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

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The structure of trichloro(trans-*but-2-enylammonium*)-*platinum(II), $PtCl_3(C_4H_{10}N)$, has been determined by single-crystal X-ray analysis. The compound crystallizes in the space group* C_{2h}^5—$P2_1/c$ *of the monoclinic system, with four monomeric molecules in a cell of dimensions* a = *10.248(3),* b = *10.388(1),* c = *8.414(1) Å, and β = 97.96(2)°. The calculated density (2.797 g.cm^{-3}) agrees well with the measured value of 2.80±0.01 g.cm^{-3}. 1326 independent reflections above background were collected at room-temperature by the equi-inclination Weissenberg method and visually estimated. The structure was refined by least-squares methods to a conventional* R *factor of 7.7%. The complex is monomeric and the platinum is four-coordinated with the three chlorine atoms and the double bond of the* trans-*crotylammonium ion, in a way analogous to that in Zeise's salt.*

Introduction

Several lines of reasoning provide evidence about the nature of complexes with empirical formula $PtCl_2$-LHCl (where L is an unsaturated amine). This evidence leads to the conclusion that they are π-complexes of the cationic ligand LH^+, and have zwitterionic character.[1,2]

In these complexes, then, the unsaturated amines are bound to the platinum by the donation of π-electrons from the double bond to the metal, with a simultaneous, synergic back-donation of *d*-electrons from the metal to the π* anti-bonding orbital of the double bond, in an analogous way to that in which ethylene is bound to platinum in Zeise's salt.[3]

A number of thermodynamic studies, carried out on complexes of platinum(II) with unsaturated amines, indicate that the π-acceptor capacity of the olefins is more important than their σ-donor capacity for the formation of stable platinum(II)-olefin bonds,[4] and that both steric and electronic effects are important in determining the stability of members of this series of compounds.[5]

It seemed opportune to investigate the structure of these complexes in the solid state to confirm the nature of the platinum-ligand bond. It was particularly important to see, especially in the case of compounds with allylic amines, whether the functional group $-\overset{+}{N}H_3$ could interact in the solid state, and hence possibly also in solution, with a chlorine atom of the same molecule through an intramolecular hydrogen bond NH ... Cl. The problem was to see to what extent the presence of the $-\overset{+}{N}H_3$ group influences the thermodynamics and the kinetics[6] of formation of these complexes.

Experimental Section

The complex [trichloro(*trans*-but-2-enylammonium)-platinum(II)], $[Cl_3Pt(C_4H_{10}N)]$, was prepared as previously described.[5] The orange-yellow crystals are stable in air and to X-rays and belong to the monoclinic system. The systematic absences, *h0l* with *l* odd and *0k0* with *k* odd (observed from Weissenberg films of *h0l, h1l, h2l,* and *hk0*, with Cu–K_α radiation) indicated the space group $P2_1/c$ (C_{2h}^5).

The unit-cell dimensions were determined from zero-layer Weissenberg films taken about the *a* and *b* axes, using Cu–K_α radiation (λ taken as 1.5418 Å). Fifty-seven reflections in the θ region greater than 65° were selected for θ measurements, made as described by Mazzone, Vaciago and Bonamico.[7] The cell parameters were refined, by least-squares analysis, to obtain optimun agreement between observed and calculated θ angles, giving the following values: *a* = 10.248(3), *b* = 10.388(1), *c* = 8.414(1) Å and β = 97.96(2)°. The standard deviations, given in parentheses, were obtained from the least-squares refinement. The measurements were taken at 23±2°C.

Assuming four molecules $PtCl_3(C_4H_{10}N)$ per unit cell, *Z* = 4, and using the refined cell parameters,

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the density was calculated to be 2.797 $g \cdot cm^{-3}$. The density obtained by flotation, in a $CHCl_3$–$CHBr_3$ mixture, was 2.80 ± 0.01 $g \cdot cm^{-3}$.

