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N,*N*′-bis[(3-hydroxy-4(4*H*)-oxypyran-2-yl)methyl]-*N*,*N*′-dimethylethylene-1,2-diammonium tetrachloridoplatinate(II) dihydrate

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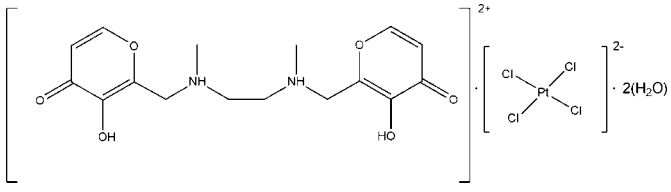
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.005 Å; R factor = 0.023; wR factor = 0.049; data-to-parameter ratio = 17.2.

The title compound $(C_{16}H_{22}N_2O_6)[PtCl_4]\cdot 2H_2O$, shows antiproliferative activity in eight tumor cell lines. The asymmetric unit consists of one solvent water molecule on a general position, and one half of each of the polyammonium cation and the tetrachloridoplatinate(II) anion, both of them located on centers of inversion. In the crystal, the cations are connected *via* hydrogen bonding between the carbonyl O atoms and the hydroxyl H atoms into zigzag chains that elongate in the *c*-axis direction. In addition, the carbonyl O atom is hydrogen-bonded to the water molecule which, in turn, interacts with the $[PtCl_4]^{2-}$ anion. Finally, the chains are linked by $N-H^{+}\cdots Cl$ interactions into a three-dimensional network.

Related literature

For the antitumor activity of maltol (systematic name: 3-hydroxy-2-methyl-4-pyrone) and polyamines, see: Casero & Woster (2001); Liang *et al.* (2006); Murakami *et al.* (2006). For background to the synthesis, solution behaviour, structural properties and biological activity of *N*,*N*′-bis[(3-hydroxy-4-pyron-2-yl)methyl]-*N*,*N*′-dimethylethylendiamine (Malten), see: Amatori *et al.* (2010, 2012).



Experimental

Crystal data

$(C_{16}H_{22}N_2O_6)[PtCl_4]\cdot 2H_2O$
M_r = 711.28
Triclinic, $P\overline{1}$
a = 6.4775 (4) Å
b = 7.0037 (4) Å
c = 13.1628 (8) Å
α = 88.810 (5)°
β = 87.033 (5)°
γ = 71.927 (6)°
V = 566.92 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 6.71 mm^{-1}
T = 150 K
0.32 × 0.22 × 0.20 mm

Data collection

Oxford Diffraction Xcalibur3 diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction 2009)
T_{min} = 0.164, T_{max} = 0.262
9431 measured reflections
2719 independent reflections
2694 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.049
S = 1.02
2719 reflections
158 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.44 e Å^{-3}
$\Delta\rho_{min}$ = −1.14 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···O2^{i}	0.73 (4)	1.98 (4)	2.655 (4)	154 (4)
O1*W*—H1*WB*···O2^{ii}	0.79 (5)	2.07 (5)	2.853 (4)	171 (5)
O1*W*—H1*WA*···Cl2	0.84 (5)	2.45 (5)	3.282 (3)	174 (5)
N1—H1*N*···Cl1^{iii}	0.74 (4)	2.79 (4)	3.380 (3)	139 (4)
N1—H1*N*···Cl1^{iv}	0.74 (4)	2.79 (4)	3.362 (3)	136 (4)

Symmetry codes: (i) $-x+2, -y+1, -z$; (ii) $-x+2, -y, -z$; (iii) $-x+2, -y+1, -z+1$; (iv) $x-1, y+1, z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PARST97* (Nardelli, 1995).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2294).

