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The Crystal Structure of the Ethylene Complex *trans*-[Pt(C_2H_4)(NH(CH_3)$_2$)Cl_2]

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[Pt(C_2H_4)(NH(CH_3)$_2$)Cl_2] is monoclinic, with the unit-cell parameters

$$a = 7{\cdot}77 \pm 0{\cdot}02,\quad b = 8{\cdot}67 \pm 0{\cdot}03,\quad c = 6{\cdot}65 \pm 0{\cdot}02\ \text{Å};\quad \beta = 102°.$$

There are two molecules in the unit cell (density observed 2·60, calculated 2·59 g.cm.$^{-3}$), and the space group is $P2_1/m$ or $P2_1$.

The [010] and [001] projections were studied, and the positions of the light atoms found by the systematic use of difference syntheses. The structure so derived has the symmetry $P2_1/m$, the principal plane of the molecule being a plane of symmetry.

It is confirmed that the ethylene molecule is symmetrically bound to the platinum atom. The carbon–carbon bond (1·47 Å) is longer than a normal double bond, though the significance to be attached to this lengthening depends on the method used to assess the errors. The bond-lengths Pt–Cl (2·30 and 2·33 Å) and Pt–N (2·02 Å) have normal values within experimental error, in spite of the high *trans*-effect of the ethylene ligand, and there is no '*trans*-lengthening' or '*cis*-shortening' of the bonds. The π-bonding theory of the *trans*-effect accounts for this result and also for the apparently contradictory observation of Bokii & Kukina (1957) that in the ion [Pt(C_2H_4)Br_3]$^-$ the bond lengths differ from their normal values.

The standard deviations of the bond-lengths were calculated from the diagonal elements only of the least-squares matrix to be CH_2–CH_2 0·18, Pt–Cl 0·04, Pt–N 0·19 Å, but this approximate method of estimating the errors may not be appropriate to this type of compound.

1. Introduction

The available evidence on the structure of ethylene complexes of platinum leads to the conclusion that they are π-complexes. The ethylene molecule is then bound to the metal by the donation of π-electrons from the ethylene ligand to the metal; there is also some back-donation of *d*-electrons from the metal to the anti-bonding orbitals of the ethylene (Chatt & Duncanson, 1953). This type of bonding can occur in the ion of Zeise's salt [Pt(C_2H_4)Cl_3]$^-$, the best-known π-complex, if the three chlorine atoms and the centre of the C–C bond occupy the four corners of a 'square-planar' arrangement round the platinum atom, and the two carbon atoms are arranged symmetrically above and below this plane.

Attempts to confirm this type of structure by X-ray methods have been made (Wunderlich & Mellor, 1954, 1955; Bokii & Kukina, 1957) and the positions of the heavier atoms found, but the coordinates of the carbon atoms were not found accurately. Two related compounds of palladium have also been studied (Dempsey & Baenziger, 1955; Holden & Baenziger, 1955), with results which also appeared to be in agreement with the proposed type of structure, though in (Pd(C_2H_4)Cl_2)$_2$ the carbon atoms appeared only rather indefinitely, and in (Pd styrene Cl_2)$_2$ the carbon–carbon bond is not perpendicular to the plane of the complex, presumably because the styrene molecule is not symmetrical about its double bond.

We therefore examined first the slightly simpler compound *trans*-[Pt(C_2H_4)(NH_3)Cl_2], which proved to be triclinic with eight molecules in the unit cell and unsuitable for full analysis. We then turned to the corresponding dimethylamine complex

trans-[Pt(C_2H_4)($NH(CH_3)_2$)Cl_2] ,

intending to carry out a full three-dimensional analysis. It is, however, unstable in X-rays and work was therefore limited to the two-dimensional studies reported in this paper.

2. Experimental

The substance crystallized from petroleum ether as poly-crystalline lumps, from which small single crystals were split off. These were found to be monoclinic, and the following unit-cell constants were measured, taking the wavelength of Cu $K\alpha$ radiation to be 1·542 Å:

$$a = 7{\cdot}77 \pm 0{\cdot}02,\ b = 8{\cdot}67 \pm 0{\cdot}03,\ c = 6{\cdot}65 \pm 0{\cdot}02\ \text{Å};\ \beta = 102°.$$

Density observed 2·60 g.cm.$^{-3}$ calculated 2·59 g.cm.$^{-3}$ for 2 molecules in the unit cell.

