Structure of Tetrakis(pyridine)platinum(II) Chloride Trihydrate: Unconstrained Anisotropic Least-Squares Refinement of Hydrogen and Non-Hydrogen Atoms From Combined X-ray–Neutron Diffraction Data*

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Abstract. $[Pt(C_5H_5N)_4]^{2+}.[Cl]_2^-.3H_2O$, $M_r = 636.452$, monoclinic, Cc, $a = 12.711$ (1), $b = 12.856$ (1), $c = 16.600$ (2) Å, $\beta = 118.544$ (8)°, $V = 2382.9$ (2) Å^3, $Z = 4$, $D_m = 1.78$ (2), $D_x = 1.774$ g cm^{-3}, $\lambda(Mo\ K\alpha_1) = 0.7093$ Å, $\mu = 63.58$ cm^{-1}, $F(000) = 1240$. $T = 296$ (1) K. Final $R(F) = 0.021$ (X-ray) for 3429 counter data. The six water H atoms were not located. Subsequently the compound was recrystallized from a pyridine–water solution and a suitable crystal thus obtained was used to collect a set of 1326 neutron diffraction data which were combined with X-ray data for further least-squares refinement. The final $R(F)$ and $R(F^2)$ indexes were 0.022 and 0.031, respectively, based on 56 atoms with 515 variables with anisotropic thermal motions. The four N atoms of the pyridine rings display the usual square-planar coordination around the metal with an average Pt–N distance of 2.024 (2) Å. Each pyridine ring is nearly planar, and the four N atoms are planar to within 0.026 (2) Å, the Pt atom deviating from this plane by 0.023 (2) Å. All water H atoms make hydrogen bonds with neighboring Cl$^-$ ions and each Cl$^-$ ion is linked to three H atoms of different water molecules, so that a three-dimensional network is formed.

Introduction. Platinum complexes have had a long history in the development of inorganic chemistry, and some of them, such as *cis*-diaminodichloroplatinum(II) (Connors & Roberts, 1974; Lippard, 1982), have been in use as antitumor drugs. Crystallographic studies on some platinum–nucleosides and platinum–nucleotides have also been reported (Bau, Gellert, Lehovec & Louie, 1979). The preparation of *cis*- and *trans*-diaminodichloroplatinum(II) has been reported by

Kauffman (1963) and their X-ray structures have appeared in the literature (Colario & Orioli, 1975). Although the formation of tetrakis(pyridine)platinum(II) chloride is mentioned (Kauffman, 1963), the degree of hydration of this compound was not given. The isolation of the title compound not only permitted the determination of its structure and the number of water molecules in a formula unit but also enabled us to demonstrate the three-dimensional network of its hydrogen-bonding scheme by the refinement based on combined X-ray and neutron data. The advantages of this kind of refinement have been discussed by Orpen, Pippard, Sheldrick & Rouse (1978).

Experimental. A brownish powder sample of the reaction product of K_2PtCl_4 and adenosine with a presumed formula $Pt(Ado.Cl_2)$ was kindly furnished by Dr J. D. Hoeschele of Health and Safety Research Division. Attempts to crystallize this presumed compound from either water or alcohol solution were not successful. The powder could be dissolved in a mixture of pyridine and dimethyl sulfoxide, and yellow crystals with large mosaic spread were obtained. When 1,2-dichloroethane was used as a solvent, crystals (compound I) suitable for X-ray analysis could be obtained. When (I) was treated further with pyridine and dimethyl sulfoxide (v/v ratio 9:1) in the presence of a small amount of water over a steam bath, large colorless air-stable crystals (compound II) were obtained upon cooling. By repeated crystallization with pyridine and water, large crystals suitable for neutron diffraction study were obtained.

