Acta Cryst. (1977). B33, 2482–2489

A Short, Highly Asymmetrical Intramolecular Hydrogen Bond: A Neutron Diffraction Study of Bis(2-amino-2-methyl-3-butanone oximato)platinum(II) Chloride 3·5 Hydrate $[Pt(C_5H_{11}N_2O)_2H]^+Cl^-.3{\cdot}5H_2O$

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(*Received* 30 *September* 1976; *accepted* 29 *January* 1977)

A neutron diffraction study of bis(2-amino-2-methyl-3-butanone oximato)platinum(II) chloride 3·5 hydrate, $[Pt(C_5H_{11}N_2O)_2H]^+Cl^-.3{\cdot}5H_2O$, has allowed a precise comparison of the short hydrogen bond and the dynamics of rotating methyl groups with the corresponding Ni compound. The triclinic unit cell ($P\bar{1}$) has dimensions: a = 12·150 (2), b = 12·549 (2), c = 6·561 (2) Å, α = 95·01 (1), β = 104·67 (1), and γ = 98·72 (1)° based on a neutron wavelength of 1·109 Å. These data were used in conjunction with a partial X-ray data set to locate all the atoms. After least-squares refinement with anisotropic temperature factors, the conventional agreement index was 0·051. The short intramolecular hydrogen bond O···O [2·472 (5) Å] is not restricted by symmetry and proves to be much more asymmetric than that in the Ni complex {O···O [2·420 (3) Å]}. The O–H bond lengths are 1·087 (8) and 1·389 (7) Å compared with 1·187 (5) and 1·242 (5) Å observed for the Ni complex. The O–H–O angle is 173·8 (5)°. The potential apparently involves a sharper, less flat, single minimum shifted well toward one O atom. The N–O bonds adjacent to the hydrogen bond are of lengths 1·344 (3) and 1·356 (3) Å with the shorter N–O distance associated with the longer O–H distance. Bond summation methods for the two O atoms reveal nearly equivalent bonding. The water molecules and Cl^- ions are extensively hydrogen-bonded to each other, to one oxime O, and to the amine H atoms of the cation. The methyl groups, particularly those attached to the sp^2 C atoms, have large rotational amplitudes (11–25°) resulting in short apparent C–H bond lengths (1·068 Å average); the bond-length shortening is well correlated with the r.m.s. rotational amplitude. Other average uncorrected bond distances involving H atoms are O–H in H_2O (0·929 Å) and N–H (1·024 Å).

Introduction

A series of related metal complexes of α-amine oxime ligands with short but variable-length O···O hydrogen bonds is currently being studied. A previous neutron diffraction study of the Ni analog of the present complex has been reported (Schlemper, Hamilton & La Placa, 1971) in which the O···O distance was 2·420 (3) Å, and the H atom was in a slightly asymmetrical position. The monohydrate of the present compound was found (Schlemper, 1969) by X-ray diffraction to have an O···O distance of 2·48 (4) Å and to be isomorphous with the Ni complex. On crystallization from water, rather than the organic solvent used for the crystal in the X-ray study, the present 3·5 hydrate is obtained with crystals of suitable size for neutron diffraction. The main purpose of this study was to compare the O–H distances in the hydrogen bond with those in the shorter hydrogen bond of the Ni complex.

Crystal data and data collection

The compound was kindly provided by Murmann (1957). Analysis: calculated for $[Pt(C_5H_{11}N_2O)_2H]^+Cl^-.3{\cdot}5H_2O$: C 22·88, N 10·67, H 5·75%; found: C 23·16, N 10·82, H 5·72%. Crystals large enough for the neutron study were obtained by slow evaporation of an aqueous solution. An earlier X-ray study of this salt was reported (Schlemper, 1969) on the monohydrate which is obtained when the 3·5 hydrate is crystallized from dichloromethane–heptane solution. The crystal used for neutron data collection was approximately 0·2 × 0·2 × 0·3 cm.

The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. The cell dimensions determined from 24 carefully centered neutron peaks are a = 12·150 (2), b = 12·549 (2), c = 6·561 (2) Å, α = 95·01 (1), β = 104·67 (1), and γ = 98·72 (1)°. The neutron wavelength (1·109 Å) was determined using the reported cell dimensions (Pérez, Leger & Houstry, 1973) and 25 carefully centered neutron reflections from a single crystal of ethylenediamine tartrate (Fair & Schlemper, 1977). The calculated density of 1·838 (1) g cm^{-3} agrees well with the density measured by flotation of 1·82 (1) g cm^{-3}.

The crystal used for intensity data collection was bounded by seven faces: (010), ($2\bar{1}1$), ($\bar{1}10$), ($\bar{1}00$), ($0\bar{1}0$), ($2\bar{1}0$), and ($00\bar{1}$) and was mounted with the c^* axis nearly coincident with the goniometer-head axis. The data were collected at the Missouri University Research Reactor using a PDP 11/40 computer-controlled Mitsubishi diffractometer modified and automated by the University of Missouri Physics

Department electronic and machine shops. A full circle and the necessary electronics for computer control were designed and built by these shops. The computer software and time-share system were provided by Gene Moum.

The data were collected by the θ–2θ step scan technique with 0·05° 2θ steps covering 1·60° for each peak. The incident beam was obtained from a Be monochromator crystal, a monitor counter was used to time the steps, and the diffracted beam was detected with a BF_3 counter. 4328 reflections were measured out to $2\theta = 85°$. Background correction, integration and Lorentz correction were accomplished with a local program. The data were corrected for absorption ($\mu = 2{\cdot}28$ cm^{-1}) with a transmission-factor range of 0·66 to 0·77. Two standards were measured after every 40 reflections, and the data were corrected for the gradual, regular decrease in the standards of a total of 3·6%. Equivalent reflections were averaged to yield 3539 independent reflections. The average disagreement between equivalent reflections was 5·9%. Of these the 2467 reflections with $F_o^2 > 2{\cdot}5\sigma$ were used in the structure solution and refinement.