The only systematically absent reflections are $0k0$ with k odd, and the space-group is therefore $P2_1$ or $P2_1/m$. The crystals showed no piezo-electric activity when tested in an apparatus similar to that of Perdok & van Suchtelen (1948), and as the refinement of the structure progressed it became increasingly probable that the correct space group is the centro-symmetric $P2_1/m$.

The intensities of the $h0l$ and $hk0$ reflections were estimated visually from Weissenberg photographs, the range of intensities being 220 to 1 and 580 to 1 for the two zones respectively, and the usual Lorentz and polarization factors were applied. Absorption corrections were not calculated since the crystals were cleavage fragments and only approximately isometric. The effects of absorption were minimized by using very small crystals with dimensions of about 0·025 mm. Wilson's (1942) method was used to find approximate values of the temperature factor for the whole molecule and of the scale factor K to place the structure factors on the absolute scale.

3. Method of analysis

During the determination of the structure of this and of other coordination compounds of platinum the following general plan was found to be effective for work on two-dimensional projections.

The approximate positions of the heaviest atoms such as platinum, and bromine if present, were found from Patterson syntheses, and an electron-density map was calculated for each projection, assuming the structure factors to have the same phases as the contributions of the heavy atoms. The main problems in interpreting these maps were to ensure that spurious peaks were not wrongly assigned to the light atoms, and to decide where, in a composite peak, the light atoms should be placed. This was accomplished by the systematic use of partial difference syntheses giving the electron-density distribution after subtracting the calculated contributions of those atoms whose parameters were fairly accurately known. The coefficients used in these syntheses were $\Delta F = (F_o - F_c')$, where F_c' included only the contributions of the atoms which were being subtracted, and F_o was given the same phase as F_c'. Reflections which were too weak to be observed were treated as follows: where $|F_c'| > |F_{\text{min.}}|$, $F_{\text{min.}}$ being the minimum observable structure factor for that reflection, ΔF was taken to be $(F_{\text{min.}} - F_c')$; where $|F_c'| \le |F_{\text{min.}}|$, the term was omitted, and ΔF taken to be zero. The necessary changes in atomic coordinates were calculated from the gradients in these maps (Cochran, 1951; Lipson & Cochran, 1953, p. 298). A least-squares method was used to calculate the changes in the temperature factor coefficients β in the expression

$$\exp\left[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{23}kl - \beta_{13}hl\right].$$

After each change in the parameters the scale factor K between observed and calculated structure factors was re-determined by a modification of Wilson's method in which log $[\Sigma F_o^2/\Sigma F_c^2]$, summed over small ranges of $(\sin\theta)/\lambda$, was plotted against the mean $(\sin^2\theta)/\lambda^2$; for this purpose F_c included the contributions of all the atoms, even when some of their positions were uncertain.

For the success of this process it was necessary to refine the parameters in the order of their importance, beginning with the positions of the heaviest atoms and then of the moderately heavy atoms (e.g. chlorine), followed by the temperature factors of the heavy and then of the moderately heavy atoms. At each stage any necessary small adjustments were made to the parameters previously refined and a further partial difference map was calculated. In this way a partial difference map was obtained representing the electron-density distribution of the light atoms only, determined by a 'direct method', diffraction effects and interference from the heavier atoms having disappeared. The assumptions made about the light-atom positions when refining the scale factor K had no important effect on this map or on the eventual determination of the correct atomic positions.

The final stage was to decide on an approximate trial structure for the light atoms only by considering the partial difference maps for both projections together, and to refine the parameters of all the atoms.