A subsequent structural analysis by X-ray diffraction revealed (I) to be *trans*-diaminodichloroplatinum(II). Our crystallographic results for compound (I) are essentially identical with those reported previously (Colario & Orioli, 1975).§ An elemental analysis of

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§ Crystal (I) found to be triclinic with symmetry $P\bar{1}$ and cell dimensions $a = 5.5289$ (9), $b = 7.090$ (1), $c = 7.645$ (1) Å, $\alpha = 79.12$ (1), $\beta = 83.92$ (1), and $\gamma = 87.78$ (1)°. The 2602 data were collected with Mo $K\alpha_1$ ($\lambda = 0.7093$ Å) to $2\theta = 70°$ and the structure was refined to $R(F) = 0.047$ and $R(F^2) = 0.101$.

compound (II)* gave the following composition: Pt, 30·19; C, 38·08; H, 4·36; N, 8·81; Cl, 11·35%. These values are consistent with the formula $PtC_{20}H_{26}N_4O_3Cl_2$ of the title compound which has the calculated composition: Pt, 30·65; C, 37·74; H, 4·12; N, 8·80; Cl, 11·14%. Crystal density of compound (II) was determined by flotation in mixtures of bromobenzene and bromoform.

X-ray data collection. Preliminary X-ray photographs showed the crystals to be monoclinic with space group either Cc or $C2/c$. Fifteen strong reflections in the 2θ range 52–56° were centered on the Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) with Nb-filtered Mo $K\alpha_1$ ($\lambda = 0.7093$ Å) radiation, and the cell constants were refined by the least-squares method. Details of intensity data collection are given in Table 1.

Solution and refinement of the structure based on X-ray data. A three-dimensional Patterson function was computed (Levy, 1977) from the corrected intensities. Attempts were made to solve the structure under $C2/c$ symmetry as well as Cc symmetry. The structural analysis including preliminary least-squares refinements unambiguously revealed that Cl⁻ ions and water O atoms do not conform to $C2/c$ symmetry, and the resulting choice of the non-centrosymmetric Cc space group was confirmed by the locations and refinement of the water H atoms from the combined X-ray and neutron data. The origin of Cc was defined in the a and c directions by fixing the x and z parameters of the independent Pt atom at zero. The structure was determined from a Patterson synthesis, and the positions for all non-hydrogen atoms were obtained from successive Fourier synthesis (Wei & Hingerty, 1984). Idealized positions calculated for the 20 hydrogen atoms attached to the pyridine carbon atoms were constrained† in the least-squares refinements with the program *ORXFLS*4, an updated version of *ORFLS* (Busing, Martin & Levy, 1962). The least-squares refinements were based on F^2, the function minimized being $\sum w|F_o^2 - s^2 F_c^2|^2$, where the weights w are reciprocals of $\sigma_c^2(F_o^2) + (0.04F_o^2)^2$. Here σ_c is the standard error from counting statistics and s is the scale factor. The refinement was carried out with isotropic extinction corrections until all parameter shifts became less than 3% of the corresponding standard deviations. The final values for $R(F)$, $R(F^2)$ and $wR(F^2)$ [defined as $(\sum w|\Delta F^2|^2/wF_o^4)^{1/2}$] are 0·021, 0·031 and 0·048, respectively. The standard deviation of an observation

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† Each H atom was constrained to be 1·0 Å from the C atom to which it was attached, and to bisect the exterior angle defined by the C atom and the two adjacent ring atoms. The isotropic temperature factor of each H atom was assumed to be $1 + B_{eq}$, where B_{eq} is the equivalent isotropic temperature factor of the C atom to which it was bound.

Table 1. *Diffraction data collection for* $[Pt(C_5H_5N)_4]^{2+}.[Cl]_2^-.3H_2O$

	X-ray data	Neutron data
Crystal dimensions (mm)	0·165 × 0·267 × 0·715*	1·33 × 1·39 × 3·57
Radiation	Mo $K\alpha_1$ (0·7093 Å)	neutron (1·537 Å)†
μ (cm⁻¹)	63·58‡	2·107
Transmission range§	0·196–0·379	0·718–0·778
Take-off angle (°)	3	–
Scan type	θ–2θ	θ–2θ
Scan step (°)	0·025	0·05
Time per step (s)	2–3	2·4–4·8
Background counting time (s)	12–48	24–48
$[(\sin\theta)/\lambda]_{max}$(Å⁻¹)	0·70	0·58
Number of unique nonzero used	3429	1336
Number of variables	273	515
Data-to-parameter ratio	12·56	9·25¶
Temperature (K)	297	297

* The largest dimension in this rectangular rod crystal corresponds to the b axis.

