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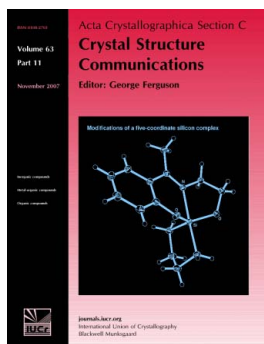
Eleonora Freire, Griselda Polla and Ricardo Baggio

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Aripiprazole salts. III. Bis(aripiprazolium) oxalate–oxalic acid (1/1)

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The asymmetric unit of the title salt [systematic name: bis(4-(2,3-dichlorophenyl)-1-{4-[(2-oxo-1,2,3,4-tetrahydroquinolin-7-yl)oxy]butyl}piperazin-1-ium) oxalate–oxalic acid (1/1)], $2C_{23}H_{28}Cl_2N_3O_2{}^+ \cdot C_2O_4{}^{2-} \cdot C_2H_2O_4$, consists of one protonated aripiprazole unit (HArip$^+$), half an oxalate dianion and half an oxalic acid molecule, the latter two lying on inversion centres. The conformation of the HArip$^+$ cation differs from that in

organized into planar ribbons parallel to (01$\bar{2}$). The oxalate anions and oxalic acid molecules form hydrogen-bonded chains running along [010], which 'pierce' the planar ribbons, interacting with them through a number of stronger N—H···O and weaker C—H···O hydrogen bonds, forming a three-dimensional network.

Comment

Aripiprazole (Arip) is an antipsychotic drug, perhaps the most characteristic representative of a modern family of atypical antipsychotics, with a different therapeutic activity to those of the classical antipsychotic drugs in standard use.
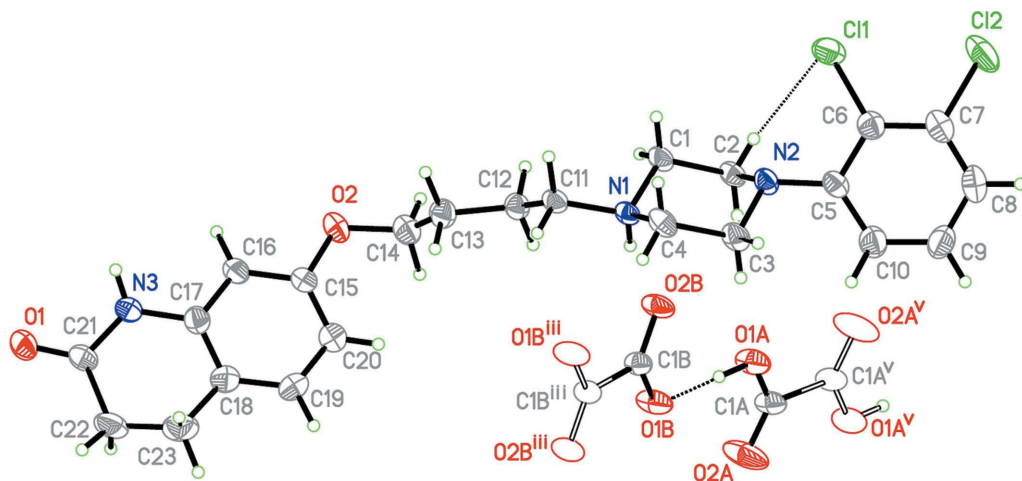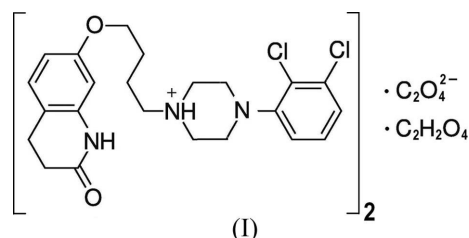

The drug crystallizes in a number of polymorphic forms, some of which have been described in the patent literature (*e.g.* Brand *et al.*, 2007; Pongo *et al*, 2009: the structural information therein is far from complete and the main source

Figure 1
A displacement ellipsoid plot of (I), drawn at the 40% probability probability level, showing the asymmetric unit (in full ellipsoids and bonds). The Arip$^+$ intramolecular hydrogen bond and the O—H···O interaction defining the anionic chain are shown with broken lines. [Symmetry codes: (iii) $-x + 2$, $-y + 1$, $-z + 1$; (v) $-x + 2$, $-y + 2$, $-z + 1$.]