A limited X-ray data set, consisting of 788 independent reflections out to $2\theta = 30°$, was collected on a Picker X-ray diffractometer to facilitate the structure solution. These data were corrected for background, integrated, and corrected for Lp. In the two days required for data collection, the standard reflections indicated approximately 40% decomposition which was manifest in visible decoloration; this is in contrast to the minimal decomposition in the approximately three months required to collect the neutron data. This is undoubtedly related to the lower energy of the thermal neutron (~0·08 eV).

Structure determination

A brief attempt was first made to solve the structure using *MULTAN*. Although there were several sets of phases with high FOM's, none of them yielded a Fourier map which gave peaks corresponding to the expected square-planar geometry around the Pt atom. The partial X-ray data set was introduced, and the Pt, Cl, N, and oxime O atoms were located using conventional Patterson and Fourier methods. Refinement of the positional parameters of these atoms with the X-ray data gave $R(F^2) = \Sigma\ |F_o^2 - F_c^2|/\Sigma\ F_o^2 = 0{\cdot}57$. At this point, use of the X-ray data set was discontinued. Those same atom positions gave $R(F^2) = 0{\cdot}79$ for the neutron data, but the subsequent Fourier map, phased on F_c, clearly revealed positions for all nonhydrogen atoms in the Pt complex as well as the presence of an atom at the center of symmetry $(0,0,\frac{1}{2})$. Refinement of the coordinates of these atoms reduced $R(F^2)$ to 0·66. A subsequent Fourier map revealed the positions of the remaining nonhydrogen atoms. Some difficulty was then encountered in locating the H atoms on the water O atoms. One of the water positions is half occupied by Cl^-, while the other half Cl^- is at the center of symmetry. This mixed occupancy results in two sets of H

Table 1. *Positional parameters for* $[Pt(C_5H_{11}N_2O)_2H]^+Cl^-.3{\cdot}5H_2O$

Numbers in parentheses in this table and elsewhere represent estimated standard deviations from the least-squares refinement. The numbering system is defined in Figs. 1 and 4.

	x	*y*	*z*
Pt	0·0727 (1)	−0·2399 (1)	0·0454 (3)
Cl(1)	0·0	0·0	0·5000
N(1)	0·0095 (1)	−0·3641 (1)	0·1745 (3)
N(2)	0·2286 (1)	−0·2769 (1)	0·0704 (3)
N(4)	0·1447 (1)	−0·1142 (1)	−0·0859 (3)
N(3)	−0·0857 (1)	−0·2019 (1)	0·0518 (4)
O(1)	0·0776 (3)	−0·4342 (3)	0·2592 (5)
O(2)	0·2606 (3)	−0·3560 (3)	0·1853 (5)
C(1)	−0·0976 (2)	−0·3796 (2)	0·1784 (4)
C(2)	−0·2984 (2)	0·2219 (2)	0·0167 (4)
C(3)	−0·1682 (2)	−0·3011 (2)	0·0695 (5)
C(4)	−0·2483 (2)	0·1402 (2)	0·1538 (4)
C(5)	−0·1480 (3)	−0·4730 (3)	0·2731 (6)
C(6)	−0·4182 (3)	0·2428 (3)	−0·0006 (6)
C(7)	0·2341 (3)	0·3548 (3)	0·1569 (6)
C(8)	−0·2507 (4)	−0·2666 (3)	0·1923 (9)
C(9)	−0·3339 (3)	0·0354 (2)	0·1318 (6)
C(10)	−0·2078 (3)	0·1938 (3)	0·3848 (5)
H(23)	0·1606 (5)	−0·4029 (4)	0·2332 (10)
H(22)	0·1693 (4)	−0·0484 (4)	0·0308 (9)
H(21)	0·0894 (4)	−0·0910 (4)	−0·2133 (9)
H(19)	−0·1244 (4)	−0·1640 (5)	−0·0703 (10)
H(20)	−0·0687 (4)	−0·1475 (4)	0·1863 (10)
H(16)	−0·2339 (7)	−0·4937 (10)	0·2163 (24)
H(17)	−0·1221 (13)	−0·4602 (10)	0·4343 (19)
H(18)	−0·1146 (10)	−0·5411 (7)	0·2399 (21)
H(4)	0·4764 (6)	−0·1950 (9)	0·1351 (17)
H(6)	0·4224 (7)	−0·3244 (8)	0·0152 (20)
H(5)	0·4465 (7)	−0·2216 (9)	−0·1314 (14)
H(7)	−0·1768 (8)	−0·3744 (7)	−0·2450 (12)
H(8)	−0·2888 (7)	−0·4311 (6)	−0·1537 (14)
H(9)	−0·2881 (7)	−0·3032 (7)	−0·2384 (16)
H(1)	−0·2972 (7)	−0·2089 (7)	0·1132 (20)
H(2)	−0·3138 (8)	−0·3355 (7)	0·1987 (20)
H(3)	−0·2041 (9)	−0·2268 (8)	0·3524 (19)
H(13)	0·3675 (6)	0·0026 (6)	0·0338 (13)
H(14)	0·4080 (6)	−0·0497 (6)	−0·1927 (14)
H(15)	0·2929 (7)	0·0218 (6)	−0·2248 (14)
H(10)	0·2789 (7)	−0·2194 (8)	−0·4367 (11)
H(11)	0·1419 (7)	−0·2667 (6)	−0·4023 (11)
H(12)	0·1728 (8)	−0·1385 (7)	−0·4903 (11)
O(3)	0·1895 (4)	0·0690 (3)	0·2561 (6)
H(25)	0·2719 (6)	0·0817 (5)	0·3318 (11)
H(24)	0·1454 (5)	0·0480 (5)	0·3530 (11)
O(5)	0·4671 (5)	−0·3410 (4)	0·4948 (8)
H(29)	0·3926 (6)	−0·3429 (5)	0·3915 (11)
H(28)	0·4977 (11)	0·2657 (15)	0·4783 (23)
H(33)	0·5365 (18)	0·3835 (25)	0·4042 (44)
O(4) [Cl(2)]	0·4394 (5)	0·0959 (5)	0·4400 (9)
H(27)	0·4733 (19)	0·0568 (18)	0·4644 (52)
H(26)	0·4654 (12)	0·1862 (15)	0·4603 (22)
O(6)	0·4620 (5)	−0·5063 (5)	−0·2281 (11)
H(30)	0·4628 (11)	−0·4444 (10)	−0·2976 (22)
H(32)	0·4870 (14)	0·5029 (14)	−0·0856 (32)
H(31)	0·4811 (8)	−0·5575 (9)	−0·3062 (18)

