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Platinum Complexes with Unsaturated Amines. XI.* The Crystal and Molecular Structure of Trichloro(*cis*-but-2-enylammonium)platinum(II)

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*A three-dimensional X-ray structure determination of trichloro(*cis*–but–2–enylammonium)platinum(II), $PtCl_3(C_4H_{10}N)$, is reported. The compound crystallizes in the space group C_{2h}^5–$P2_1/c$ of the monoclinic system with four formula units in a cell of dimensions a = 7.2254(4), b = 7.521(1), c = 16.596(1) Å, β = 97.77(2)°. The calculated density (2.777 g.cm^{-3}) is in good agreement with the observed density of 2.79 ± 0.01 g.cm^{-3}. Data were collected by the equi-inclination Weissenberg technique and intensities were estimated visually. The structure was refined by block-diagonal matrix least-squares methods to a final conventional R factor of 8.0% for 1381 observed reflections. The structure consists of discrete square-planar $PtCl_3(C_4H_{10}N)$ molecules in which the platinum the three chlorine atoms and the midpoint of the olefinic double bond form a plane, with the platinum,at the centre. The structure is compared with that of the analogous trichloro(*trans*–but–2–enylammonium)platinum(II).*

Introduction

Olefinic hydrocarbons with *cis* configuration coordinate to metal atoms more strongly than those with *trans* configuration.[1] This conclusion is derived from the observation that, for isomeric olefins, the ΔG of formation of olefin complexes is in general higher for the *cis* than for the *trans*-isomers.[2,3,4,5,6]

A similar result has been obtained for the two isomers *cis*- and *trans*-but-2-enylamine on the formation of olefin complexes with platinum(II).[7,8] Enthalpy and entropy changes for the reaction

$$[PtCl_4]^{=} + (ol)^+ \rightleftharpoons [(ol^+)PtCl_3^-] + Cl^- \qquad (1)$$

(where the term $(ol)^+$ refers to *cis*-crotylammonium and to *trans*-crotylammonium) were obtained from the temperature dependence of the equilibrium constants which were determined using spectrophotometric methods.

From the data collected, given in Table I, it can be seen that, in this case, differences in equilibrium constants between complexes of the isomeric olefins are largely due to enthalphy effects.

Table I. Thermodynamic data for reaction (1)

	trans—$CH_3 . CH$: [7] $CH . CH_2 . NH_3^+$	*cis*—$CH_3 . CH$:[8] $CH . CH_2NH_3^+$
K_{30}° (σ%)	450(2.5)	1075(0.86)
K_{45}° (σ%)	304(1.2)	675(0.65)
K_{60}° (σ%)	209(1.0)	415(1.37)
Δ*H*° (kcal/mole)	–5.1 ± 0.25	–6.0 ± 0.2
ΔS° (e.u.)	–4.6 ± 0.7	–5.9 ± 0.6

While no deductions can be made until the enthalpies of solution of the free olefins and of the complexes have been obtained, it seemed opportune to study the crystal structure of the complex with the *cis*-but-2-enylamine, to see, on comparing it with that of the complex with the *trans*-isomer,[9] whether the differences in the thermodynamic parameters derive from some structural difference.

Experimental Section

Preparation of the ligand and of the complex. Commercial 1,3-dichloro-2-butene, purified by distillation (b.p. 127-129°C), was converted into 2-butyn-1-ol.[10] Following the procedure described by Ettlinger and Hodgkins,[11] *cis*-but-2-enylamine hydrochloride was prepared from the acetylenic alcohol. The hydrochloride, crystallized twice from anhydrous ethanol and ether, gave an infrared spectrum identical to that reported in the literature,[12] and melted at 137-138°C (lit.[12] 138°C).

(*) Part X, see ref. (9).