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supplementary materials

Acta Cryst. (2012). E**68**, m1323–m1324 [doi:10.1107/S1600536812040949]

N,*N*′-bis[(3-hydroxy-4(4*H*)-oxypyran-2-yl)methyl]-*N*,*N*′-dimethylethylene-1,2-diammonium tetrachloridoplatinate(II) dihydrate

Vieri Fusi, Luca Giorgi, Eleonora Macedi, Paola Paoli and Patrizia Rossi

Comment

Maltol (3-hydroxy-2-methyl-4-pyrone) is a natural compound, which exhibits interesting antineoplastic activities (Murakami *et al.*, 2006). At the same time, linear polyamines are also known antitumor agents (Liang *et al.*, 2006; Casero & Woster, 2001). For these reasons we synthesized and studied compound *N*,*N*′-bis((3-hydroxy-4-pyron-2-yl)methyl)-*N*,*N*′-dimethylethylendiamine (Malten) coupling two Maltol units to an aliphatic diamine. Malten has shown antiproliferative activity in eight tumor cell lines (Amatori *et al.*,2010; Amatori *et al.*, 2012). In the asymmetric unit of the title compound half of the polyammonium cation $[H_2Malten]^{2+}$ and of the tetrachloroplatinate(II) counterion are present, together with a crystallization water molecule. The two halves of each ion are related by a center of symmetry (Fig. 1). The $[H_2Malten]^{2+}$ polyammonium chain, which joins the two aromatic rings, has an all-*trans* conformation and defines a plane which forms an angle of 65.4 (2)° with each of them. In the crystal lattice the $[H_2Malten]^{2+}$ cations are each linked by two pairs of complementary O—H···O hydrogen bonds into centrosymmetric dimers, which are further linked into chains along the *c* axis (Fig. 2 and Table 1). Moreover, the carbonyl O atom (O2) is H-bonded to the lattice water molecule, which is also linked to the $(PtCl_4)^{2-}$ anion by O—H···Cl interactions. Finally, the cations and anions are linked by N—H^+···Cl interactions.

Experimental

Malten·2$HClO_4$ was dissolved in H_2O, K_2PtCl_4 was added and the pH adjusted to 3. Crystals suitable for X-ray analysis formed in one day at room temperature.

Refinement

The O—H and N—H H atoms were located in the Fourier difference map and refined with varying coordinates isotropic. The C—H H atoms were introduced in calculated position and refined isotropic with U_{iso}(H) 1.2 times U_{eq}(C) (1.5 for methyl H atoms).

Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction 2009); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PARST97* (Nardelli, 1995).

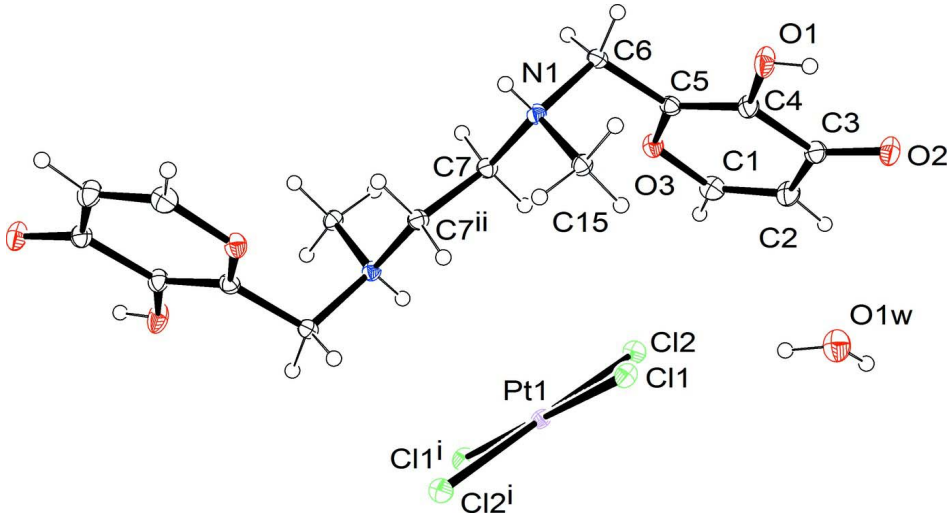

Figure 1

Crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 30% probability level. Symmetry codes: i) = -*x* + 2, -*y*, -*z* + 1; ii) = -*x* + 1, -*y* + 1, -*z* + 1.

