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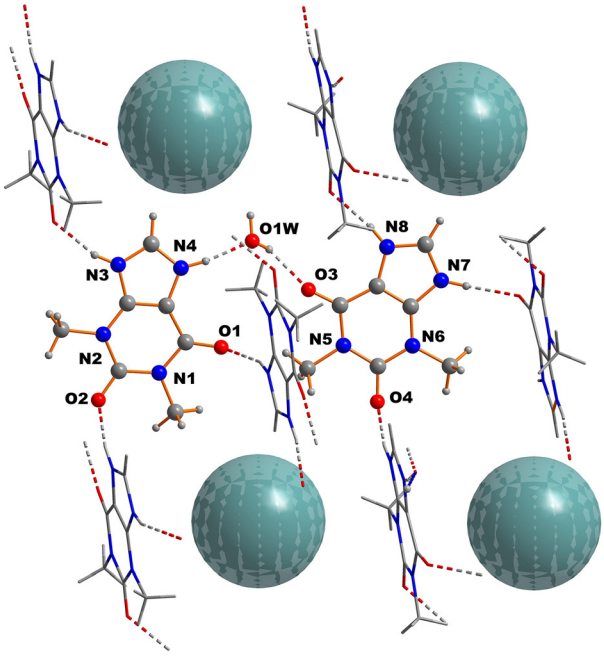
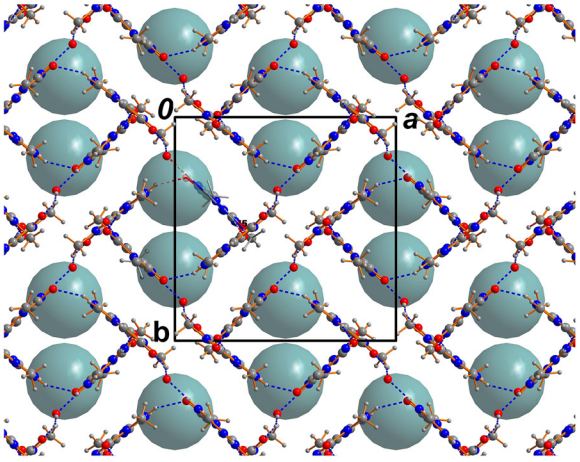
Hydrogen bonding and π···halogen interactions in the crystal structure of bis(theophyllinium) hexachloridoplatinate(IV) monohydrate





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Abstract

$C_{14}H_{20}Cl_6N_8O_5Pt$, monoclinic, $P2_1/n$ (no. 14), a = 13.4907(2) Å, b = 13.32240(10) Å, c = 13.8035(2) Å, β = 102.241(1)°, Z = 4, V = 2424.48(5) Å^3, $R_{gt}(F)$ = 0.0256, $wR_{ref}(F^2)$ = 0.0740, T = 290 K.

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1 Source of material and general procedures

All chemicals were obtained from commercial sources and used as purchased (Tables 1 and 2).