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Table II. Final positional and thermal parameters.[a] Standard deviations are given in parentheses

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Pt	−0.0990(1)	0.1116(1)	0.1093(1)	142(2)	4(3)	−6(1)	146(2)	−1(1)	39(0)
Cl(1)	−0.2509(8)	0.2701(9)	0.0015(4)	191(11)	−2(19)	−34(9)	215(12)	38(9)	50(3)
Cl(2)	0.1681(8)	0.2768(8)	0.0992(4)	164(10)	−51(18)	2(8)	213(12)	1(9)	48(3)
Cl(3)	0.0647(8)	−0.0415(9)	0.2153(4)	190(11)	31(19)	−13(8)	209(11)	10(9)	40(2)
N	−0.1067(44)	−0.3524(46)	0.0925(19)	428(97)	278(137)	−69(59)	364(82)	−66(51)	58(14)
C(1)	−0.2741(38)	−0.2699(38)	0.1286(19)	232(55)	46(89)	71(46)	204(55)	−7(42)	58(13)
C(2)	−0.3187(27)	−0.0822(27)	0.0908(17)	112(34)	−208(59)	20(33)	132(39)	−17(31)	61(12)
C(3)	−0.3764(27)	0.0530(42)	0.1399(16)	83(31)	51(76)	2(30)	325(64)	−9(45)	47(11)
C(4)	−0.4025(37)	0.0438(42)	0.2275(18)	213(51)	40(95)	35(41)	250(57)	−22(44)	47(12)

[a] Coefficients b_{ij} are defined by $T = \exp[-10^{-4}(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$.

Trichloro(*cis*-but-2-enylammonium)platinum(II) was prepared (yield 65%) by method 1 described by Denning and Venanzi.[13] The product that crystallized decomposed at 205-225°C (Found Pt, 52.3%, $C_4H_{10}Cl_3NPt$ requires Pt, 52.2%).

Determination of the Unit Cell and Collection of Intensity Data. The yellow crystals are stable in air and to X-rays, and belong to the monoclinic system. From Weissenberg photographs of the reciprocal lattice layers $0kl$ and $h0l$ through $h2l$ the systematic absences were found to be $h0l$ when l is odd and $0k0$ when k is odd. These absences are consistent with the space group $C_{2h}^5-P2_1/c$.

The unit-cell dimensions were determined from zero-layer Weissenberg films taken, at 23±2°C, about the a and b axes using Cu—Kα radiation (λ taken as 1.5418 Å). Eighty seven reflections in the high region of θ were selected for θ measurements, made as described elsewhere.[14] The best agreement between observed and calculated θ angles was reached for the following values of the unit-cell parameters, refined by a least-squares procedure: $a = 7.2254(4)$, $b = 7.521(1)$, $c = 16.596(1)$ Å, $\beta = 97.77(2)°$. The standard deviations given in parentheses were formally obtained by a least-squares treatment of the measured data, with no correction for absorption.

The observed density of 2.79 ± 0.01 g.cm^{-3}, obtained by flotation in a $CHCl_3$—$CHBr_3$ mixture, is in good agreement with the value of 2.777 g.cm^{-3} calculated for four molecules $PtCl_3(C_4H_{10}N)$ in the unit-cell.

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs, taken about the a (7 layers, 0—6kl), b (7 layers, h0—6l), and c (4 layers hk0—3) axes, at room temperature, with Ni-filtered Cu—Kα radiation. The approximate dimensions of the three crystals used were, respectively, 0.05×0.10×0.20, 0.05×0.08×0.18, and 0.07×0.07×0.17 mm, with the long dimension in each case along the spindle axis.

The intensities were corrected for Lorentz and polarization effects, and for spot extension.[15] Absorption corrections were applied as for cylindrical specimens ($\mu = 376$ cm^{-1}); no extinction corrections were applied.

The observed structure amplitudes belonging to different layers were scaled together according to the method of Hamilton, Rollett, and Sparks,[16] using a weighting function of the form $w = (\Delta F_o)^{-2}$, the numbers ΔF_o being proportional to the standard deviations $\sigma(F_o)$, derived from the standard deviations $\sigma(I)$ on the intensities I. 1381 independent non-zero reflections (68% of the possible ones with Cu—Kα radiation) were collected and used in the analysis.

Solution and Refinement of the Structure. A structure factor calculation with all atoms located from Patterson and Fourier maps ($\bar{B} = 2.95$ Å^2 by Wilson's method) gave $R = 0.149$.