atom positions for O(5) and O(6). Refinement of the scattering factor of O(4) gave 0·74 ± 0·01, which is in good agreement with the theoretical value of 0·77 based on equal occupancy by Cl and O. The final agreement indices were $R(F^2) = 0{\cdot}074$ and $\omega R(F^2) = [\Sigma\,\omega(F_o^2 - F_c^2)^2/\Sigma F_o^4]^{1/2} = 0{\cdot}096$ where $\omega = 1/\sigma^2$ and $\sigma^2 = \sigma^2(\text{counting}) + (0{\cdot}03F_o^2)^2$. The standard deviation of an observation of unit weight was 1·51. In this last refinement there were 495 variables including anisotropic vibration of all atoms and an isotropic extinction parameter $[g = 3{\cdot}90\,(10) \times 10^{-4}]$. The maximum shift in any parameter on the last cycle was less than 5% of its standard deviation. Neutron atomic scattering lengths (Bacon, 1972) were H −0·374, O 0·580, Pt 0·95, Cl 0·96, N 0·94, and C 0·66 × 10^{-12} cm. No attempt was made to refine the structure in space group $P1$ because the final $R(F^2)$ index of 0·074 was near the agreement index between equivalent and duplicate measurements (0·059) and because insufficent data (2467 reflections) were measurable to handle the number of variables (~990) in $P1$. The $R(F^2)$ value is also consistent with the value of $\Sigma\ \sigma(F^2)/\Sigma\ F_o^2 = 0{\cdot}085$. The agreement between 'chemically equivalent' bond distances and angles in this compound as well as the agreement with corresponding parameters in the previous X-ray study of the monohydrate (Schlemper, 1969) and with corresponding ligand parameters in the Ni complex (Schlemper, Hamilton & La Placa, 1971) also supports the choice of $P\bar{1}$. Statistics on the normalized structure factors were also indicative of a centrosymmetric space group.

The final positional parameters are given in Table 1.*

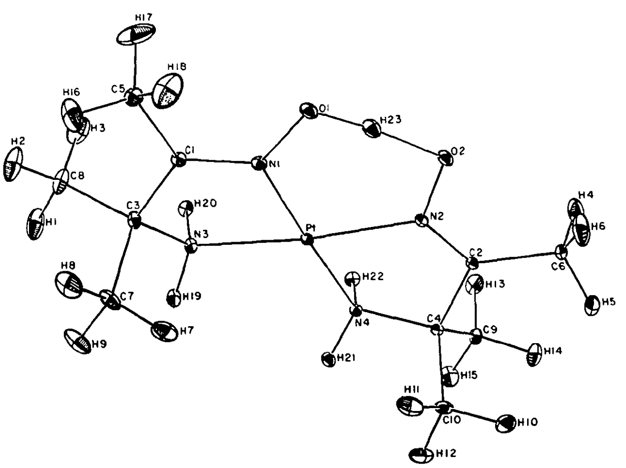

Fig. 1. Perspective view of the $[Pt(C_5H_{11}N_2O)_2H]^+$ cation showing the atom labeling and the anisotropic thermal motion.

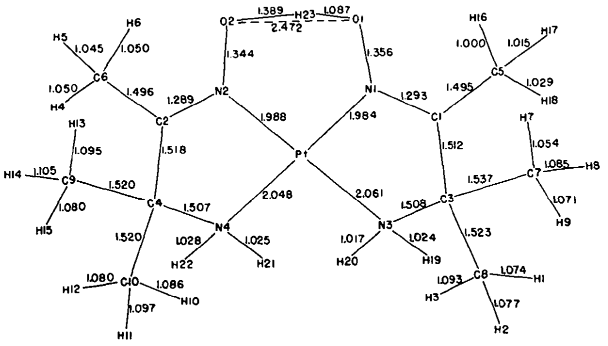

Fig. 2. Bond distances in $[Pt(C_5H_{11}N_2O)_2H]^+$. Standard deviations are: Pt–N 0·002, C–N 0·003–0·004, C–C 0·003–0·005, C–H 0·007–0·014, N–H and O–H 0·006–0·008 Å.

Discussion

Structure of the platinum complex

The structure consists of discrete mononuclear Pt complex cations (Fig. 1), Cl^- ions, and water molecules. The Pt^{II} atom is in the normal square-planar coordination. The closest nonhydrogen intermolecular contact to the Pt involves a methyl C atom at 3·65 Å. As in the Ni complex (Schlemper, Hamilton & La Placa, 1971), the metal–N(amine) distance is significantly longer than the metal–N(oxime) distance. The difference (0·07 Å) is, however, more pronounced than in the Ni case (0·04 Å). The average Pt–N(amine) distance of 2·054 (6) Å is in fair agreement with other studies, *e.g.* 2·030 (6) Å observed in $[Pt(NH_2CH_2CH_2NH_2)_2]^{2+}$ (Robinson, Schlemper & Murmann, 1975).