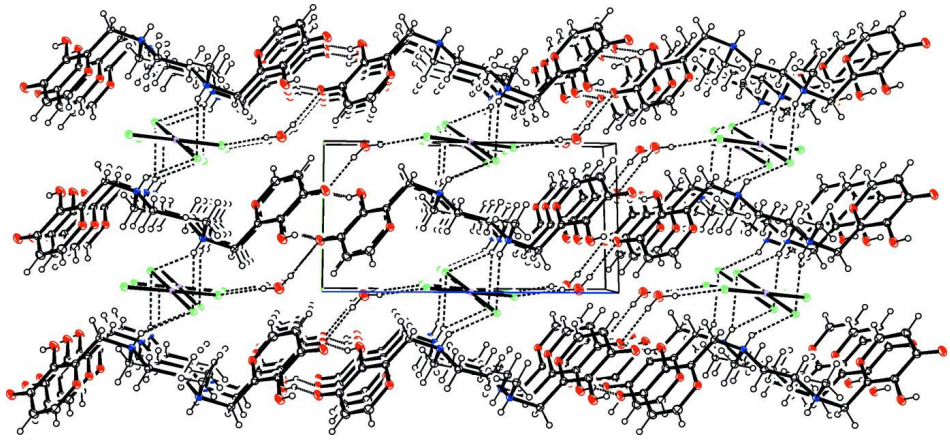

Figure 2

Crystal structure of the title compound with view along the *a* axis. Intermolecular hydrogen bonding is shown as dashed lines.

N,*N*′-bis[(3-hydroxy-4(4*H*)-oxypyran-2-yl)methyl]-*N*, *N*′-dimethylethylene-1,2-diammonium tetrachloridoplatinate(II) dihydrate

Crystal data

$(C_{16}H_{22}N_2O_6)[PtCl_4]\cdot 2H_2O$
$M_r = 711.28$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.4775\ (4)$ Å
$b = 7.0037\ (4)$ Å
$c = 13.1628\ (8)$ Å
$\alpha = 88.810\ (5)°$
$\beta = 87.033\ (5)°$
$\gamma = 71.927\ (6)°$
$V = 566.92\ (6)$ Å^3
$Z = 1$
$F(000) = 346$
$D_x = 2.083$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7279 reflections
$\theta = 4.1–29.2°$
$\mu = 6.71$ mm^{-1}

T = 150 K
Prismatic, light yellow

0.32 × 0.22 × 0.20 mm

Data collection

Oxford Diffraction Xcalibur3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.4547 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction 2009)
T_{min} = 0.164, T_{max} = 0.262

9431 measured reflections
2719 independent reflections
2694 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 29.3°, θ_{min} = 4.1°
h = −8→8
k = −9→9
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.049
S = 1.02
2719 reflections
158 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.44 e Å^{-3}
$\Delta\rho_{min}$ = −1.14 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Pt1	1.0000	0.0000	0.5000	0.01531 (6)
Cl1	1.25762 (12)	0.12554 (11)	0.42237 (6)	0.01926 (15)
Cl2	0.82520 (13)	0.02992 (11)	0.34889 (6)	0.02098 (16)
O1	0.8029 (5)	0.6477 (4)	0.1284 (2)	0.0298 (6)
O2	0.8598 (4)	0.3386 (4)	−0.00821 (17)	0.0278 (5)
O3	0.3953 (4)	0.4312 (3)	0.22157 (16)	0.0218 (5)
N1	0.5757 (4)	0.6487 (4)	0.3876 (2)	0.0169 (5)
C1	0.4294 (6)	0.2757 (5)	0.1565 (3)	0.0261 (7)
H1	0.3424	0.1924	0.1649	0.031*
C2	0.5823 (6)	0.2365 (5)	0.0809 (3)	0.0263 (7)
H2	0.5998	0.1263	0.0394	0.032*
C3	0.7197 (5)	0.3601 (5)	0.0625 (2)	0.0224 (7)
C4	0.6815 (5)	0.5228 (5)	0.1358 (2)	0.0205 (6)