The structure was refined by block-diagonal (4×4 and 9×9) least-squares methods. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. The weighting scheme used, $w = (a+F_o+bF_o^2)^{-1}$, was checked at intervals, and a and b adjusted, by means of a least-squares procedure, to keep a relatively constant average of $w|F|^2$ both in ranges of increasing F_o values and increasing $\sin\theta/\lambda$ values.[17] For the last cycles of the refinement the least-squares procedure gave $a = 16.3$ and $b = 0.0102$.

The initial refinement, with individual isotropic thermal parameters assigned to all atoms, converged to a R factor of 0.109. A further refinement was carried out in which all atoms were allowed to vibrate anisotropically. This refinement converged to $R = 0.080$.

No attempt was made to include the contribution of the hydrogen atoms. No region of the electronic density exceeded $\pm 3\sigma(\rho)$ on the final difference Fourier synthesis [$\sigma(\rho) = 0.63$ e . Å^{-3}].

Table III. Root-mean-square amplitudes of vibration (Å)

	Min.	Intermed.	Max.
Pt	0.186	0.205	0.240
Cl(1)	0.199	0.242	0.295
Cl(2)	0.199	0.249	0.264
Cl(3)	0.202	0.247	0.255
N	0.249	0.268	0.412
C(1)	0.220	0.251	0.289
C(2)	0.070	0.249	0.290
C(3)	0.144	0.255	0.307
C(4)	0.226	0.251	0.278

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Table IV. Observed structure amplitudes and final calculated structure factors (in electrons ×10). F(000) = 663.6