† Be (101) monochromator with pyrolytic graphite filter to reduce $\lambda/2$ contribution to an estimated value of less than 2%.

‡ Linear absorption coefficient for Mo $K\alpha$ radiation.

§ Method of Busing & Levy (1957) with 512 integration points.

¶ This ratio is for the combined refinement with both X-ray and neutron data.

of unit weight, defined as $[w|\Delta F^2|^2/(n-p)]^{1/2}$, where n is the number of observations and p the number of variables fitted to the data set, is 0·905. A final difference Fourier synthesis showed no residual peak greater than 0·51 or less than −0·53 e Å⁻³. The atomic scattering factors used were those of Cromer & Waber (1974). Dispersion corrections of platinum and chlorine for Mo $K\alpha$ were also included (Cromer, 1974).

Neutron data collection. Because the analysis of X-ray data did not reveal the H atoms of the water molecules, clearly neutron data were desirable. Neutron diffraction intensities were measured with the neutron wavelength of 1·537 Å from a crystal of size 1·33 × 1·39 × 3·57 mm using a Huber four-circle diffractometer at the Oak Ridge High Flux Isotope Reactor. A monochromator of Be 101 was used. A complete set of 1191 unique reflections (including zero intensities) was measured for $2\theta < 100°$; another 145 reflections were measured out to $100 < 2\theta < 126°$ with the diffractometer in the parallel mode, but many reflections in the latter range were not accessible. The intensity data were corrected for absorption using a linear absorption coefficient of 2·107 cm⁻¹ (Koester & Yelon, 1982).* Details of data collection are also given in Table 1.

Refinement of structure based on X-ray and neutron data. Least-squares refinement based on combined X-ray and neutron data was performed with the program *ORXFLS*. All necessary modifications were made in user subroutine *WEIGHT*, which is called

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Table 2. *Positional and isotropic thermal parameters for* $[Pt(C_5H_5N)_4]^{2+}.[Cl]_2^-.3H_2O$