The atomic scattering factors were taken from the *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (Vol. II, 1935). The values for oxygen and fluorine were used for the CH_2 and CH_3 groups respectively; this is a convenient approximation which takes account of the correct number of electrons, though by its use the values derived for the temperature factors

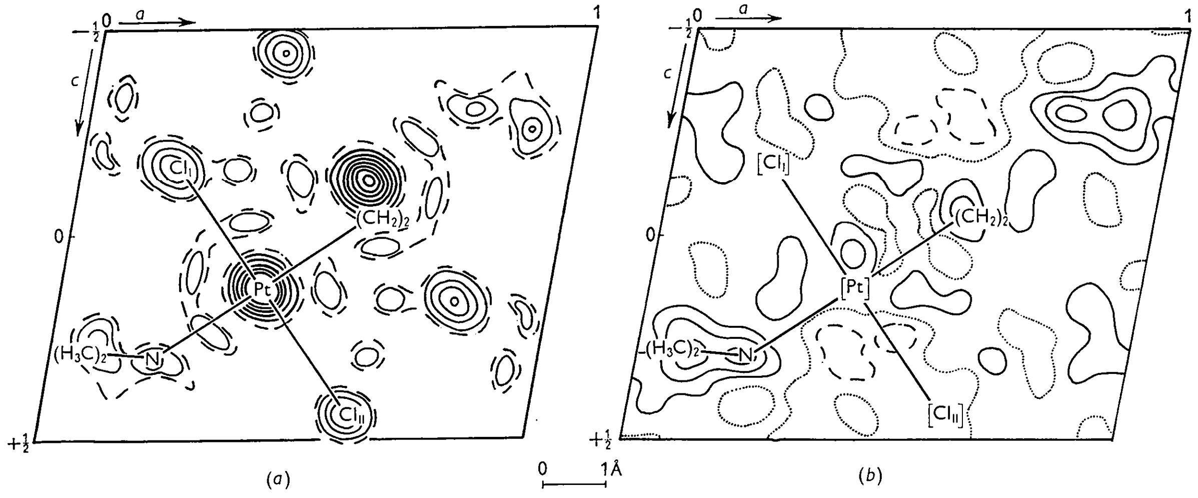

Fig. 1. (*a*) Electron-density distribution projected down [010]. The structure factors were given the same signs as the platinum contributions. Contours at every 25 e.Å^{-2} round platinum, 5 e.Å^{-2} elsewhere; 5 e.Å^{-2} contour broken. (*b*) Electron-density distribution projected down [010] after subtracting the contributions of the platinum and chlorine atoms. Contours at every 4 e.Å^{-2}, positive contours continuous, zero contour dotted, negative contours broken.

for these groups cease to have any direct physical meaning. For this reason only isotropic temperature factors were derived for the light atoms.

4. Results

The [010] *projection*

The uncertainty about the space group does not affect the [010] projection, since it is centro-symmetric in either case. The first Fourier map (Fig. 1(*a*)) shows clearly the positions of the platinum and chlorine atoms, and indicates the position of the dimethylamine group. The ethylene molecule cannot be distinguished, because the position *trans*- to the dimethylamine group is overlapped by the platinum atom of a neighbouring molecule. The early partial difference maps contained a small peak near this *trans*- position, and the trial structure of Fig. 1(*a*) was confirmed by the partial difference map showing the light atoms only (Fig. 1(*b*)), in which the principal peaks can readily be assigned.

There are a number of irregularities in Fig. 1(*b*) which could not be accepted in a purely organic structure. There are peaks 6 e.Å^{-2} high, large enough to be caused by a single carbon atom, but these are only half the height of the principal peaks. There are areas of negative electron density (-8 e.Å^{-2}), which, however, are not near any of the assumed atomic positions. Finally, the nitrogen atom peak (14 e.Å^{-2}) is much higher than expected. These irregularities appear to have no structural significance, but are attributable to the normal errors of observation which inevitably lead to larger background variations in the electron-density maps when a heavy atom is present. The structure shown in Fig. 1(*b*) was therefore taken to be correct.