other reported salts and resembles more the conformation of neutral Arip units in reported polymorphs and solvates. The intermolecular interaction linking HArip$^+$ cations is also similar to those in reported Arip compounds crystallizing in the space group $P\bar{1}$, with head-to-head N—H···O hydrogen bonds generating centrosymmetric dimers, which are further

of structural information on aripiprazole consists of a paper by Tessler & Goldberg (2006), complemented by two excellent works by Braun *et al.* (2009*a,b*). In the first of the Braun *et al.* papers, a number of different polymorphic forms of the Arip molecule are reported, while in the second paper, different solvates (ethanol, methanol, 1,2-dichloroethane, water *etc.*) are studied.

The situation with AripH$^+$ salts is different and even if they have been mentioned in the patent literature, no structures
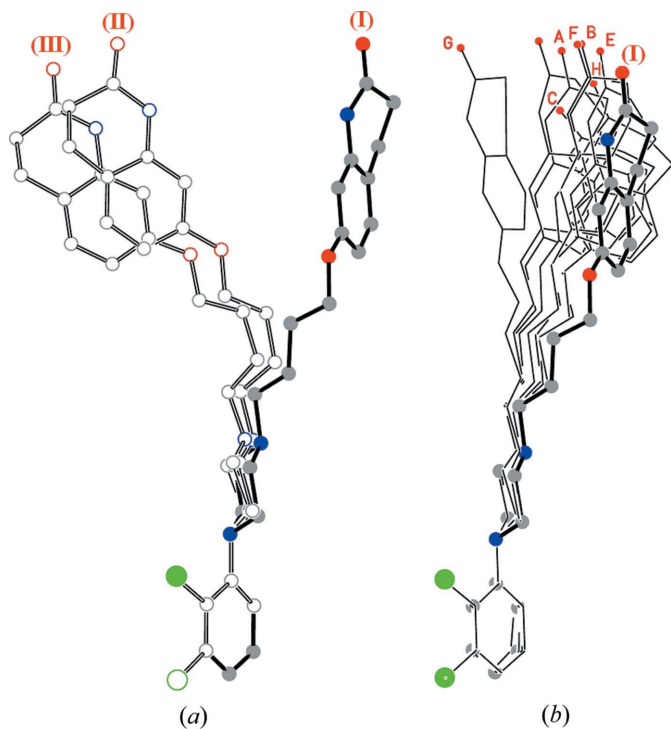
Figure 2
A comparison of the stereodisposition of the present structure [(I), bold] with (a) reported Arip⁺ salts and (b) different solvates (**A** and **B**; Braun *et al.*, 2009*a*) and polymorphs (**C** to **H**; Braun *et al.*, 2009*b*). Compound codes: (II) is the nitrate salt, (III) is the perchlorate salt, **A** is an ethanol solvate (CSD refcode MELFEP01), and **B**, **C**, **D/E**, **F/G** and **H** are methanol solvates (CSD refcodes MELFOZ01 to MELFIT05).

had been reported until very recently when we presented the crystal structures of aripiprazole nitrate, hereafter (II) (Freire *et al.*, 2012*a*), and aripiprazole perchlorate, hereafter (III) (Freire *et al.*, 2012*b*). As discussed in these original reports, the protonated state of Arip results in interesting structural properties caused by N—H donor behaviour, which prompted us to proceed with the analysis of other AripH⁺ salts. We present here the results for a third AripH⁺ salt, *viz.* bis(aripiprazolium) oxalate–oxalic acid (1/1), 2(AripH⁺)·Oxal²⁻·H₂Oxal, (I) (H₂Oxal is oxalic acid).

The asymmetric unit of (I) consists of one protonated aripiprazole unit (HArip⁺), half an oxalate dianion and half an oxalic acid molecule, the latter two lying on inversion centres (Fig. 1).

The AripH⁺ cation in (I) is similar to those in (II) and (III) with respect to bond lengths and angles. However, the conformation of the cation in (I) differs from that of the cations in (II) and (III), mainly in the central region, as shown in Table 1 and Fig. 2(*a*). In fact, the shape of the cation in (I) resembles more those of the neutral Arip units found in the polymorphs and solvates described by Braun *et al.* (2009*a*,*b*) (Fig. 2*b*).