C5	0.5256 (5)	0.5510 (5)	0.2108 (2)	0.0187 (6)
C6	0.4731 (5)	0.7161 (5)	0.2869 (2)	0.0190 (6)
H6A	0.3166	0.7682	0.2984	0.023*
H6B	0.5233	0.8244	0.2595	0.023*
C7	0.4568 (5)	0.5266 (5)	0.4470 (2)	0.0181 (6)
H7A	0.4719	0.4039	0.4103	0.022*
H7B	0.3033	0.6018	0.4532	0.022*
C15	0.8152 (5)	0.5442 (5)	0.3735 (2)	0.0181 (6)
H15A	0.8821	0.6290	0.3351	0.027*
H15B	0.8389	0.4207	0.3376	0.027*
H15C	0.8778	0.5159	0.4388	0.027*
O1W	1.1440 (5)	−0.0251 (4)	0.1423 (2)	0.0343 (6)
H1N	0.559 (6)	0.742 (6)	0.417 (3)	0.028 (11)*
H1O	0.888 (7)	0.623 (6)	0.088 (3)	0.024 (11)*
H1WA	1.062 (9)	−0.020 (8)	0.194 (4)	0.059 (16)*
H1WB	1.128 (7)	−0.105 (7)	0.104 (3)	0.040 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.01339 (9)	0.01279 (9)	0.02021 (9)	−0.00476 (6)	0.00072 (6)	−0.00306 (6)
Cl1	0.0169 (4)	0.0185 (4)	0.0241 (4)	−0.0084 (3)	0.0032 (3)	−0.0031 (3)
Cl2	0.0223 (4)	0.0208 (4)	0.0219 (4)	−0.0092 (3)	−0.0040 (3)	−0.0009 (3)
O1	0.0347 (15)	0.0327 (14)	0.0275 (13)	−0.0200 (12)	0.0137 (12)	−0.0108 (11)
O2	0.0310 (14)	0.0309 (13)	0.0237 (12)	−0.0136 (11)	0.0074 (10)	−0.0087 (10)
O3	0.0236 (12)	0.0246 (12)	0.0197 (11)	−0.0112 (10)	−0.0005 (9)	−0.0021 (9)
N1	0.0197 (14)	0.0154 (13)	0.0168 (12)	−0.0074 (11)	0.0002 (10)	−0.0020 (10)
C1	0.0284 (19)	0.0261 (18)	0.0283 (17)	−0.0143 (15)	−0.0056 (15)	0.0001 (14)
C2	0.0310 (19)	0.0242 (17)	0.0271 (17)	−0.0134 (15)	0.0003 (15)	−0.0062 (13)
C3	0.0251 (18)	0.0222 (16)	0.0196 (15)	−0.0064 (13)	−0.0035 (13)	−0.0020 (12)
C4	0.0236 (17)	0.0208 (16)	0.0191 (15)	−0.0096 (13)	−0.0003 (13)	−0.0030 (12)
C5	0.0218 (16)	0.0177 (15)	0.0172 (14)	−0.0065 (13)	−0.0041 (13)	0.0014 (11)
C6	0.0220 (16)	0.0170 (15)	0.0170 (14)	−0.0047 (12)	−0.0027 (12)	0.0018 (11)
C7	0.0171 (15)	0.0176 (15)	0.0200 (15)	−0.0060 (12)	0.0006 (12)	0.0009 (11)
C15	0.0158 (15)	0.0189 (15)	0.0194 (14)	−0.0051 (12)	0.0007 (12)	−0.0008 (11)
O1W	0.0380 (17)	0.0383 (16)	0.0315 (15)	−0.0187 (13)	−0.0001 (13)	−0.0064 (12)

