINGTON and C. J. WRIGHT, J. Chem. Soc. Faraday II 69, 275 (1973).
- [8] J. HOWARD, T. C. WADDINGTON and C. J. WRIGHT, J. Chem. Soc. Faraday II 72, 513 (1976).
- [9] J. HOWARD and T. C. WADDINGTON, J. Chem. Soc. Faraday II 74, 1975 (1978).

- [10] G. A. KUKINA, G. B. BOKII and F. A. BRUSENTSEV, *Zh. Strukt. Khim.* 5, 730 (1964).
- [11] J. A. WUNDERLICH and D. P. MELLOR, Acta Crystallogr. 7, 130 (1954).
- [12] J. A. WUNDERLICH and D. P. MELLOR, Acta Crystallogr. 8, 57 (1955).
- [13] G. B. BOKII and G. A. KUKINA, Kristallografiya 2, 400 (1957).
- [14] G. B. BOKII and G. A. KUKINA, *Zh. Strukt. Khim.* 6, 706 (1965).
- [15] M. BLACK, R. H. B. MAIS and P. G. OWSTON, Acta Crystallogr. 25B, 1753 (1969).
- [16] J. A. J. JARVIS, B. T. KILBOURN and P. G. OWSTON, Acta Crystallogr. 26B, 876 (1970).
- [17] J. A. J. JARVIS, B. T. KILBOURN and P. G. OWSTON, Acta Crystallogr. 27B, 366 (1971).
- [18] W. C. HAMILTON, K. A. KLANDERMAN and R. SPRATLEY, Acta Crystallogr. 25A, 5172 (1969).
- [19] R. A. LOVE, T. F. KOETZLE, G. J. B. WILLIAMS, L. C. ANDREWS and R. BAU, *Inorg. Chem.* 14, 2653 (1975).
- [20] S. MARICIC, C. R. REDPATCH and J. A. S. SMITH, J. Chem. Soc. 4905 (1963).
- [21] B. F. G. JOHNSON and J. A. SEGAL, J. Chem. Soc. Chem. Commun. 1312 (1972).
- [22] K. S. WHEELOCK, J. H. NELSON, L. C. CUSACHS and H. B. JONASSEN, J. Am. Chem. Soc. 92, 5110 (1970).
- [23] M. A. M. MEESTER, D. J. STUFKENS and K. VRIEZE, Inorg. Chim. Acta 16, 191 (1976).
- [24] H. BOUCHER and B. BOSNICH, *Inorg. Chem.* 16, 717 (1977).
- [25] L. J. BUNCE, D. H. C. HARRIS and G. C. STIRLING, The Dido (6H) long wavelength inelastic neutron spectrometer. AERE Harwell Report R6246 (1970).
- [26] M. B. H. HARRYMAN and J. B. HAYTER, The optimisation of flux and energy resolution on the Dido time-of-flight spectrometers. AERE Harwell Report USS/P23 (1972).

- [27] D. H. C. HARRIS, S. J. COCKING, P. A. EGELSTAFF and F. J. WEBB, in *The IAEA Conference on Inelastic Scattering of Neutrons in Solids*, Vol. 1, p. 107, Chalk River 1962. IAEA Agency, Vienna (1963).
- [28] P. H. GAMLEN, N. F. HALL and A. D. TAYLOR, Molecular spectroscopy by the beryllium filter machine. AERE Harwell Report RRL74/693 (1974).
- [29] A. H. BASTON and D. H. C. HARRIS, Neutron beam instruments at Harwell. AERE Harwell Report AERE-R9278 MPD/NBS/97 (1978).
- [30] A. H. BASTON, The collection and processing of data from three time-of-flight neutron spectrometers. AERE Harwell Report AERE-M2570. HMSO, London (1972).
- [31] R. E. GHOSH, Computer programs for analysis of neutron time-of-flight data. AERE Harwell Report USS/P19(REV) (1974).
- [32] J. HOWARD, K. ROBSON and T. C. WADDINGTON, Chem. Phys. 61, 53 (1981).
- [33] J. HOWARD, T. C. WADDINGTON and C. J. WRIGHT, J. Chem. Soc. Faraday II 73, 1768 (1977).
- [34] J. HIRAISHI, Spectrochim. Acta 25A, 749 (1969).
- [35] M. J. GROGAN and K. NAKAMOTO, J. Am. Chem. Soc. 90, 918 (1968).
- [36] M. J. GROGAN and K. NAKAMOTO, J. Am. Chem. Soc. 88, 5454 (1966).
- [37] F. A. COTTON, R. FRANCIS and W. D. HORROCKS, J. Phys. Chem. 64, 1534 (1960).
- [38] YU N. KUKUSHKIN and V. N. SPEVAK, Zh. Neorg. Khim. 17, 3176 (1972).
- [39] YU. N. KUKUSHKIN and I. V. PAKHOMOVA, Zh. Neorg. Khim. 15, 1882 (1970).
- [40] J. S. KOEHLER and D. M. DENNISON, Phys. Rev. 57, 1006 (1940).