The results from this projection suggest that the space group is $P2_1/m$. The interatomic distances usually found in platinous complexes are within the ranges Pt–Cl = 2·30–2·35 Å and Pt–N = 2·00–2·03 Å (see Discussion § 5). The projected bond lengths found here are Pt–Cl_{I} = 2·30 Å, Pt–Cl_{II} = 2·33 Å, and Pt–N = 2·02 Å, which are so very similar to the normal bond lengths that the bonds must, within experimental error, be perpendicular to the [010] axis: the platinum, chlorine and nitrogen atoms will then all lie in a plane parallel to the (010) plane. The shape of the peak assigned to the two methyl groups in Fig. 1(*b*) shows that these two groups are superposed, and from the shape of the ethylene peak it can be concluded, with slightly less certainty, that the two methylene groups are also superposed. The (PtCl_2N) plane is therefore probably a plane of symmetry, as required by the space group $P2_1/m$.

The [001] *projection*

The choice of $P2_1/m$ as the correct space group is supported by the Patterson function $P(U, V)$ which indicates the existence of planar molecules parallel to the plane (010).

The early stages of the work on this projection were valid for both space groups. The x-coordinate of the platinum atom was found from the Patterson function and had the same value as in the [010] projection; the y-coordinate was taken to be $\frac{1}{4}$, which is the value required for $P2_1/m$, and is a possible value for $P2_1$. The electron-density map calculated by giving the observed structure factors the same phases as the contributions of the platinum atom (Fig. 2(*a*)), shows the two chlorine atoms with the same x-coordinates as in the [010] projection and with y-coordinates of $\frac{1}{4}$. This confirms that the plane defined by the platinum and chlorine atoms is parallel to (010), within ex-

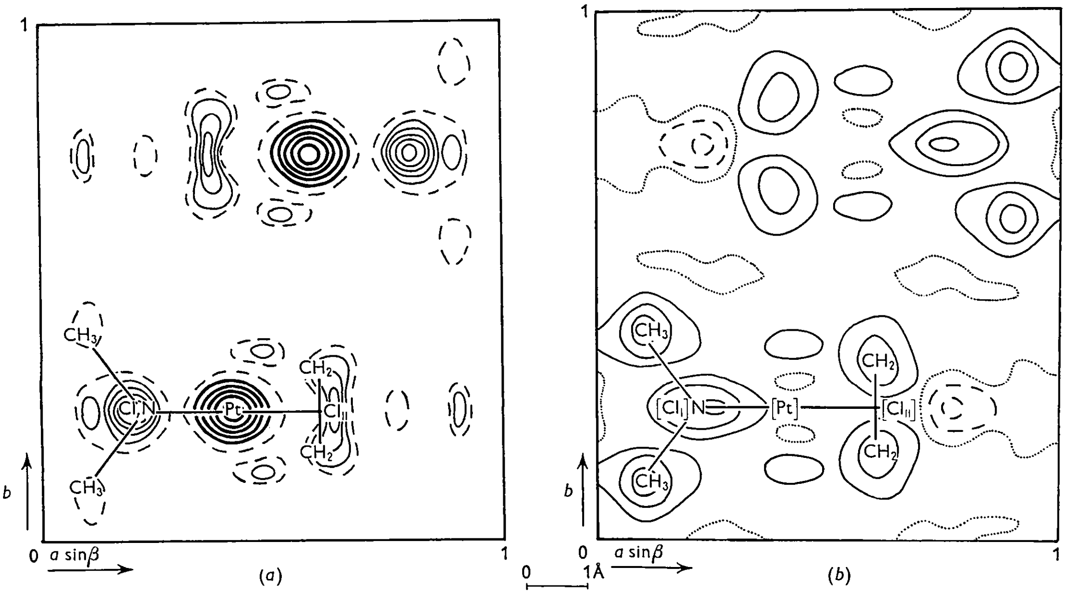

Fig. 2. (*a*) Electron-density distribution projected down [001]. The structure factors were given the same signs as the platinum contributions. Contours at every 25 e.Å^{-2} round platinum, 5 e.Å^{-2} elsewhere; 5 e.Å^{-2} contour broken. (*b*) Electron-density distribution projected down [001] after subtracting the contributions of the platinum and chlorine atoms. Contours at every 2 e.Å^{-2}, positive contours continuous, zero contour dotted, negative contours broken.

perimental error; a small departure from this would not be detected, but large departures would be indicated by an abnormally high β_{22} coefficient in the temperature factor of the chlorine atoms, and this was not found.