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.14 × 0.07 × 0.02 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	17.3 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy,
θ_{max}, completeness:	74.0°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	36111, 4890, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4839
$N(param)_{refined}$:	318
Programs:	DIAMOND,[1] CrysAlis^{PRO},[2] SHELX[3–5]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Pt1	0.49999 (2)	0.18203 (2)	0.23125 (2)	0.01197 (8)
Cl1	0.46938 (8)	0.08039 (8)	0.35868 (7)	0.0287 (2)
Cl2	0.52633 (7)	0.28561 (6)	0.10376 (6)	0.01848 (18)
Cl3	0.50510 (7)	0.04200 (6)	0.13350 (7)	0.01947 (18)
Cl4	0.67420 (7)	0.17041 (6)	0.29112 (7)	0.01872 (18)
Cl5	0.32720 (7)	0.19171 (7)	0.16946 (7)	0.02033 (19)
Cl6	0.49605 (8)	0.32525 (7)	0.32617 (7)	0.0239 (2)
O1	0.5517 (2)	0.2302 (2)	0.8053 (2)	0.0199 (5)
O2	0.8083 (2)	0.0096 (2)	0.9296 (2)	0.0203 (6)
O3	0.3991 (2)	0.4420 (2)	0.6796 (2)	0.0206 (5)
O4	0.3137 (2)	0.5313 (2)	0.97049 (19)	0.0193 (5)
N1	0.6861 (2)	0.1260 (2)	0.8672 (2)	0.0148 (6)
N2	0.7721 (2)	0.0343 (2)	0.7628 (2)	0.0167 (6)
N3	0.7204 (2)	0.0837 (2)	0.5887 (2)	0.0184 (6)
H31	0.760125	0.044971	0.561845	0.022*
N4	0.6051 (2)	0.1937 (2)	0.6036 (2)	0.0180 (6)
H41	0.557143	0.239412	0.588991	0.022*
N5	0.3575 (2)	0.4908 (2)	0.8252 (2)	0.0155 (6)
N6	0.2195 (2)	0.5993 (2)	0.8293 (2)	0.0158 (6)
N7	0.1354 (2)	0.6604 (2)	0.6646 (2)	0.0166 (6)
H71	0.087387	0.697952	0.680009	0.020*
N8	0.2316 (2)	0.5857 (2)	0.5777 (2)	0.0171 (6)
H81	0.257139	0.565931	0.527295	0.020*
C1	0.6207 (3)	0.1753 (3)	0.7905 (3)	0.0157 (7)
C2	0.7587 (3)	0.0539 (3)	0.8575 (3)	0.0158 (7)
C3	0.7165 (3)	0.0871 (3)	0.6869 (3)	0.0156 (7)
C4	0.6525 (3)	0.1501 (3)	0.5407 (3)	0.0205 (8)
H4	0.640493	0.163702	0.471632	0.025*
C5	0.6444 (3)	0.1547 (3)	0.6971 (3)	0.0155 (7)
C6	0.6742 (3)	0.1478 (3)	0.9692 (3)	0.0207 (8)
H6A	0.626125	0.100066	0.987810	0.031*
H6B	0.648496	0.216256	0.972213	0.031*
H6C	0.740023	0.141407	1.015276	0.031*
C7	0.8467 (3)	−0.0406 (3)	0.7459 (3)	0.0232 (8)
H7A	0.899571	−0.007362	0.718630	0.035*
H7B	0.812744	−0.091287	0.698877	0.035*
H7C	0.877397	−0.072998	0.808797	0.035*
C8	0.3464 (3)	0.4931 (3)	0.7223 (3)	0.0148 (7)
C9	0.2975 (3)	0.5403 (3)	0.8799 (3)	0.0144 (7)
C10	0.2070 (3)	0.6064 (3)	0.7295 (3)	0.0144 (7)
C11	0.1523 (3)	0.6453 (3)	0.5729 (3)	0.0169 (7)
H11	0.113188	0.673291	0.513721	0.020*
C12	0.2674 (3)	0.5596 (3)	0.6765 (3)	0.0143 (7)
C13	0.4376 (3)	0.4265 (3)	0.8818 (3)	0.0202 (8)
H13A	0.494049	0.468284	0.915941	0.030*
H13B	0.461749	0.380391	0.836491	0.030*
H13C	0.410440	0.387788	0.930686	0.030*
C14	0.1515 (3)	0.6516 (3)	0.8823 (3)	0.0240 (8)
H14A	0.089726	0.611819	0.878682	0.036*
H14B	0.133739	0.717377	0.851819	0.036*
H14C	0.185648	0.660502	0.951851	0.036*
O1W	0.4628 (3)	0.3273 (2)	0.5431 (2)	0.0324 (7)
H1W	0.457 (5)	0.384 (2)	0.574 (4)	0.049*
H2W	0.463 (5)	0.341 (5)	0.4808 (15)	0.049*

The title compound was synthesized by dissolving 0.18 g (1 mmol) theophylline (180.16 g/mol) and 0.14 $PtCl_4$ (0.5 mmol) in 1 mL concentrated hydrochloric acid. Short-time warming until both components were dissolved, yielded a yellow/orange solution. From the aforementioned solution a large number of block crystals grew upon slow cooling to room temperature within minutes.