As usual in this type of structure, the most interesting features are the noncovalent interactions defining the spatial arrangement. In (I), only hydrogen bonds are present (Table 2) and neither π–π nor C—H···π contacts are observed despite the presence of many aromatic rings.

The first entry in Table 2 corresponds to an intramolecular C—H···Cl contact, characteristic for the 4-(2,3-dichloro-
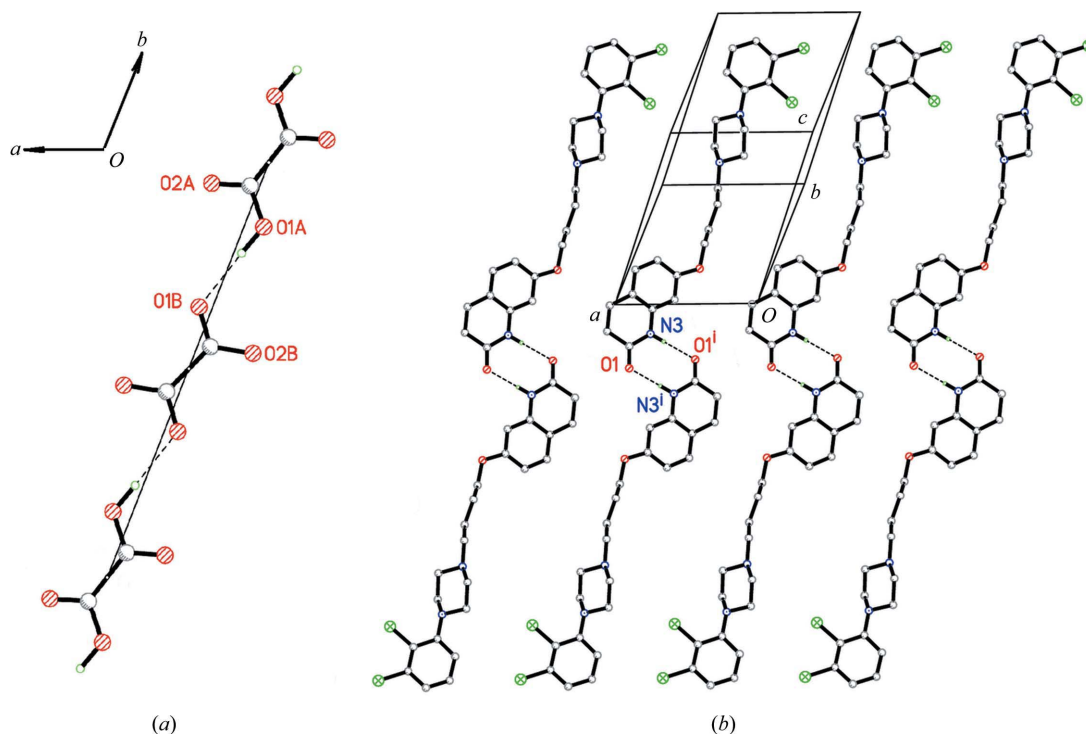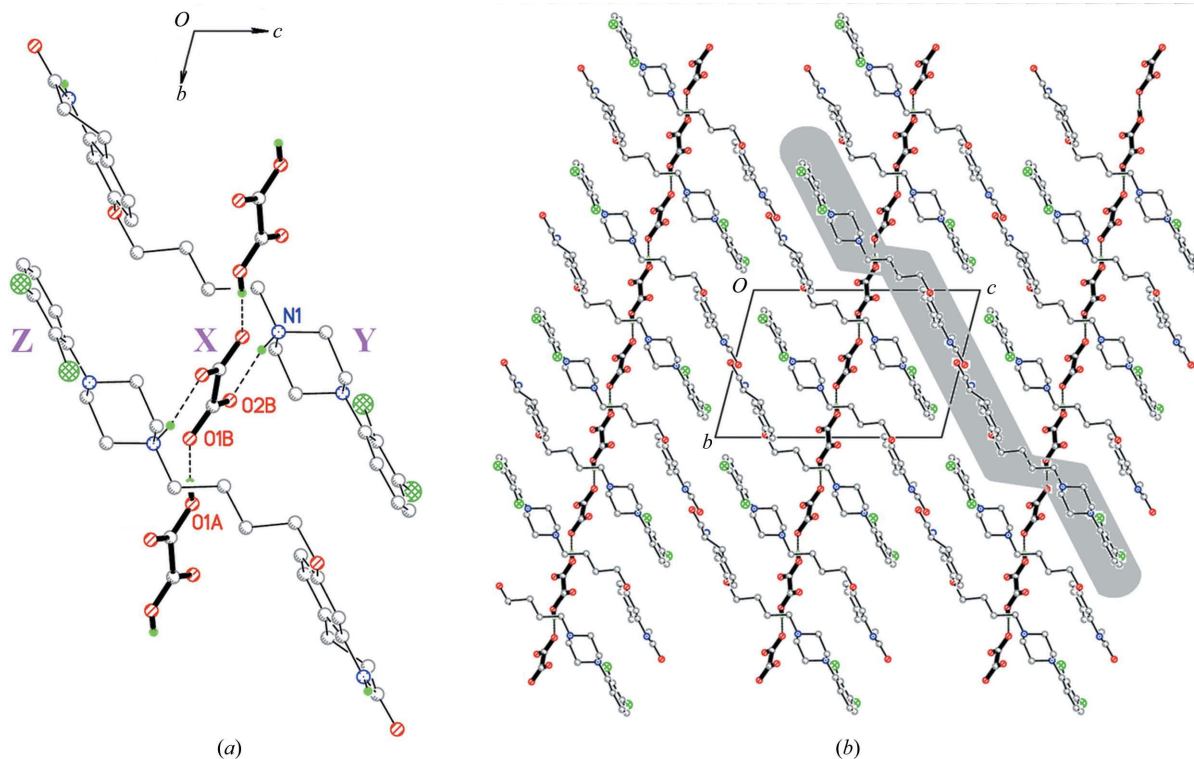