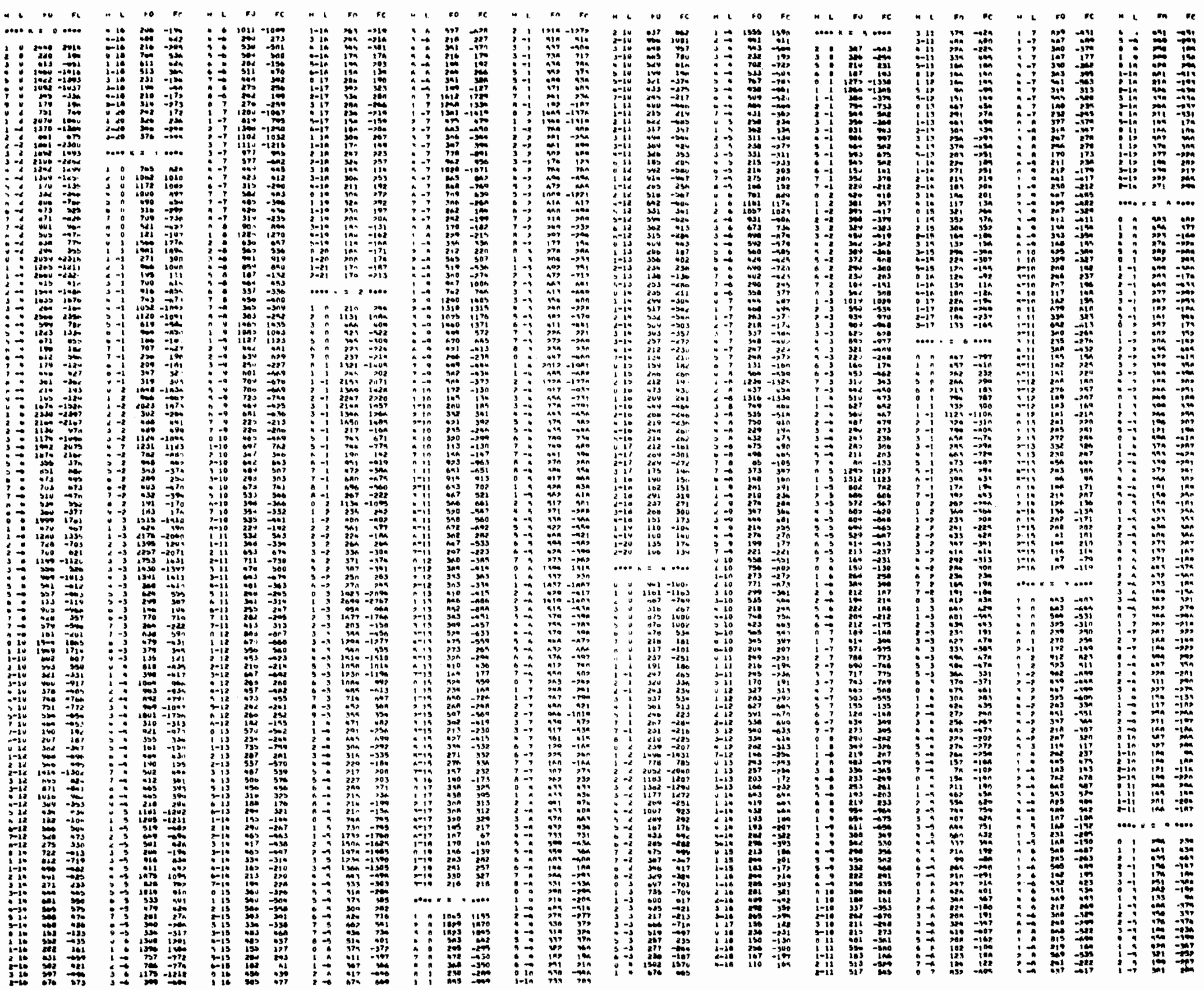

Table II gives the final positional and anisotropic thermal parameters for the non-hydrogen atoms; their thermal vibration ellipsoids are defined in Table III. The final values of $|F_o|$ and F_c (in electrons×10) for the reflections used in the analysis are presented in Table IV. Atomic scattering factors were taken from Ref. (18). The effects of anomalous dispersion were included in the structure factors,[19] the values of $\Delta f'$ for Pt and Cl being those from Ref. (20).

The calculations were carried out on the UNIVAC 1108 computer of Rome University.*

Results and Discussion

A perspective view of the molecule of the complex is shown in Figure 1; bond-lengths and -angles, together with their standard deviations, are given in Table V.

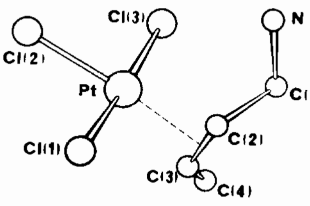

Figure 1. [Trichloro(*cis*-but-2-enylammonium)platinum(II)]. A perspective view of the molecule.

In trichloro(*cis*–but–2–enylammonium)platinum-(II), I, as in trichloro(*trans*–but–2–enylammonium)-platinum(II),[9] II, platinum is four-coordinated with a square-planar configuration, if the midpoint (MP) of the olefinic double bond is considered to be one

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Table V. Bond lengths (Å) and bond angles (degrees).[a] Standard deviations are given in parentheses

Pt—Cl(1)	2.301(6)	Cl(1)—Pt—Cl(2)	88.9(2)
Pt—Cl(2)	2.320(6)	Cl(1)—Pt—Cl(3)	177.5(2)
Pt—Cl(3)	2.293(6)	Cl(1)—Pt—MP[b]	87.1(7)
Pt—C(2)	2.15(2)	Cl(2)—Pt—Cl(3)	88.6(2)
Pt—C(3)	2.18(2)	Cl(2)—Pt—MP[b]	175.1(6)
Pt—MP[b]	2.05(2)	Cl(3)—Pt—MP[b]	95.4(7)
N—C(1)	1.55(5)	C(2)—Pt—C(3)	37.8(10)
C(1)—C(2)	1.56(4)	N—C(1)—C(2)	109.6(24)
C(2)—C(3)	1.40(4)	C(1)—C(2)—C(3)	119.0(25)
C(3)—C(4)	1.49(4)	C(2)—C(3)—C(4)	128.3(27)

[a] Although the olefinic carbon atoms C(2) and C(3) cannot be said to be bound to platinum, their distances from the metal, as well as the angle C(2)—Pt—C(3), are reported. [b] MP defines the midpoint of the olefinic double bond.

of the vertices. The atoms Pt, Cl(1), Cl(2), Cl(3), and the MP point are coplanar within the limits of experimental errors.