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs, taken about the *a* (4 layers, 0–3*kl*), *b* (9 layers, *h*0–8*l*), and *c* (8 layers, *hk*0–7) axes, at room temperature with Ni–filtered Cu–K_α radiation. The approximate dimensions of the three crystals used were respectively $0.07 \times 0.07 \times 0.08$, $0.07 \times 0.09 \times 0.11$, and $0.06 \times 0.08 \times 0.09$ mm, with the long dimension in each case along the spindle axis.

The intensity data were corrected for Lorentz and polarization effects, and for spot extension.[8] Absorption corrections were applied as for cylindrical specimens ($\mu = 379$ cm^{-1}), but no extinction corrections were applied.

Table I. Analysis of $<w|\Delta F|^2>$ as a function of F_{obs}

Range of F_o	Number of reflections	$<w\|\Delta F\|^2>$
6.1- 13.3	83	0.346
13.3- 16.5	83	0.334
16.5- 19.0	83	0.356
19.0- 21.6	83	0.374
21.6- 24.0	83	0.364
24.0- 27.2	83	0.280
27.2- 30.0	83	0.305
30.0- 33.3	83	0.330
33.3- 38.3	83	0.289
38.3- 43.0	83	0.300
43.0- 49.2	83	0.393
49.2- 57.5	83	0.456
57.5- 67.2	83	0.296
67.2- 83.0	83	0.236
83.0-110.7	82	0.302
110.7-351.2	82	0.372

The observed structure amplitudes were placed on a common scale by the method of Hamilton, Rollett and Sparks,[9] using a weighting function of the form $w = (\Delta F_o)^{-2}$, where the numbers ΔF_o are proportional to the standard deviations $\sigma(F_o)$, which are in turn calculated from the standard deviations $\sigma(I)$ in the intensities I.

1326 independent non-zero reflections (65% of the possible ones with Cu–K_α radiation) were collected and used in the structure refinement.

The structure was solved by the usual combination of Patterson and Fourier maps. At this stage a structure factor calculation ($\bar{B} = 3.17$ Å^2 by Wilson's method) gave $R = 0.216$. Five cycles of isotropic block-diagonal (4×4) least-squares refinement reduced R to 0.086. The refinement was continued, using anisotropic thermal parameters, until convergence was achieved: this required four further cycles of block-diagonal (9×9) least-squares refinement ($R = 0.077$).

The function minimized during the refinement 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 altered, by means of a least-squares procedure, to keep a relatively constant average of $w|\Delta F|^2$ over regions of F_o.[10] For the last four cycles of the refinement the least-squares procedure gave $a = 13.4$ and $b = 0.0082$. Table I gives an idea of the adequacy of these values in the weighting scheme used.

No attempt was made to include the contribution of the hydrogen atoms. No region of electronic density exceeded $\pm 3\sigma(\rho)$ $e \cdot Å^{-3}$ on the final difference Fourier synthesis ($\sigma(\rho) = 0.40$ $e \cdot Å^{-3}$).

Table II gives the final atomic parameters for the non-hydrogen atoms within the crystal-chemical unit.

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	0.2099(1)	–0.0274(1)	–0.0071(1)	103(1)	–2(2)	45(2)	90(1)	13(2)	141(1)
Cl(1)	0.0693(6)	–0.2018(6)	–0.0373(8)	137(6)	–11(11)	38(12)	105(5)	0(13)	184(9)
Cl(2)	0.1274(7)	0.0398(7)	–0.2669(8)	157(7)	10(12)	48(13)	125(6)	26(14)	166(8)
Cl(3)	0.3412(7)	0.1516(7)	0.0169(10)	151(7)	–56(12)	–4(17)	133(7)	92(16)	264(13)
N	0.1420(22)	0.1309(23)	0.3335(32)	135(23)	19(40)	3(56)	111(21)	–70(55)	259(43)
C(1)	0.2621(28)	0.0479(27)	0.3556(38)	121(25)	25(46)	7(61)	125(29)	–40(64)	231(47)
C(2)	0.2400(24)	–0.0663(26)	0.2422(30)	117(23)	49(40)	21(50)	112(24)	16(51)	164(34)
C(3)	0.3466(27)	–0.1184(28)	0.1771(31)	140(27)	18(49)	–66(54)	128(28)	13(58)	163(33)
C(4)	0.3677(28)	–0.2590(26)	0.1459(38)	153(29)	29(45)	14(67)	88(21)	38(61)	245(50)