The Raman spectra were measured using a Bruker MULTIRAM spectrometer (Nd: YAG-laser at 1064 nm; InGaAs detector) with an apodized resolution of 8 cm^{-1} in the region of 4000–70 cm^{-1}.

2 Experimental details

A single crystal of the title compound was directly selected from the mother liquor and rapidly transferred to the Xcalibur four-circle diffractometer equipped with an EOS detector.[2] An absorption correction (Gaussian method) was applied.[2] The structure solution and the refinement were successfully carried out using the SHELX program system.[3–5] Pseudosymmetry is present in this structure, as the complex $[PtCl_6]^{2-}$ anions almost occupy positions that meet the conditions of a higher symmetry (right part of the figure).[6,7]

All hydrogen atoms were seen in the Fourier map after all non-hydrogen atoms were located. C-bound hydrogen atoms were included using a riding model. Coordinates of nitrogen- and oxygen bound atoms were refined using distance restraints and individually refined U_{iso} parameters.

3 Comment

3.1 Introduction

Theophylline is a natural product and was first described by Kossel after its isolation from tea leaves which is responsible for the naming up to now.[8,9] There is still a fundamental interest in this compound, the corresponding solid state phases[10,11] and its co-crystals.[12–15] Nowadays theophylline is often used as pharmaceutical agent due to its effects on the respiratory system.[16–19] We have already shown that methylxanthines like caffeine[20] and especially theophylline[21–24] are excellent tectons to construct hydrogen bonded networks. A database check (Cambridge Structural database[25]) showed that not more than about twenty crystal structures have been deposited so far, that contain a theophyllinium cation. From the reaction of theophylline (systematic name:

1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) with hydrochloric in the presence of one half of an equivalent of $PtCl_4$, block crystals of the title compound were obtained.

3.2 Structural comments

The asymmetric unit of the title structure consists of two *N*-protonated theophyllinium cations (TheoH), one hexachloridoplatinate(IV) dianion and one water molecule, which are all located in general positions. Bond lengths within the TheoH cation are all in the expected ranges.[21–24] The same is true for the hexachloridoplatinate(IV) anion.[26] The TheoH cation I (N1···N4) is connected to three neighboring TheoH cations and one water molecule by NH···O hydrogen bonds (see left part of the figure). The TheoH cation II (N5···N8) accepts one OH···O hydrogen bond from a water molecule and it is involved in hydrogen bonds with three neighboring TheoH cations. The water molecule furthermore donates a OH···Cl hydrogen bond (H···Cl: 2.28(2) Å; O···Cl: 3.121(3) Å; O–H···Cl = 160°). These connections create a network of the cationic sub structure with the flat theophyllinium cations to be oriented perpendicular to each other (see the left part of the Figure). It should not go unmentioned that the C–H group of the five membered ring of each TheoH cation forms a weak hydrogen bond to neigboring hexachloridoplatinate(IV) anions (C4···Cl4: 3.530(4) Å; C11···Cl2: 3.574(4) Å) Finally it should be mentioned that there is a halogen-π interaction between the chlorido ligand Cl3 and the N7 atom of the cation II (3.198(3) Å). All the aforementioned intermolecular interactions create a complex hydrogen bonded framework. In the right part of the figure the packing is shown with view along [001]. It is clearly visible that the TheoH cations are oriented almost perpendicular (82.1°) to each other to create the network including the water molecules.

3.3 Raman spectroscopy

There are three very strong signals in the Raman spectrum at 346, 319 and 163 cm^{-1} respectively. These signals must be assigned to the $[[PtCl_6]^{2-}$ anion and perfectly agree with reported spectra.[27,28]

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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