	x	y	z	$B_{eq}(\text{Å}^2)^*$
Pt	0	0·00750 (2)	0	2·454 (7)
Cl(1)	−0·2743 (2)	−0·1378 (1)	−0·0667 (1)	4·90 (5)
Cl(2)	−0·0084 (2)	−0·4089 (1)	0·0729 (2)	6·31 (7)
O(A)	0·2386 (4)	0·1585 (3)	0·0419 (3)	5·7 (2)
O(B)	0·0137 (9)	−0·4964 (4)	0·2609 (8)	8·4 (3)
O(C)	−0·0047 (5)	0·4006 (4)	−0·0426 (4)	7·5 (2)
N(11)	0·0979 (2)	−0·0546 (2)	0·1268 (2)	3·08 (8)
C(21)	0·1979 (4)	−0·0059 (2)	0·1870 (3)	3·5 (1)
C(31)	0·2669 (4)	−0·0425 (3)	0·2761 (3)	4·4 (1)
C(41)	0·2317 (4)	−0·1320 (3)	0·3020 (3)	4·8 (2)
C(51)	0·1309 (4)	−0·1831 (3)	0·2392 (3)	5·3 (2)
C(61)	0·0647 (4)	−0·1424 (3)	0·1516 (3)	4·3 (1)
N(12)	0·0639 (2)	−0·1020 (2)	−0·0527 (2)	2·92 (8)
C(22)	0·0097 (4)	−0·1948 (2)	−0·0770 (3)	4·0 (1)
C(32)	0·0502 (4)	−0·2725 (3)	−0·1136 (3)	4·7 (2)
C(42)	0·1484 (4)	−0·2532 (3)	−0·1257 (3)	4·4 (1)
C(52)	0·2048 (4)	−0·1571 (3)	−0·0995 (3)	4·5 (1)
C(62)	0·1601 (4)	−0·0832 (3)	−0·0635 (3)	3·8 (1)
N(13)	−0·0910 (2)	0·0741 (2)	−0·1246 (2)	2·98 (8)
C(23)	−0·1815 (4)	0·0241 (3)	−0·1945 (3)	3·9 (1)
C(33)	−0·2416 (4)	0·0653 (3)	−0·2816 (3)	5·0 (1)
C(43)	−0·2076 (4)	0·1619 (3)	−0·2974 (4)	5·1 (2)
C(53)	−0·1167 (4)	0·2149 (3)	−0·2251 (3)	4·9 (1)
C(63)	−0·0586 (4)	0·1681 (3)	−0·1398 (3)	4·0 (1)
N(14)	−0·0624 (2)	0·1156 (2)	0·0559 (2)	2·85 (8)
C(24)	−0·0059 (4)	0·2068 (2)	0·0854 (3)	4·0 (1)
C(34)	−0·0434 (4)	0·2805 (3)	0·1262 (3)	4·7 (2)
C(44)	−0·1430 (4)	0·2599 (3)	0·1369 (3)	4·6 (1)
C(54)	−0·2018 (4)	0·1662 (3)	0·1061 (3)	4·6 (1)
C(64)	−0·1595 (3)	0·0956 (3)	0·0659 (3)	3·9 (1)
H(21)	0·2208 (9)	0·0630 (8)	0·1616 (7)	6·1 (4)
H(31)	0·3467 (10)	−0·0023 (9)	0·3234 (7)	7·3 (4)
H(41)	0·2820 (11)	−0·1596 (10)	0·3712 (8)	7·1 (5)
H(51)	0·1020 (15)	−0·2554 (10)	0·2561 (10)	8·8 (7)
H(61)	−0·0186 (12)	−0·1784 (9)	0·0989 (9)	7·5 (5)
H(22)	−0·0669 (11)	−0·2056 (8)	−0·0673 (10)	7·0 (5)
H(32)	0·0064 (11)	−0·3454 (9)	−0·1308 (11) .	8·6 (7)
H(42)	0·1813 (12)	−0·3128 (8)	−0·1537 (9)	7·2 (5)
H(52)	0·2834 (12)	−0·1388 (9)	−0·1051 (11)	7·9 (6)
H(62)	0·2008 (10)	−0·0083 (8)	−0·0407 (10)	6·7 (5)
H(23)	−0·2082 (10)	−0·0508 (8)	−0·1776 (8)	6·7 (4)
H(33)	−0·3120 (13)	0·0228 (11)	−0·3333 (9)	8·4 (6)
H(43)	−0·2491 (12)	0·1980 (10)	−0·3642 (8)	8·0 (5)
H(53)	−0·0887 (13)	0·2922 (11)	−0·2345 (10)	8·7 (5)
H(63)	0·0126 (11)	0·2051 (8)	−0·0831 (9)	7·4 (5)
H(24)	0·0694 (11)	0·2183 (8)	0·0752 (9)	6·9 (5)
H(34)	0·0008 (13)	0·3533 (8)	0·1479 (10)	8·6 (7)
H(44)	−0·1727 (13)	0·3180 (10)	0·1709 (9)	8·0 (6)
H(54)	−0·2830 (13)	0·1475 (10)	0·1102 (10)	8·1 (7)
H(64)	−0·2015 (9)	0·0205 (8)	0·0394 (9)	6·3 (5)
H(1A)	0·2320 (9)	0·2200 (7)	0·0061 (7)	5·6 (4)
H(2A)	0·3185 (10)	0·1330 (8)	0·0583 (7)	6·2 (4)
H(1B)	0·0723 (12)	−0·4564 (11)	0·3093 (9)	8·1 (6)
H(2B)	0·0072 (12)	−0·4689 (10)	0·2084 (10)	7·4 (6)
H(1C)	0·0643 (10)	0·4001 (8)	−0·0485 (7)	6·5 (4)
H(2C)	−0·0008 (10)	0·4574 (9)	−0·0057 (7)	6·8 (4)

E.s.d.'s are given in all tables and in the text. The digits in parentheses correspond to the least significant digits of the parameters.