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

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

	Min.	Intermed.	Max.
Pt	0.214	0.227	0.234
Cl(1)	0.239	0.254	0.269
Cl(2)	0.236	0.265	0.287
Cl(3)	0.238	0.271	0.344
N	0.232	0.259	0.322
C(1)	0.242	0.254	0.303
C(2)	0.216	0.245	0.273
C(3)	0.207	0.266	0.306
C(4)	0.211	0.280	0.306

In Table III the root-mean-square displacements for the same atoms are reported. Structure factors based on the final parameters are compared with the observed structure amplitudes in Table IV. Atomic scattering factors were as given by Cromer and Mann.[11] The effects of anomalous dispersion were included in the structure factors,[12] the values of $\Delta f'$ for Pt and Cl being those computed by Cromer.[13]

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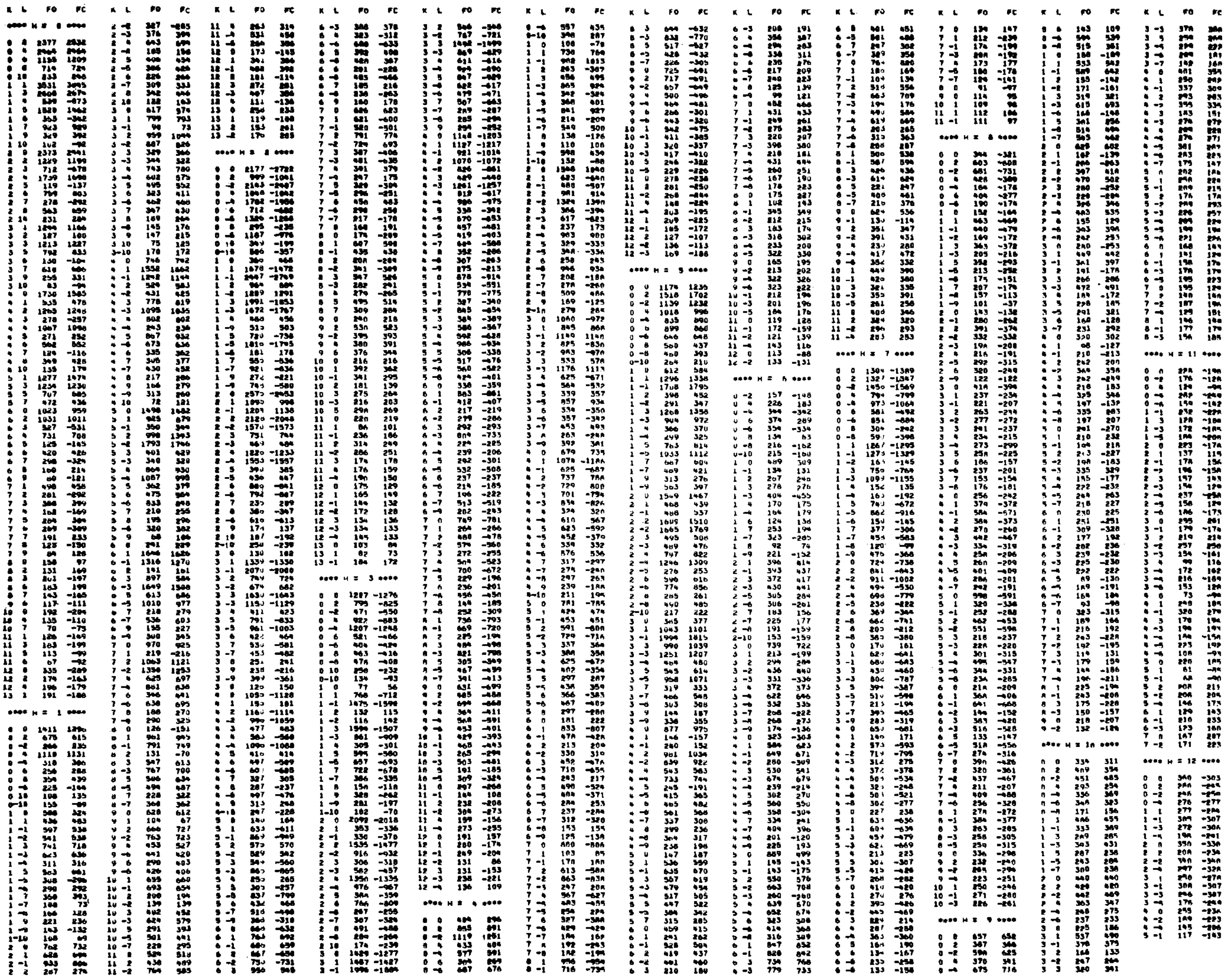
Table IV. Observed structure amplitudes and final calculated structure factors (in electrons × 10). F(000)=663.6