The bond distances and angles in the Pt complex are given in Figs. 2 and 3 respectively. The average nonhydrogen distances and angles are compared with those from the X-ray study of the monohydrate in Table 2. Despite the large standard deviations in the X-ray study there is excellent agreement in all distances and angles including the intramolecular O···O hydrogen bond distance. The ligand distances are also in good agreement with those observed in the corresponding Ni complex (Schlemper, Hamilton & La Placa, 1971). The largest difference is in the N–C(sp^3) distances, 1·493 (2) Å in the Ni complex and 1·508 (2) Å in the Pt complex.

As in the Ni complex there are significant differences in 'chemically equivalent' bond distances, *e.g.* Pt–N(3) [2·061 (2) Å] and Pt–N(4) [2·048 (2) Å]. Again one of the larger differences, N(1)–O(1) [1·356 (3) Å] and N(2)–O(2) [1·344 (3) Å], is attributable to the asymmetric hydrogen bond, and other differences may be indirectly related to this hydrogen-bonding difference. In any case the chemically reasonable m (C_s) symmetry is

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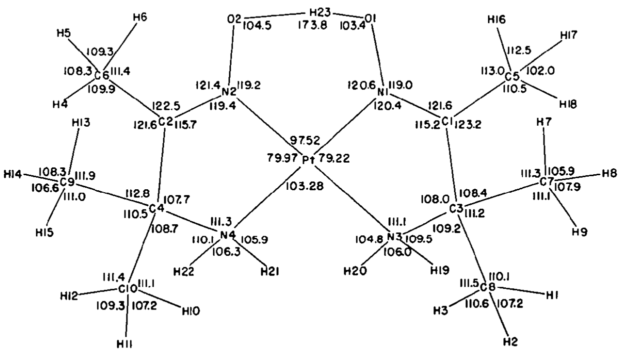
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32500 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.



C2–C6–H5	110.9	Pt–N3–H19	116.0	C1–C5–H17	111.7
H4–C6–H6	106.8	C3–N3–H20	109.1	H16–C5–H18	106.5
H13–C9–H15	108.5	Pt–N4–H22	115.0	H7–C7–H9	109.6
C4–C9–H14	111.3	C4–N4–H21	108.1	C3–C7–H8	110.9
C4–C10–H11	110.4	C1–C3–C8	112.2	C3–C8–H2	110.4
H10–C10–H12	107.3	N3–C3–C7	107.8	H1–C8–H3	106.9
C2–C4–C10	105.2			N4–C4–C9	109.0

Fig. 3. Bond angles in $[Pt(C_5H_{11}N_2O)_2H]^+$. Standard deviations are 0·1–0·4° for angles involving nonhydrogen atoms; 0·4–0·7° for angles involving one H, and 0·6–1·1° for angles involving two H atoms.

Table 2. *Comparison of average bond distances and angles in the two hydrates of* $[Pt(C_5H_{11}N_2O)_2H]^+Cl^-$ *and in the corresponding nickel complex*

The first line of each entry is from the present neutron study of the 3·5 hydrate, the second line from the X-ray study (Schlemper, 1969) of the monohydrate, and the third line from the neutron study of the Ni complex (Schlemper, Hamilton & La Placa, 1971).

Distances		Angles	
*M**–N(amine)	1·986 (2) Å	N(oxime)–*M*–N(oxime)	97·5 (1)°
	1·99 (3)		98 (1)
	1·866 (4)		97·34 (6)
M–N(oxime)	2·054 (6)	N(amine)–*M*–N(amine)	103·3 (1)
	2·03 (3)		101 (1)
	1·908 (1)		96·53 (6)
N–O	1·350 (6)	N(amine)–*M*–N(oxime)	79·6 (4)
	1·36 (4)		80·1 (1)
	1·340 (5)		83·1 (2)
N–C(sp^2)	1·291 (2)	*M*–N–O	119·9 (7)
	1·26 (4)		119 (1)
	1·288 (2)		122·5 (2)
N–C(sp^3)	1·508 (1)	*M*–N–C(sp^2)	119·9 (5)
	1·53 (4)		120 (1)
	1·493 (2)		118·3 (1)
C(sp^2)–C(sp^3)	1·505 (9)	*M*–N–C(sp^3)	111·2 (1)
	1·52 (4)		111 (1)
	1·502 (11)		111·0 (1)
C(sp^3)–C(sp^3)	1·525 (6)		
	1·53 (4)		
	1·526 (6)		
O···O	2·472 (5)		
	2·48 (4)		
	2·420 (3)		

* *M* = Pt or Ni.

not quite achieved. The ligand puckering is also very similar to that observed in the Ni complex, *i.e.* most of the nonhydrogen atoms off to one side of the Pt–N square plane.

The amine groups

The average N–H bond length is 1·024 (3) Å, and the range is 1·017–1·028 Å compared with an average of 1·024 (4) Å in the Ni complex. The rigid-body thermal-motion correction, as described later, would increase the average by 0·004 Å. As in the Ni complex, there are again marked deviations from tetrahedral angles for the amine groups, with each amine group having one Pt–N–H angle of about 105° and the other of about 115°.