The analysis was continued, using the same atom-by-atom process as before, until the partial difference map showing the light atoms only was obtained (Fig. 2(*b*)). The phases of the structure factors were determined by the platinum and chlorine atoms, and since these had been found to lie in the positions $\pm(x, \frac{1}{4})$ which conform to the symmetry $P2_1/m$, the difference map must also have the symmetry $P2_1/m$. Thus Fig. 2(*b*) has the mirror plane of symmetry at $y=\frac{1}{4}$ imposed upon it, though it does not follow that the light atoms must be symmetrically placed on either side of the mirror plane.

On close examination Fig. 2(*b*) shows no distortion which might be expected to result from forcing a wrong symmetry. It contains five peaks per molecule which are reasonably circular and agree very well in both height (6–7 e.Å^{-2}) and position with the trial structure of Fig. 2(*a*). These peaks have the same x-coordinates as the light atoms in the [010] projection. There are few spurious peaks, and the only notable irregularity is a negative area (−4 e.Å^{-2}), which is not related to the proposed structure. There seems no doubt therefore that the structure is correct, and that the space group is $P2_1/m$.

Final refinement

The approximate positions of the atoms having thus been found, the parameters of all the atoms were then refined for the two projections independently. After a few cycles the coefficients β_{11} in the temperature factor expressions for the two projections were seen to have closely similar values (Table 1), indicating that large errors due to the absorption of X-rays had been avoided by the use of small crystals. A set of parameters was then drawn up, taking a compromise between the values from the two projections for the x-coordinates and β_{11} coefficients, and a final cycle of refinement was calculated with the results summarized in Tables 2 and 3 and Fig. 3.

Table 1. *Parameters common to both projections*

Projection	[010]		[001]	
Atom	x	β_{11}	x	β_{11}
Pt	0·4112	0·0090	0·4115	0·0130
Cl_I	0·197	0·0138	0·199	0·0156
Cl_{II}	0·626		0·623	
N	0·221		0·222	
CH_3	0·091		0·100	
CH_2	0·600		0·600	

Table 2. *Final atomic coordinates and standard deviations*

(Expressed as decimal parts of the cell edge)

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Pt	0·4112	0·2500	0·1323	0·0007	—	0·0008
Cl_I	0·197	0·250	−0·164	0·0037	—	0·0040
Cl_{II}	0·625	0·250	0·436			
N	0·222	0·250	0·300	0·0171	—	0·0196
CH_3	0·095	0·106	0·262	0·0084	0·0084	0·0108
CH_2	0·600	0·165	−0·050	0·0098	0·0104	0·0150

Table 3. *Temperature factors*

Pt	$\exp -[0{\cdot}0110h^2+0{\cdot}0094k^2+0{\cdot}0074l^2+0{\cdot}0087hl]$
Cl	$\exp -[0{\cdot}0147h^2+0{\cdot}0401k^2+0{\cdot}0189l^2+0{\cdot}0067hl]$
N	$\exp -[4{\cdot}00\,(\sin^2\theta)/\lambda^2]$
CH_2	$\exp -[8{\cdot}40\,(\sin^2\theta)/\lambda^2]$
CH_3	$\exp -[8{\cdot}40\,(\sin^2\theta)/\lambda^2]$

The standard deviations quoted in Table 2 were calculated from equations of the form

$$\sigma^2(x) = \frac{\Sigma w \Delta F^2}{(n-v)\Sigma w(\partial F/\partial x)^2},$$

where n is the number of reflections and v is the number of variable parameters. The weights used were $w=(F_{\text{min.}}/F_o)^2$ where $|F_o|>|F_{\text{min.}}|$, and $w=(F_o/F_{\text{min.}})^2$ where $|F_o|\le|F_{\text{min.}}|$; the values taken for $|F_{\text{min.}}|$ were approximately twice the average minimum observable F. The formula quoted by Lipson & Cochran (1953, p. 288) gave lower values for the standard deviations, whilst the formulae of Cruickshank (1949 and 1954) gave values which were lower still, being approximately half those given in Table 2. Since these other equations are of doubtful validity where the substance contains atoms of widely differing atomic numbers and where some of the atoms are in special positions, only the standard deviations obtained from the least-squares equations are quoted here. It is debatable whether even these values give a reliable measure of the accuracy of the determination, since so many sources of uncertainty are ignored by the simple least-squares equation.