The olefinic double bond slightly deviates (4.5°) from the direction perpendicular to the coordination plane (see Figure 2).

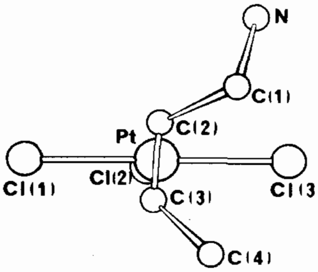

Figure 2. [Trichloro(*cis*-but-2-enylammonium)platinum(II)]. A projection along the platinum-olefin axis of the molecule.

All the bond distances in I compare well with the corresponding ones in II. A slight difference occurs in the length of the Pt–Cl bond *trans* to the olefin, which, in I, is 2.320(6) Å, a little shorter than in II (2.339(7) Å). The Pt–Cl bonds *cis* to the olefin are shorter than that which is *trans*, their lengths average 2.297(4) Å and agree with the values found in II [which average 2.299(5) Å] and with the sum of the covalent radii (2.29 Å). Like the *trans*-isomer, *cis*-but-2-enylamine exercises a small *trans*-bond-lengthening effect.

The C(1)–C(2)=C(3)–C(4) part of the ligand is almost exactly planar, maximum deviation (0.0007 Å) from the best plane through the four carbon atoms, $0.926x+0.271y+0.134z = 2.100$ in terms of monoclinic coordinates, being insignificant. This plane is nearly normal to that of coordination (the dihedral angle being 89°), and makes a dihedral angle of 23° with the plane normal to the platinum-olefin axis and passing through the MP point ($-0.885x-0.463y+0.168z = 2.594$ in terms of monoclinic coordinates). C(2) and C(3) lie approximately on this latter plane (0.02 Å being their deviations from it), whilst C(1) and C(4) are 0.46 Å above, and Pt 2.05 Å below. As in the complex with the *trans*-isomer, C(1) and C(4) are displaced away from the platinum atom.

No twisting of the olefin *p* orbitals occurs in *cis*-crotylamine on cordination of its double bond to platinum. Thus the differences in the thermodynamic parameters (particularly ΔH) observed in reaction 1 for the two isomeric ligands *cis*- and *trans*-crotylamine do not derive from the possible relief of the strain due to bond opposition present in the *cis*-isomer, as suggested by Muhs and Weiss.[5]

The only structural difference, which may contribute to the difference in ΔH, concerns the angle between the direction of the olefinic double bond and the coordination plane (85,5° in I, 81.5° in II). The *trans*-isomer is more deviated from the direction perpendicular to the coordination plane, which is assumed to be the most stable in olefin complexes.[22] However no deductions can be made until the enthalpies of solution of the free olefins and of the complexes have been obtained.

The nitrogen atom of the ligand molecule approximates with short contacts to four chlorine atoms. Three of these contacts, listed in Table VI, agree with a value of a NH ... Cl hydrogen bond, the fourth being somewhat longer. A system of hydrogen bonds, one of them probably being bifurcated,[23] stabilizes the structure of trichloro(*cis*-but-2-enylammonium)platinum(II) in the solid state.

Table VI. Short contacts (Å) between nitrogen and chlorine atoms[a]

N	Cl(3)	3.24
N	Cl(1) (−*x*, −*y*, −*z*)	3.25
N	Cl(2) (−*x*, −*y*, −*z*)	3.20
N	Cl(3) (−*x*, *y* − ½, ½−*z*)	3.47

[a] The first one is an intramolecular short contact (the value of the angle C(1)—N ... Cl(3), 74°, should exclude the possibility of an intramolecular N—H ... Cl hydrogen bond in solution), the following ones refer to atoms whose equivalent positions are given in parentheses.

The coordinates reported and the drawings refer to the molecule with C(2)*R*:C(3)*S* configuration.[24] The molecule with configuration C(2)*S*:C(3)*R* is related to the former by a glide plane in the crystal, in which the optically active[25] complex is present in the form of a racemate.

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