Geometric parameters (Å, º)

Pt1—Cl1^{i}	2.3018 (8)	C2—C3	1.431 (5)
Pt1—Cl1	2.3018 (8)	C2—H2	0.9300
Pt1—Cl2^{i}	2.3132 (7)	C3—C4	1.462 (4)
Pt1—Cl2	2.3132 (7)	C4—C5	1.348 (5)
O1—C4	1.345 (4)	C5—C6	1.491 (4)
O1—H1O	0.73 (4)	C6—H6A	0.9700
O2—C3	1.243 (4)	C6—H6B	0.9700
O3—C1	1.356 (4)	C7—C7^{ii}	1.526 (6)
O3—C5	1.363 (4)	C7—H7A	0.9700
N1—C15	1.499 (4)	C7—H7B	0.9700
N1—C7	1.501 (4)	C15—H15A	0.9600

N1—C6	1.514 (4)	C15—H15B	0.9600
N1—H1N	0.74 (4)	C15—H15C	0.9600
C1—C2	1.337 (5)	O1W—H1WA	0.84 (5)
C1—H1	0.9300	O1W—H1WB	0.79 (5)
Cl1^{i}—Pt1—Cl1	180.00 (4)	O1—C4—C3	119.7 (3)
Cl1^{i}—Pt1—Cl2^{i}	90.28 (3)	C5—C4—C3	121.2 (3)
Cl1—Pt1—Cl2^{i}	89.72 (3)	C4—C5—O3	121.9 (3)
Cl1^{i}—Pt1—Cl2	89.72 (3)	C4—C5—C6	124.4 (3)
Cl1—Pt1—Cl2	90.28 (3)	O3—C5—C6	113.7 (3)
Cl2^{i}—Pt1—Cl2	180.0	C5—C6—N1	112.9 (2)
C4—O1—H1O	115 (3)	C5—C6—H6A	109.0
C1—O3—C5	118.6 (3)	N1—C6—H6A	109.0
C15—N1—C7	113.3 (2)	C5—C6—H6B	109.0
C15—N1—C6	111.5 (2)	N1—C6—H6B	109.0
C7—N1—C6	110.8 (2)	H6A—C6—H6B	107.8
C15—N1—H1N	109 (3)	N1—C7—C7^{ii}	111.9 (3)
C7—N1—H1N	107 (3)	N1—C7—H7A	109.2
C6—N1—H1N	106 (3)	C7^{ii}—C7—H7A	109.2
C2—C1—O3	123.1 (3)	N1—C7—H7B	109.2
C2—C1—H1	118.5	C7^{ii}—C7—H7B	109.2
O3—C1—H1	118.5	H7A—C7—H7B	107.9
C1—C2—C3	121.5 (3)	N1—C15—H15A	109.5
C1—C2—H2	119.2	N1—C15—H15B	109.5
C3—C2—H2	119.2	H15A—C15—H15B	109.5
O2—C3—C2	125.6 (3)	N1—C15—H15C	109.5
O2—C3—C4	120.7 (3)	H15A—C15—H15C	109.5
C2—C3—C4	113.7 (3)	H15B—C15—H15C	109.5
O1—C4—C5	119.1 (3)	H1WA—O1W—H1WB	109 (5)

Symmetry codes: (i) −*x*+2, −*y*, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O2^{iii}	0.73 (4)	1.98 (4)	2.655 (4)	154 (4)
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N1—H1*N*···Cl1^{v}	0.74 (4)	2.79 (4)	3.380 (3)	139 (4)
N1—H1*N*···Cl1^{vi}	0.74 (4)	2.79 (4)	3.362 (3)	136 (4)

Symmetry codes: (iii) −*x*+2, −*y*+1, −*z*; (iv) −*x*+2, −*y*, −*z*; (v) −*x*+2, −*y*+1, −*z*+1; (vi) *x*−1, *y*+1, *z*.