The methyl groups

The C–H distances range from 1·00–1·10 Å before thermal-motion correction; the shorter distances are associated with the greater thermal motion. As in the Ni complex, the greatest thermal motion is observed for the methyl groups attached to the sp^2 C atoms which show an average uncorrected distance of 1·032 Å. The sp^3 C atoms have an average uncorrected C–H distance of 1·085 Å. After thermal-motion correction (subsequent section) the values are C–H(sp^2) (1·111 Å) and C–H(sp^3) (1·113 Å). These values are in excellent agreement with each other and with the corresponding values from the Ni complex of 1·120 and 1·108 Å respectively. A discrepancy from tetrahedral geometry is observed in that the average H–C–H angle [107·8 (1·6)°] is, as might be expected, significantly smaller than the average C–C–H angle [111·0 (5)°]. These values are almost identical to those in the nickel complex and represent considerably smaller deviations from tetrahedral angles than those observed for the amine groups.

Chloride–water disorder and intermolecular hydrogen bonding

There is extensive hydrogen bonding involving the water molecules, Cl^- ions, amine moieties, and one of the oxime O atoms. This hydrogen bonding network is shown in projection in Fig. 4. The hydrogen-bond angles and donor atom—acceptor atom distances are given in Table 3. Because one site is occupied half by water [O(4)] and half by Cl^- [Cl(2)], there is some disorder in the intermolecular hydrogen bonding. This disorder involves the H atoms on O(5) and O(6), the H positions [H(28), H(33), and H(32)] being determined by the occupancy of the surrounding Cl(2), O(4) positions. One H on each of the O(5) and O(6) water molecules is ordered, H(29) on O(5) and H(31) on O(6), while the other H has two possible positions (see Fig. 4). In all cases, each H atom of the water molecules and amine groups is involved in one and only one hydrogen bond. The X–H···Y angles are all nearly linear with a range of 163·7–174·2°. The H···O distances (1·792–2·004 Å) are in the normal range of intermolecular hydrogen bonds.

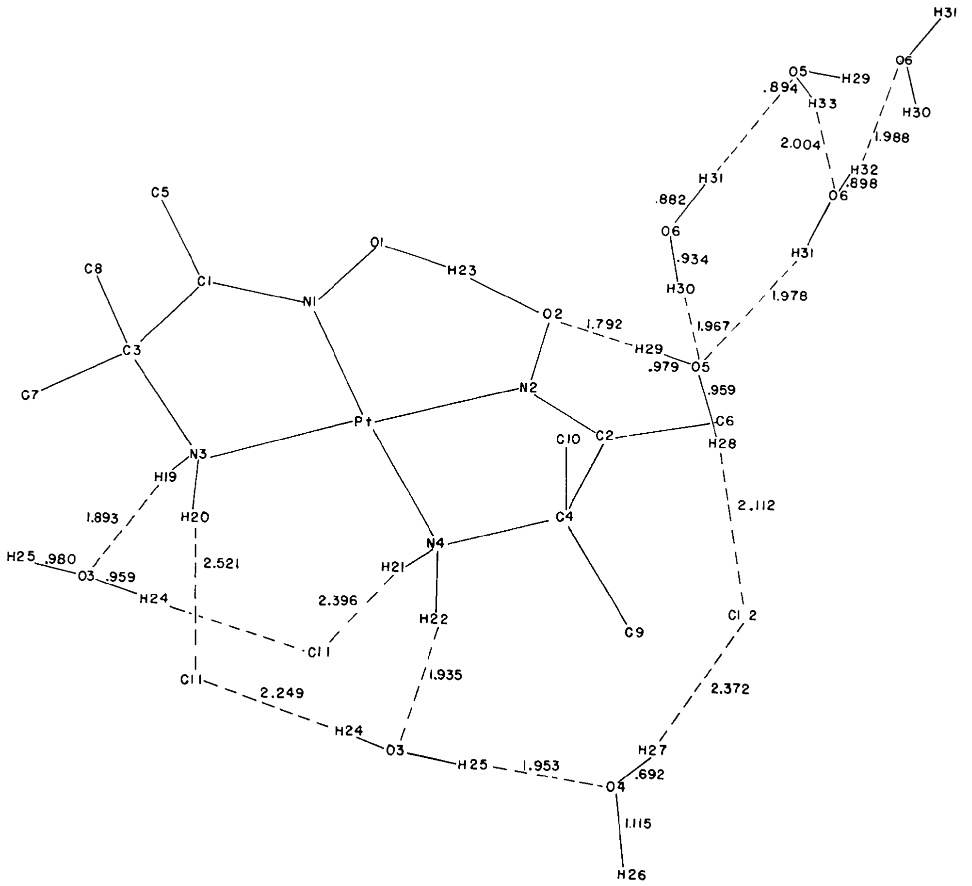


Fig. 4. A projection of the hydrogen bonding between water molecules, Cl^- ions, and the Pt complex. Not shown is the hydrogen bond from H(26) to water O(5) (see Table 3).