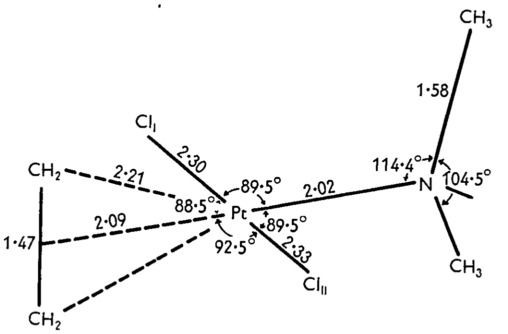

Fig. 3. The molecular configuration, with inter-atomic distances (in Å) and angles. The estimated standard deviations are: Pt–Cl, 0·04 Å; Pt–N, 0·19 Å; Pt–CH_2, 0·15 Å; CH_2–CH_2, 0·18 Å; N–CH_3, 0·22 Å; angles round Pt, 5°; angles round N, 12°.

The values of the reliability index

$$\Sigma\big||F_o|-|F_c|\big|/\Sigma|F_o|$$

were 0·136 for the [010] and 0·080 for the [001] projections, including those unobserved terms for which $|F_c|>|F_{\text{min.}}|$, and the r.m.s. electron densities in the final $(\varrho_o-\varrho_c)$ synthesis were 2·97 and 1·86 e.Å^{-2} respectively. The final values of observed and calculated structure factors are given in Table 4.

5. Discussion

This work shows that the positions of carbon atoms can be found in a platinum complex containing only a few light atoms, using two-dimensional data. No special experimental techniques were necessary, except for the use of very small crystals, but a cautious method of analysis was necessary to avoid mistakes in interpretation.

The results confirm the view that the ethylene molecule is linked to the metal atom by a symmetrical bond, with the two carbon atoms equidistant from the platinum atom, and the C–C bond perpendicular to the plane of the complex. The observed C–C bond length of 1·47 Å is greater than the expected double-bond length of 1·34 Å, though in view of the large standard deviation this difference is of uncertain significance. An attempt was made to 'force' the carbon atoms closer, since the peaks of the chlorine atom and the methylene groups in the [001] projection (Fig. 2(*a*)) overlap to some extent, and it seemed possible that the coordinates derived for the methylene groups might be influenced by the parameters used for the chlorine atom. The temperature coefficients of the chlorine atom were then re-adjusted, but after a further cycle of refinement the carbon atoms were found to be back in their original positions, 1·47 Å apart. This lends support to the possibility that the bond is in fact longer than a double bond. The interpretation of the infra-red spectra of ethylene complexes, on the other hand, indicates that the C–C bond differs only a little from its state in free ethylene (Chatt & Duncanson, 1953; Powell & Sheppard, 1958). Holden & Baenziger (1955) found the C–C bond in the complex (Pd styrene Cl_2)$_2$ to have a normal length for a double bond (1·32 Å), but in this case also the standard deviation (0·15 Å) was large and definite conclusions about the bond-length were difficult to reach.

The Pt–CH_2 distance, 2·21 Å, is only a little longer than the sum of the atomic radii (2·09 Å if the radius of the platinous ion is taken to be 1·32 Å), but here again the standard deviation is large. There is, unfortunately, no accurate value of the length of a normal single bond between platinum(II) and carbon available for comparison.