The calculations were carried out on the IBM 7040 computer of Rome University.*

Results and Discussion

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

Platinum is four-coordinated with the three chlorine atoms and the double bond of the *trans*-crotylammonium ion. The centre of this double bond lies approximately on a line passing through the metal atom and the chlorine in *trans*-position, directly in line to interact with the dsp^2 hybrid bonding orbital of the platinum. The coordination around the metal atom is square-planar if the midpoint (MP) of the olefinic double is considered to be one of the vertices. The atoms Pt, Cl(1), Cl(2), Cl(3), and the MP point are coplanar within the experimental errors.

The olefinic carbon atoms C(2) and C(3) are almost equidistant from the platinum atom, and the line passing through them is tilted to make an angle of 81.5° with the coordination plane, Figure 2. Steric interferences of C(1) with Cl(3) and of C(4) with Cl(1) are the likely cause of the slight deviation of

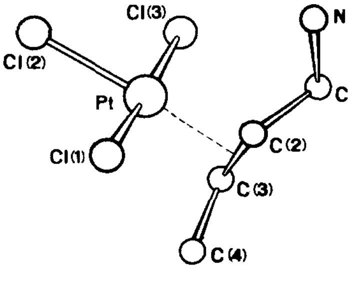


Figure 1. [Trichloro(*trans*-but-2-enylammonium)platinum(II)]. A perspective view of the molecule.

(*) The programmes used were all from the programme library of the « Laboratorio di Strutturistica Chimica del C.N.R. », prepared by Dr. A. Domenicano. The more relevant programmes are listed at the entries from 7528 to 7535 in the 1966 I.U.Cr. « World List of Crystallographic Computer Programs ».

the ligand from that orientation, which is assumed to be the most stable for square planar platinum(II) olefin complexes, *i.e.* with the double bond direction perpendicular to the cordination plane.[14,15]

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

Pt–Cl(1)	2.307(6)	Cl(1)–Pt–Cl(2)	89.5(2)
Pt–Cl(2)	2.339(7)	Cl(1)–Pt–Cl(3)	177.2(2)
Pt–Cl(3)	2.288(7)	Cl(1)–Pt–MP[b]	91.0(8)
Pt–C(2)	2.12(3)	Cl(2)–Pt–Cl(3)	88.4(3)
Pt–C(3)	2.16(3)	Cl(2)–Pt–MP[b]	175.3(8)
Pt–MP[b]	2.02(3)	Cl(3)–Pt–MP[b]	91.3(8)
N–C(1)	1.49(4)	C(2)–Pt–C(3)	38.1(10)
C(1)–C(2)	1.52(4)	N–C(1)–C(2)	108.9(22)
C(2)–C(3)	1.40(4)	C(1)–C(2)–C(3)	119.5(23)
C(3)–C(4)	1.51(4)	C(2)–C(3)–C(4)	125.7(26)