* The equivalent isotropic temperature factors were calculated by the relation given by Hamilton (1959): $B_{eq} = 8\pi^2(U_{11}a^{*2}a^2 + U_{22} + U_{33}c^{*2}c^2 + 2U_{13}a^*c^*ac\cos\beta)/3$, where $U_{ij} = \beta_{ij}/2\pi^2a_i^*a_j^*$ (a^*'s are reciprocal-cell constants).

before each structure factor is calculated. Scattering-factor tables and anomalous-scattering factors were entered as for an X-ray problem. On each cycle the neutron data were included first, followed by the X-ray data.

On the first entry of each cycle, subroutine *WEIGHT* replaced the X-ray anomalous-scattering factors with neutron scattering factors and set indicators for a neutron problem. On the first X-ray reflection of each cycle, the X-ray anomalous-scattering factors were restored and indicators were set for an X-ray problem.

Table 3. *Selected bond lengths* (Å) *and bond angles* (°)

(*a*) Pyridine ring systems

	$I = 1$	$I = 2$	$I = 3$	$I = 4$
Pt—N(1*I*)	2·028 (3)	2·021 (2)	2·016 (3)	2·031 (2)
N(1*I*)—C(2*I*)	1·338 (4)	1·340 (4)	1·345 (4)	1·339 (4)
C(2*I*)—C(3*I*)	1·393 (5)	1·389 (5)	1·378 (6)	1·378 (5)
C(3*I*)—C(4*I*)	1·377 (6)	1·378 (5)	1·381 (6)	1·385 (6)
C(4*I*)—C(5*I*)	1·372 (6)	1·390 (5)	1·383 (6)	1·380 (6)
C(5*I*)—C(6*I*)	1·388 (6)	1·381 (5)	1·383 (5)	1·380 (5)
C(6*I*)—N(1*I*)	1·337 (4)	1·339 (4)	1·339 (4)	1·347 (4)
C(2*I*)—H(2*I*)	1·08 (1)	1·07 (1)	1·10 (1)	1·06 (1)
C(3*I*)—H(3*I*)	1·07 (1)	1·06 (1)	1·05 (1)	1·06 (1)
C(4*I*)—H(4*I*)	1·07 (1)	1·08 (1)	1·08 (1)	1·11 (1)
C(5*I*)—H(5*I*)	1·09 (1)	1·07 (1)	1·09 (1)	1·09 (1)
C(6*I*)—H(6*I*)	1·10 (1)	1·07 (1)	1·06 (1)	1·09 (1)
C(6*I*)—N(1*I*)—C(2*I*)	119·5 (3)	119·4 (3)	118·9 (3)	119·1 (3)
N(1*I*)—C(2*I*)—C(3*I*)	121·8 (3)	121·8 (3)	122·5 (4)	122·1 (3)
C(2*I*)—C(3*I*)—C(4*I*)	118·7 (4)	119·0 (3)	118·6 (4)	119·0 (3)
C(3*I*)—C(4*I*)—C(5*I*)	119·2 (4)	118·8 (3)	119·1 (4)	119·1 (3)
C(4*I*)—C(5*I*)—C(6*I*)	119·6 (4)	119·3 (3)	119·3 (4)	119·1 (4)
C(5*I*)—C(6*I*)—N(1*I*)	121·2 (4)	121·7 (3)	121·6 (3)	121·7 (3)