Ethylene complexes of divalent platinum are of chemical interest because the ethylene group has a very high *trans*-effect, making the group which is *trans* to it, the dimethylamine group in this instance, very much more labile than usual. Various theories of the *trans*-effect have been proposed, and are summarized by Basolo & Pearson (1958). The theory based on the electrostatic interactions of charged ligands cannot be relevant in this case, unless the normally neutral ethylene molecule is so polarized in the complex as to behave as if it were charged. A second explanation is that the ethylene molecule weakens the *trans*-bond, assuming, incorrectly, that chemically reactive bonds are necessarily weak. If this were so,

Table 4. *Observed and calculated structure factors*

hkl	$\|F_o\|$	F_c	*hkl*	$\|F_o\|$	F_c	*hkl*	$\|F_o\|$	F_c	*hkl*	$\|F_o\|$	F_c
000	—	308	306	<18	37	704	<14	−24	390	39	−33
1	108	108	7	26	22				10	<21	−3
2	24	—20				80$\bar{6}$	39	−49			
3	111	−104	40$\bar{8}$	47	−40	$\bar{5}$	37	−34	400	90	−85
4	105	−94	$\bar{7}$	<21	−13	$\bar{4}$	<17	3	1	89	85
5	43	−39	$\bar{6}$	49	49	$\bar{3}$	65	43	2	69	64
6	36	19	$\bar{5}$	60	68	$\bar{2}$	73	56	3	81	−84
7	71	61	$\bar{4}$	42	42	$\bar{1}$	<20	17	4	48	−44
8	<13	39	$\bar{3}$	<14	−5	0	<20	−9	5	59	60
			$\bar{2}$	73	−77	1	47	−40	6	37	34
10$\bar{8}$	32	−31	$\bar{1}$	79	−78	2	38	−29	7	42	−39
$\bar{7}$	74	−68	0	81	−85	3	25	−10	8	<31	−23
$\bar{6}$	47	−40	1	<16	10				9	30	26
$\bar{5}$	<20	3	2	54	56	90$\bar{4}$	<13	18	10	<16	15
$\bar{4}$	121	116	3	72	72	$\bar{3}$	<14	−14			
$\bar{3}$	115	94	4	39	33	$\bar{2}$	41	−32	500	100	100
$\bar{2}$	27	24	5	<20	−13	$\bar{1}$	36	−28	1	41	−38
$\bar{1}$	44	34	6	31	−32	0	<14	−11	2	91	−95
0	89	−133				1	<13	15	3	34	31
1	122	−129	50$\bar{7}$	49	47				4	68	73
2	90	−98	$\bar{6}$	<20	−5	020	201	−201	5	<27	−23
3	73	52	$\bar{5}$	47	−47	4	102	115	6	41	−48
4	63	61	$\bar{4}$	100	−91	6	97	−85	7	<26	16
5	61	64	$\bar{3}$	53	−50	8	63	54	8	38	33
6	<21	20	$\bar{2}$	32	24	10	39	−31	9	<20	−10
7	29	−25	$\bar{1}$	92	88						
			0	87	100	100	145	−133	600	64	−68
20$\bar{8}$	14	0	1	<18	24	1	105	−91	1	<26	−12
$\bar{7}$	44	44	2	<20	−19	2	138	133	2	55	59
$\bar{6}$	52	58	3	76	−68	3	76	65	3	<27	14
$\bar{5}$	66	60	4	39	−42	4	98	−96	4	43	−48
$\bar{4}$	29	−28	5	<17	9	5	63	−56	5	<27	−11
$\bar{3}$	105	−97	6	22	25	6	62	57	6	39	39
$\bar{2}$	151	−148				7	47	38	7	<27	8
$\bar{1}$	44	−35	60$\bar{7}$	51	−54	8	43	−40	8	28	−28
0	26	47	$\bar{6}$	<18	−20	9	31	−22			
1	95	104	$\bar{5}$	24	−20	10	32	27	700	<27	25
2	144	139	$\bar{4}$	86	74				1	<27	26
3	28	31	$\bar{3}$	57	50	200	45	46	2	<27	−26
4	48	−36	$\bar{2}$	29	21	1	49	44	3	<27	−25
5	77	−82	$\bar{1}$	52	−46	2	34	−32	4	<26	25
6	39	−42	0	80	−68	3	83	−87	5	<26	27
7	<16	−2	1	44	−40	4	28	25	6	<26	−21
			2	<21	−5	5	66	70	7	<21	−19
30$\bar{8}$	<13	25	3	<21	32	6	<21	−25			
$\bar{7}$	<18	−22	4	<18	28	7	48	−47	800	<25	−9
$\bar{6}$	73	−73	5	32	26	8	30	18	1	31	−35
$\bar{5}$	79	−80				9	39	32	2	<24	9
$\bar{4}$	20	−16	70$\bar{6}$	41	42	10	<24	−12	3	35	34
$\bar{3}$	72	53	$\bar{5}$	<18	15				4	<22	−8
$\bar{2}$	137	165	$\bar{4}$	43	−34	300	<16	6	5	29	−28
$\bar{1}$	79	100	$\bar{3}$	54	−47	1	84	−82	6	<17	6
0	<11	7	$\bar{2}$	58	−51	2	<18	−8			
1	85	−103	$\bar{1}$	<21	−3	3	68	69	900	<24	−11
2	92	−98	0	<21	24	4	<22	6	1	30	37
3	48	−47	1	52	55	5	65	−68	2	<22	11
4	<20	5	2	46	34	6	<26	−3	3	22	−32
5	51	53	3	<17	−5	7	52	52	4	<15	−9
						8	<26	3			