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

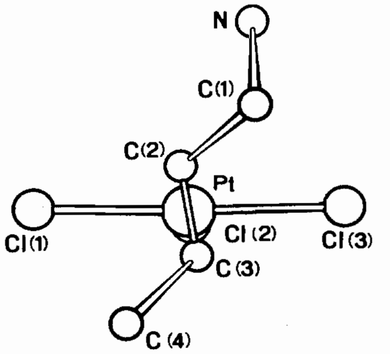


Figure 2. [Trichloro(*trans*-but-2-enylammonium)platinum(II)]. A projection along the platinum-olefin axis of the molecule.

The Pt–C distances, between platinum and the olefinic carbon atoms, as well as the Pt–MP distance, agree well with those found in Zeise's salt.[16,17]

The Pt–Cl bond lengths, between platinum and the chlorine atoms *cis* to the olefin are almost equivalent: they average 2.299(5) Å and agree with the sum of the covalent radii (2.29 Å). The Pt–Cl bond *trans* to the olefin is significantly longer (2.339(7)), showing that the π-bonding olefin exercises a small *trans*-bond-lengthening effect.

The C(1) . C(2) : C(3) . C(4) part of the ligand is not planar: the C(1) and C(4) carbon atoms are displaced away from the platinum atom. Considering the plane normal to the Pt-olefin axis and passing through the MP point ($0.298x-0.334y+0.844x = 2.706$, in terms of monoclinic coordinates), it can be seen that, while this plane contains the C(2) and C(3) carbon atoms (at planar deviations of 0.02 Å), the C(1) and C(4) carbon atoms are respectively 0.45 Å and 0.35 Å above the plane, platinum being 2.02 Å below. The internal rotation angle around the –C=C– bond is 143.2°. This fact agrees with the work of Hamilton on a neutron-diffraction study of Zeise's salt,[16] in which the hydrogen atoms of the cordinated ethylene « bend back significantly ».

The C(2)–C(3) bond length of 1.40 Å shows the typical lengthening of the olefin bond on coordination.

The nitrogen atom of the ligand molecule appears to interact with chlorine atoms; in fact it approximates, with short contacts, to six of them. The distance of these contacts, listed in Table VI, are all shorter than the sum of the ionic radii (3.62 Å) and three of them agree with the value of a hydrogen bond N–H ... Cl,[18,19] the other three being somewhat longer. Although the positions of the hydrogen atoms of the $-\overset{+}{N}H_3$ group are unknown, the arrangement of the six chlorine atoms around the nitrogen indicates the possibility that, in the solid state, the structure of trichloro(*trans*-but-2-enylammonium)platinum(II) is stabilized by a hydrogen bond network, similar to that found in the structure of glycylglycine hydrochloride,[20] in which each of the hydrogen atoms on the $-\overset{+}{N}H_3$ group mediates two short contacts between nitrogen and two other acceptor atoms, one of the contacts being shorter than the other.

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

N	Cl(3)		3.58
N	Cl(1)	(–*x*, ½+*y*, ½–*z*)	3.42
N	Cl(1)	(–*x*, –*y*, –*z*)	3.15
N	Cl(2)	(–*x*, –*y*, –*z*)	3.26
N	Cl(2)	(*x*, ½–*y*, ½+*z*)	3.52
N	Cl(3)	(*x*, ½–*y*, ½+*z*)	3.28

[a] The first one is an intramolecular short contact, the following ones refer to chlorine atoms, the equivalent positions of which are given in parentheses.

It is to be noted that the value of the angle C(1)–N ... Cl(3) (65°) should exclude the possibility of formation of an intramolecular hydrogen bond, N–H ... Cl, in solution, for complexes with allylic amines.

The optically active complex[21] is present in the crystal in the form of the racemate, the C(2)*R*:C(3)*R* and C(2)*S*:C(3)*S* configurations[22] being related by the glide plane. The coordinates reported and the drawings refer to the molecule with C(2)*R*:C(3)*R* configuration.

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