Table 3. *Hydrogen-bond distances and angles*

Bond (*X*–H···*Y*)	*X*···*Y* (Å)	*X*–H (Å)	H···*Y*(Å)	*X*–H···*Y*(°)
O(3)–H(24)···Cl(1)	3·180 (3)	0·96 (1)	2·249 (7)	163·7 (7)
N(4)–H(21)···Cl(1)	3·398 (3)	1·025 (6)	2·396 (6)	165·6 (4)
N(3)–H(20)···Cl(1)	3·536 (3)	1·024 (7)	2·521 (6)	171·1 (4)
O(5)–H(29)···O(2)	2·769 (4)	0·98 (1)	1·792 (8)	174·2 (7)
N(3)–H(19)···O(3)	2·896 (3)	1·017 (8)	1·893 (7)	168·6 (5)
N(4)–H(22)···O(3)	2·953 (3)	1·028 (6)	1·935 (7)	170·3 (4)
O(4)–H(26)···O(5)	3·065 (4)	1·11 (2)	1·96 (2)	172·2 (12)
O(6)–H(30)···O(5)	2·880 (4)	0·93 (2)	1·97 (1)	165·1 (12)
O(6)–H(31)···O(5)	2·856 (4)	0·88 (2)	1·98 (1)	173·6 (8)
O(3) H(25)···O(4)	2·925 (4)	0·980 (9)	1·953 (9)	170·9 (6)
O(5)–H(28)···Cl(2)	3·065 (3)	0·96 (2)	2·11 (2)	173·1 (12)
O(4)–H(27)···Cl(2)	3·065 (4)	0·69 (2)	2·38 (2)	169·9 (28)
O(6)–H(32)···O(6)	2·882 (4)	0·90 (2)	1·99 (2)	174·0 (15)
O(5)–H(33)···O(6)	2·880 (4)	0·89 (4)	2·01 (4)	166·1 (18)
O(1)–H(23)···O(2)	2·472 (5)	1·087 (8)	1·389 (7)	173·8 (5)

The O(4), Cl(2) position is somewhat poorly resolved. The coordinates of O(4) and Cl(2) are undoubtedly not exactly identical, but no distinction was made in the refinement. This probably accounts for the poorly defined geometry of that water, O(4)–H(27) (0·692 Å) and O(4)–H(26) (1·115 Å). These H atoms were assigned occupancy factors of ½ as were H(28), H(30), H(32), and H(33).

The unresolved difference in Cl(2) and O(4) positions probably also accounts for the short H(25)···Cl(2)[O(4)] distance (1·953 Å). The $H(H_2O){\cdots}Cl$ distances involving the fully occupied special position are normal, 2·249, 2·396, and 2·521 Å as compared with, for example, those in the Ni complex (2·240 to 2·445 Å).

The shortest intermolecular hydrogen bond involves interaction of H(29) on the O(5) water with oxime O(2) (1·792 Å). This oxime O atom is the one with the longer intramolecular O–H distance. This is in sharp contrast to the Ni complex where the oxime O atoms are not involved in any intermolecular hydrogen bonds. The consequence of this will be discussed in a subsequent section.

Thermal motion

For most of the atoms, the minimum and maximum amplitudes vary by much less than a factor of two. However, one of the half-occupancy H atoms [H(30)] shows a minimum r.m.s. of 0·076 and maximum of 0·288. The H atoms on the methyl groups have the largest amplitudes, particularly those on the sp^2 C atoms. The directions of vibration for the cation can be seen in Fig. 1. As usually observed, the maximum amplitude of vibration for each terminal atom is nearly perpendicular to the bond while the minimum is nearly along the bond. The larger amplitudes of vibration of the H atoms led to a treatment of the thermal motion in which the terminal methyl groups are treated as hindered rotors as in the corresponding Ni complex (Schlemper, Hamilton & La Placa, 1971).

The thermal motion parameters of the 17 nonhydrogen atoms in the Pt complex were fitted to a general rigid-body model of 21 parameters as described by Schomaker & Trueblood (1968). The anisotropic β_{ij} were first converted to mean square amplitudes U_{ij}, referred to a Cartesian axis system with axes parallel to the crystal **a**, **c*** × **a**, and **c*** axes. The translation tensor (**T**), libration tensor (**L**), and interaction tensor (**S**), referred to the same axis system, are as follows:

$$\mathbf{T}\,(\text{Å}^2)=\begin{pmatrix} 0.034\,(2) & 0.005\,(2) & -0.004\,(2)\\ 0.005\,(2) & 0.019\,(2) & -0.005\,(2)\\ -0.004\,(2) & -0.005\,(2) & 0.016\,(3)\end{pmatrix}$$

$$\mathbf{L}\,(\text{deg}^2)=\begin{pmatrix} 16.9\,(22) & 6.6\,(11) & -2.6\,(9)\\ 6.6\,(11) & 12.5\,(9) & -3.1\,(8)\\ -2.6\,(9) & -3.1\,(8) & 6.3\,(8)\end{pmatrix}$$

$$\mathbf{S}\,(\text{deg Å})=\begin{pmatrix} 0.12\,(5) & -0.12\,(4) & 0.08\,(3)\\ -0.02\,(3) & -0.08\,(3) & 0.15\,(2)\\ 0.08\,(2) & 0.07\,(2) & -0.03\end{pmatrix}.$$

The principal axes of libration and translation are nearly coincident. The r.m.s. lengths along the principal axes are: **L** 4·8, 2·8, 2·2°; **T** 0·19, 0·14, 0·11 Å. The precision of these quantities is about 10%. The r.m.s. translational amplitudes are slightly smaller than those of the Ni compound, probably due to the heavier Pt atom. The librational amplitudes are almost identical to the Ni complex. The maximum amplitude of libration is nearly around the long axis of the molecule and of translation along this axis as observed in the Ni complex. The screw components are somewhat larger than in the Ni case, but still small. The effective translations in the non-intersecting-axis description are −0·017, 0·015, and 0·018 Å. The 'center of reaction', as in the Ni complex, lies within 0·4 Å of the center of mass of the 17 nonhydrogen atoms. The r.m.s. deviation of the experimental U_{ij} from those calculated from the least-squares values of **T**, **L**, and **S** is 0·0054 Å^2. The estimated precision of the U_{ij} from the least-squares refinement is about 0·002 to 0·003 Å, so that there are significant nonrigid-body motions. Because of the small size of the screw components, the data were analyzed in the same manner as in the Ni complex in terms of only **T** and **L**, with the origin of the libration axes at the center of mass of the 17 nonhydrogen atoms. The resulting r.m.s. deviation of U_{ij} was 0·0078 Å^2. The r.m.s. lengths and directions of the principal axes of **T** and **L** show little change: **L** 4·1, 2·9, 2·2°; **T** 0·19, 0·14, 0·12 Å.