evidence for bond-weakening might be found from the bond-lengths. Crystallographic evidence that the *trans*-bond is considerably longer and the *cis*-bonds shorter than normal in the ion [Pt(C_2H_4)Br_3]$^-$ has been given by Bokii & Kukina (1957), though the absence of detailed results and estimates of error throws some doubt on their conclusions. Better evidence has been given by Holden & Baenziger (1955) for this effect in a styrene complex of palladium. It is in fact difficult to judge whether a given bond is longer or shorter than normal since there are so few accurate determinations of bond-lengths in platinum compounds. The structures of several platinous and platinic amino-chloro-complexes have been reported, the Pt–Cl bond lengths lying in the range 2·30–2·35 Å, and most of the Pt–N bonds between 2·00 and 2·03 Å, but the errors in the bond lengths are rarely stated (Bokii, Vainstein & Babareko, 1951; Bokii, 1954; Porai-Koshits, 1954*a* and *b*; Porai-Koshits & Romanova, 1954). In their study of Magnus' Green Salt, $[Pt(NH_3)_4][PtCl_4]$, Atoji, Richardson & Rundle (1957) found Pt–Cl = 2·34 Å (s.d. 0·005 Å) and Pt–N = 2·06 Å (s.d. 0·025 Å). The bond lengths found by us therefore appear to have normal values, within their experimental error, and there is no evidence of large changes in the lengths of either *cis* or *trans* bonds attributable to the *trans*-effect of the ethylene group in this complex.

These apparently conflicting results can be reconciled by the alternative explanation, that ligands of high *trans*-influence have little effect on the σ-bonds, but modify the molecular π-bonding system involving the *d*-orbitals of the metal (Chatt, Duncanson & Venanzi, 1955). This affects the reactivity of the molecule as a whole, but does not weaken the *trans*-bond. If the *trans*-bond has some double-bond character, however, the changes in the π-bonding system will reduce the amount of double-bond character and the *trans*-bond will be lengthened. This could explain the examples of bond-lengthening mentioned above, since both metal–chlorine and metal–bromine bonds may have some double-bond character. The *trans*-bond in the present example, on the other hand, is a Pt–N bond which can have no double-bond character and is therefore unchanged by the *trans*-influence of the ethylene molecule.

In this discussion it has been assumed that the standard deviations given in Table 2 are a true measure of the errors. The range of Pt–Cl bond lengths reported for various structures, however, is smaller by a factor of two or three than would be expected from our calculated standard deviation of 0·04 Å. Since most of these determinations were made by two-dimensional methods their accuracies will be comparable with that of the present work, and it therefore appears that the method of estimating the errors used in this paper may not be appropriate to compounds which contain both light and very heavy atoms. The errors will then be much less than the values quoted, and the variations in bond length discussed above will have correspondingly greater significance.

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