N(11)—Pt—N(12)	90·0 (1)	N(12)—Pt—N(13)	90·2 (1)
N(13)—Pt—N(14)	91·2 (1)	N(14)—Pt—N(11)	88·6 (1)

(*b*) H-bonds (O—H···Cl⁻)

	O—H	H···Cl	O···Cl	O—H···Cl
O(A) H(1A) Cl(1ⁱ)	0·97 (1)	2·17 (1)	3·140 (4)	176·6 (9)
O(A) H(2A) Cl(2ⁱ)	0·97 (1)	2·16 (1)	3·127 (4)	169·7 (9)
O(B) H(1B) Cl(1ⁱⁱ)	0·94 (2)	2·38 (1)	3·325 (9)	177 (1)
O(B) H(2B) Cl(2ⁱ)	0·91 (2)	2·30 (1)	3·202 (11)	177 (1)
O(C) H(1C) Cl(1ⁱ)	0·93 (2)	2·27 (1)	3·179 (5)	168·0 (9)
O(C) H(2C) Cl(2ⁱⁱⁱ)	0·94 (1)	2·19 (1)	3·124 (5)	175·1 (10)

(*c*) H···Cl···H angles

H(14ⁱᵛ)···Cl(1)···H(1Bᵛ)	134·9 (4)
H(1Bᵛ)···Cl(1)···H(1Cᵛ)	65·5 (4)
H(1Cⁱᵛ)···Cl(1)···H(14ⁱᵛ)	84·3 (4)
H(24ⁱᵛ)···Cl(2)···H(2B)	78·5 (4)
H(2B)···Cl(2)···H(2Cᵛⁱ)	108·2 (4)
H(2Cᵛⁱ)···Cl(2)···H(24ⁱᵛ)	117·5 (4)

(*d*) H—O—H angles

H(1A)—O(A)—H(2A) 102·7 (9)		H(1B)—O(B)—H(2B) 106 (1)
H(1C)—O(C)—H(2C) 109 (1)		

Symmetry codes: (i) $\frac{1}{2}+x$, $\frac{1}{2}+y$, z; (ii) $\frac{1}{2}+x$, $-\frac{1}{2}-y$, $\frac{1}{2}+z$; (iii) x, $1+y$, z; (iv) $-\frac{1}{2}+x$, $-\frac{1}{2}+y$, z; (v) $-\frac{1}{2}+x$, $-\frac{1}{2}-y$, $-\frac{1}{2}+z$; (vi) x, $-1+y$, z.

Neutron scattering factors (Koester & Yelon, 1982) used were: Pt, 0·95; C, 0·6648; H, −0·3741; N, 0·930; O, 0·5805; and Cl, 0·9579 (all in units of 10^{-12} cm). The least-squares refinement, again based on the F^2 data, was carried out with isotropic extinction corrections (Zachariasen, 1967) for the neutron data and anisotropic corrections (Coppens & Hamilton, 1970) for the X-ray data, until the ratios of change to e.s.d. became negligible. The final discrepancy factors are shown below.

	$R(F)$	$R(F^2)$	$wR(F^2)$	Standard deviation of an observation of unit weight
X-ray data	0·021	0·031	0·049	0·883
Neutron data	0·039	0·051	0·067	0·905
Combined data	0·022	0·031	0·053	0·941

Final difference Fourier syntheses showed no residual peaks greater than 0·53 or less than −0·51 e Å⁻³ for the X-ray data. The maximum and minimum residual peaks were 0·4 and −0·4 × 10¹¹ cm⁻², respectively, for the neutron data. These latter values can be compared with −8 × 10¹¹ cm⁻² obtained for a hydrogen peak in an observed Fourier synthesis with only the neutron data.

Because anomalous X-ray scattering is important, both absolute orientations were tested.

The final coordinates and equivalent isotropic temperature factors (Hamilton, 1959) are listed in Table 2. Selected bond lengths and angles calculated with program ORFFE (Busing, Martin & Levy, 1964) are given in Table 3. All figures were prepared by use of program ORTEP (Johnson, 1976).