The amplitudes of vibration of the H atoms were corrected for the rigid-body motions obtained above for the $S = 0$ case. The resulting ΔU's ($U_{\rm exp} - U_{\rm rigid\,body}$) were analyzed in terms of hindered rotation as in the Ni complex to derive r.m.s. amplitudes of rotation (θ), estimated vibrational frequencies (ω), and corresponding barrier heights (V_0) (Table 4). In every case, by far the largest amplitude of the difference ellipsoid was in the direction corresponding to hindered rotation. The other values were always small and frequently near zero. The average values for the H atoms of each methyl group are used in Table 4.

The most significant result of this analysis is that, as in the Ni case, the methyl groups on the sp^2 C atoms have larger amplitudes and lower frequencies than the methyl groups on the sp^3 C atoms. The agreement between the corrected bond distances is remarkable, and the absolute values are in good agreement with those obtained in the Ni case.

Table 4. *Thermal motion analysis for the methyl groups of the cation*

The U' are mean square amplitudes $U_{\rm exp}-U_{\rm rigid\,body}$ (×10^3 Å^2). The principal components are along different but analogous natural axes* for each methyl group. $r_{\rm C-H}$ is the uncorrected bond length, θ is the r.m.s. amplitude of rotation, ω is the estimated vibrational frequency, and V_0 is the corresponding barrier height.

Methyl carbon	U'_{11}	U'_{22}	U'_{33}	$r_{\rm C-H}$ (Å)	$\langle\theta\rangle$ (°)	$r_{{\rm C-H}/\cos\langle\theta\rangle}$ (Å)	ω (cm^{-1})	V_0 (kcal mol^{-1})
C(5)	11 (6)	218 (51)	26 (11)	1·017 (10)	24·7	1·119	109	0·60
C(6)	9 (4)	115 (11)	3 (15)	1·050 (3)	17·9	1·103	151	1·14
C(7)	15 (4)	66 (13)	24 (16)	1·072 (11)	13·5	1·102	199	1·98
C(8)	21 (4)	70 (23)	29 (9)	1·083 (8)	13·7	1·115	193	1·87
C(9)	17 (1)	40 (1)	7 (5)	1·095 (9)	11·3	1·117	256	3·27
C(10)	9 (5)	64 (13)	19 (19)	1·089 (6)	13·1	1·118	202	2·04

* The natural axes are defined so that U'_{22} corresponds to hindered rotation, *i.e.* axis 1 along the C–C bond, axis 3 in the C–C–H plane, and axis 2 taken to make an orthogonal system.

Intramolecular hydrogen bond

The short intramolecular hydrogen bond O···O [2·472 (5) Å] is significantly longer than that [2·420 (3) Å] observed for the corresponding Ni complex. The effect of this 0·05 Å elongation on the position of the H atom between the O atoms is dramatic (Fig. 5). While the difference in O—H distance in the Ni case was only 0·055 Å, it is 0·302 Å in this complex: O(1)—H(23) 1·087 (8) Å and O(2)—H(23) 1·389 (7) Å. This elongation can be associated with the larger size of Pt^{II} compared with Ni^{II}. The O···O distance is the same as that [2·48 (4) Å] observed in the X-ray study (Schlemper, 1969) of the monohydrate of the same salt. In order to achieve this O···O distance there are some significant differences in bond angles in this complex compared with the Ni complex (Fig. 5). Because of the bite of the ligand, the intrachelate ring angles are smaller in this complex. To maintain the square-planar coordination of the metal ion the other two *cis* N—Pt—N angles must be larger than in the Ni complex. This increase is almost exclusively in the N(amine)—Pt—N(amine) angle from 96·5° in the Ni complex to 103·3° in the Pt complex. Another change which decreases the O···O distance in the Pt complex is a Pt—N—O angle approximately 2° smaller than the Ni—N—O angle. Despite these adjustments in bond angles, the O···O distance is ~0·05 Å longer than in the Ni complex.

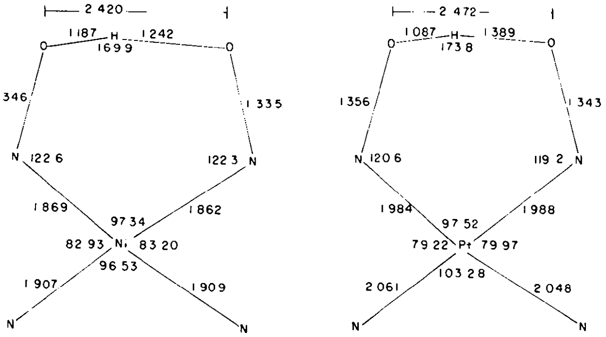


Fig. 5. Illustration of the effect of metal-ion size on the hydrogen bond and metal coordination geometry for the Ni^{II} and the Pt^{II} complexes.

The longer O—H distance involves the O atom which has an intermolecular hydrogen-bond interaction with a water H [H(29)] such that O(2)···H(29) equals 1·792 Å. This hydrogen bond is not affected by the disorder discussed earlier and thus has a very real effect on the symmetry of the short hydrogen bond. An analysis of the bonding of the oxime O atoms can be made using the approach of Brown & Shannon (1973). In this approach, the bond strength (s) for a bond of length R is given by $s = s_0(R/R_0)^{-n}$, where s_0 = ideal strength of a bond of length R_0 and n is constant for a given cation–anion pair, and the bond summation (s_T) for a given atom is given by $s_T = \Sigma_{i=1}^{CN} s_i$ where CN is the coordination number of that atom. For bonding to the oxime O atoms, the following values were used: R_0 = 1·184 for H and 1·241 for N (taken from $NaNO_3$), s_0 = 0·5 for H and $1\frac{2}{3}$ for N, and n = 2·2 for H and 4·0 (chosen from other He core atom—O values) for N. If only those atoms within 2·4 Å of the O atoms are considered in the bond summation, s_T = 1·772 for O(1) and 1·767 for O(2). The value for O(2) would have been only 1·567 in the absence of the intermolecular hydrogen bond to H(29). There are several methyl H atoms between 2·48 and 3·05 Å from each of the oxime O atoms. If these are included, the values of s_T (2·18 and 2·15) are again nearly identical for each O atom. Since a value for $s_T \simeq 2$ is expected for O, these longer contacts are probably given too much weight in this analysis, but they do need to be considered as significant interactions. A similar analysis of the bonding of the oxime O atoms in the Ni complex gives s_T = 1·807 for O(2) and s_T = 1·806 for O(1) considering only those atoms within 2·4 Å. In the Ni case, this includes one intramolecular methyl hydrogen for each oxime O atom which contributes about 0·11 to each of the values of s_T. Inclusion of the methyl H contacts between 2·4 and 3·05 Å gives s_T = 2·16 and 2·03 in good agreement with the Pt complex. From an examination

Table 5. *Asymmetry of short* O···O *hydrogen bonds from neutron diffraction studies*

Compound	O···O	O—H	H···O	Δ(O—H)	Reference
$[Ni(C_5H_{11}N_2O)_2H]^+Cl^-.H_2O$	2·420 (3)	1·187 (5)	1·242 (5)	0·055	Schlemper, Hamilton & La Placa (1971)
$(NH_2)_2CO.H_3PO_4$	2·421 (3)	1·207 (6)	1·223 (6)	0·016	Kostansek & Busing (1972)
$[H_5O_2]^+[C_6H_2(NO_2)_3SO_3]^-.2H_2O$	2·436 (2)	1·128 (4)	1·310 (4)	0·182	Lundgren & Tellgren (1974)
$C_6(NO_2)_2(OH)_2O_2.6H_2O$	2·44	1·18	1·27	0·09	Williams & Peterson (1969)
$[Pt(C_5H_{11}N_2O)_2H]^+Cl^-.3{\cdot}5H_2O$	2·472 (5)	1·087 (7)	1·389 (7)	0·302	This work
$KHO(CH_2COO)_2$	2·476 (2)	1·152 (3)	1·326 (3)	0·174	Albertsson & Grenthe (1973)
$H_2C_2O_4.2H_2O$	2·506 (4)	1·026 (7)	1·480 (7)	0·454	Sabine, Cox & Craven (1969)
$NaH_2PO_4.2H_2O$	2·536 (3)	1·023 (5)	1·515 (5)	0·492	Barth, Catti & Ferraris (1976)
$NaH_2PO_4.2H_2O$	2·577	1·028 (6)	1·553 (6)	0·525	Barth, Catti & Ferraris (1976)
InOOH	2·537 (3)	1·079 (7)	1·458 (7)	0·379	Lehmann *et al.* (1970)
$H_3PO_4.\frac{1}{2}H_2O$	2·563 (1)	1·017 (2)	1·556 (2)	0·537	Dickens *et al.* (1974)
$Ca(H_2PO_4)_2.H_2O$	2·595 (3)	1·016 (3)	1·584 (4)	0·568	Schroeder, Prince & Dickens (1975)
$Ca(H_2PO_4)_2.H_2O$	2·622 (3)	0·987 (5)	1·679 (4)	0·692	Schroeder, Prince & Dickens (1975)
$Ca(H_2PO_4)_2.H_2O$	2·626	0·987 (5)	1·653 (5)	0·676	Schroeder, Prince & Dickens (1975)

of these bond summations, the oxime O atoms appear to achieve a quite constant summation. When the intramolecular O—H distance lengthens, the corresponding N—O distance shortens, and other interactions with the O, such as the intermolecular hydrogen bond of O(2) with water, occur.

The rigid-body thermal parameters were subtracted from the thermal parameters for the individual atoms in the O—H—O bridge. For the treatment neglecting the screw motion, the H difference ellipsoid is almost perfectly isotropic with r.m.s. components of 0·12 (1) Å in both the bond-parallel and bond-perpendicular directions. The difference ellipsoids for the O atoms are very small with an average r.m.s. of 0·03 (3) Å. This is in marked contrast to the Ni complex where the H difference ellipsoid shows significant elongation along the O—H—O direction, suggesting a broad, single minimum potential with appreciable static disorder accounting for the elongation of the H difference ellipsoid along the bond. In this case, based on the spherical nature of the H difference ellipsoid, the potential appears to be less broad, and the H atom position to be quite ordered.

In Table 5 the asymmetry of the H atom in short O···O hydrogen bonds is compared for several careful neutron diffraction studies. A gradual, but apparently not quite regular, increase in the asymmetry of the H atom position is observed with increasing O···O distance. This is most easily seen in the values of Δ(O—H). The entries in this table are restricted to studies where the H atom is not crystallographically restricted by symmetry. The irregularities in Δ(O—H) as a function of O···O may be related to crystal packing effects such as other weak hydrogen bonds to one or both of the O atoms as observed in this study. Since the monohydrate of this complex has been shown (Schlemper, 1969) to have the same O···O distance with no intermolecular hydrogen bonds to either O atom, a careful location of the H atom in that hydrogen bond would be useful, and attempts are under way to obtain crystals large enough for a neutron diffraction study.

The authors gratefully thank R. Kent Murmann who provided the compound used for this study, and G. K. Johnson who provided helpful discussion on the oxygen bond summation. Acknowledgement is made of the National Science Foundation which supported this work (Grant CHE74-08958-A02).

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