Discussion. The major importance of this work is the unconstrained anisotropic refinement of the structure of $[Pt(C_5H_5N)_4]^{2+}.[Cl]_2^-.3H_2O$ with combined X-ray and neutron diffraction data. The results of X-ray structural analysis *per se* show the correctness of the non-hydrogen part of the structure. With the combined data not only are all of the H atoms located, but also the hydrogen-bonding scheme is clearly revealed. Since the resulting positional and thermal parameters for non-hydrogen atoms for the combined data are in close agreement with those based on the X-ray data alone, only the results based on the combined data are presented in this work.*

The crystal structure consists of discrete ions in which the independent Pt atom exhibits the usual square-planar coordination with the four pyridine N atoms, as shown in Fig. 1. The $[Pt(C_5H_5N)_4]^{2+}$ cation shows approximate C_{2h}–$2/m$ symmetry [the twofold axis bisects the angle N(11)–Pt–N(14)]. The average Pt–N distance of 2·024 (1) Å is not significantly different from the mean Pt–N distance found in *cis*-dichloro-bis(pyridine)platinum(II) [2·04(1)Å] (Colario & Orioli, 1975) and in *trans*-dichlorobis(pyridine)platinum(II) [2·020 (4) Å] (unpublished results). Each pyridine ring is essentially planar as shown in Table 4, and the four nitrogens are planar to within 0·026 (1) Å with the Pt atom deviating from this plane by 0·023 (2) Å. The angles between the plane normals for the neighboring pyridine rings are within a range of 82·9 (1) and 87·2 (1)°; the dihedral angles between the mean plane of the four N atoms system and those of the four pyridine rings range from 66·8 (1) to 86·4 (1)°.

Fig. 2 shows the hydrogen-bonding scheme of water to the neighboring Cl⁻ anions. The two H atoms of each water molecule are hydrogen-bonded to two different Cl⁻ ions, and each Cl⁻ in turn is bonded to hydrogens from three different water molecules. The detailed bonding parameters are shown in Table 3. These hydrogen-bond parameters are in accord with those quoted by Hamilton & Ibers (1968) for O—H···Cl bonds and are consistent with those reported for $CaCl_2.6H_2O$ and $SrCl_2.6H_2O$ (Agron & Busing, 1986).

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* Lists of structure factors, anisotropic thermal parameters and a figure showing the atom arrangement around the Pt atom have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51289 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Equations of best molecular planes and distances* (Å) *of atoms from these planes*

$$(a)\ 0.7860X + 0.5915Y - 0.2177Z - 0.0795 = 0$$
$$(b)\ 0.7558X - 0.5382Y - 0.6432Z - 0.0118 = 0$$
$$(c)\ 0.1786X - 0.3504Y + 0.7224Z - 0.0243 = 0$$
$$(d)\ 0.8747X - 0.4253Y - 0.6222Z - 0.1334 = 0$$
$$(e)\ 0.1818X - 0.4072Y + 0.6994Z - 0.1031 = 0$$

(a)

N(11)	0·026 (1)
N(12)	−0·026 (1)
N(13)	0·025 (1)
N(14)	−0·026 (1)
Pt*	−0·023 (2)

(b)		(c)		(d)		(e)	
N(11)	−0·010 (2)	N(12)	−0·003 (2)	N(13)	0·004 (2)	N(14)	0·002 (2)
C(21)	0·009 (2)	C(22)	0·001 (3)	C(23)	−0·007 (3)	C(24)	−0·002 (3)
C(31)	0·001 (3)	C(32)	0·004 (3)	C(33)	−0·002 (3)	C(34)	−0·000 (3)
C(41)	−0·009 (3)	C(42)	−0·006 (3)	C(43)	0·012 (3)	C(44)	0·001 (3)
C(51)	0·009 (3)	C(52)	0·003 (3)	C(53)	−0·014 (3)	C(54)	−0·001 (2)
C(61)	0·001 (3)	C(62)	0·001 (2)	C(63)	0·006 (3)	C(64)	−0·001 (2)
Pt*	−0·064 (5)	Pt*	−0·010 (5)	Pt*	0·092 (5)	Pt*	0·064 (5)

Root-mean-square deviations of the fitted atoms for planes (a), (b), (c), (d) and (e) are 0·026 (1), 0·007 (1), 0·003 (1), 0·009 (2) and 0·001 (1) Å, respectively. Calculations were performed with program ORFFE4, an updated version of ORFFE (Busing, Martin & Levy, 1964). X, Y, and Z represent direct-axis coordinates expressed in Å.

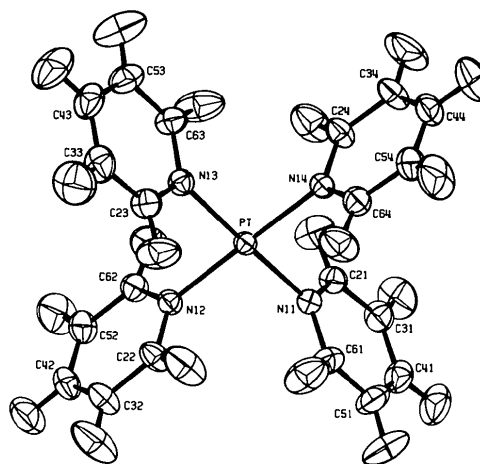* Atoms not included in the calculation of the least-squares plane.

Fig. 1. A perspective view of the $[Pt(C_5H_5N)_4]^{2+}$ cation. H atoms are numbered according to the C atoms to which they are bound. Thermal ellipsoids enclose 50% probability.
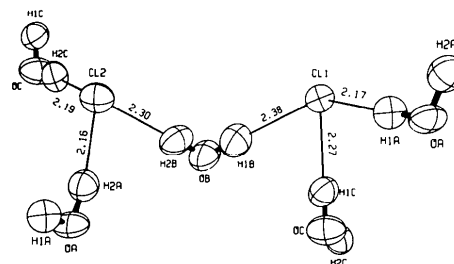

Fig. 2. A view of the hydrogen-bonding scheme. Each Cl is hydrogen-bonded to the neighboring H atoms of three different water molecules, whereas each water is connected to two different Cl atoms. Thermal ellipsoids enclose 35% probability.

In this structure, both C—H distances [1·06 (1)–1·11 (1) Å] and O—H distances of water [0·91 (2)–0·97 (1) Å] were determined. The average C—H and O—H distances are 1·078 (2) and 0·943 (5) Å, respectively.

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Structure of Histaminium Tetraaquadisulfatomanganate(II) Monohydrate*

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Abstract. $C_5H_{11}N_3^{2+}.[Mn(SO_4)_2(H_2O)_4]^{2-}.H_2O$, $M_r = 450.28$, monoclinic, $P2_1/n$, $a = 6.819$ (1), $b = 18.129$ (2), $c = 13.109$ (2) Å, $\beta = 93.74$ (1)°, $V = 1617.2$ (5) Å³, $Z = 4$, $D_m = 1.86$ (1), $D_x = 1.849$ Mg m⁻³, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 0.418$ mm⁻¹, $F(000) = 932$, room temperature, $R = 0.032$ for 2275 observed reflections. The structure contains a histaminium dication in *syn–anti* conformation. Two monodentate sulfate ligands and four water molecules form a slightly distorted octahedral environment around the Mn^{2+} ion. The structure contains a complicated network of O—H···O, N—H···O and C—H···O hydrogen bonds.

Introduction. In the vicinity of some biomembranes the predominant form of histamine is a dication (Durrant, Ganellin & Parsons, 1975). Therefore some structures of histaminium salts have already been studied (Veidis, Palenik, Schaffrin & Trotter, 1969; Bonnet & Jeannin, 1972; Yamane, Ashida & Kakudo, 1973; Bonnet,

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