Figure 3
The two different substructures in (I), showing (a) the anionic oxalate chain and (b) an assembly of dimers of Arip⁺ cations. [Symmetry code: (i) −x + 1, −y − 1, −z.]

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Figure 4
Packing diagrams of (I), viewed down *a*, showing (*a*) a detailed view of the N—H···O interaction linking both substructures, and (*b*) the relative orientation of both substructures. The anionic chains (in bold) run in the plane of the figure, while the strand of cationic dimers are shown in projection (one of them in a shadowed background).

phenyl)piperazin-1-yl group in all reported Arip derivatives.

The next two entries in Table 2 define two well differentiated supramolecular substructures, *viz.* an anionic chain, comprising oxalate anions and oxalic acid molecules, and a ribbon of AripH$^+$ cation dimers. The first of these is an (Oxal^{2-}···H$_2$Oxal)$_n$ chain parallel to [010] (Fig. 3*a*), generated by an O—H···O hydrogen bond. The one-dimensional structure intersects the (010) crystallographic plane at $x = 1$, $z = \frac{1}{2}$ and embeds the inversion centres at $y = \frac{1}{2}$ and $y = 0,1$. These chains are well separated from each other by [100] and [001] translations.
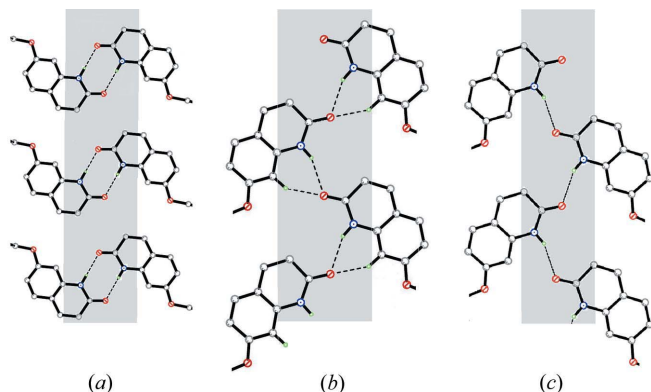

Figure 5
The three different synthons found for the intermolecular Arip$^+$···Arip$^+$ interactions in (*a*) (I), (*b*) (II) and (*c*) (III).

The elemental building block of the cationic substructure is a head-to-head dimer. Cations in the dimer are linked by an N—H···O hydrogen bond (Table 2, third entry), which is characteristic of many Arip structures (see below). The elongated dimers thus formed [tail-to-tail C···C distance = 37.11 (2) Å] are oriented approximately along [021] and form ribbons parallel to (01$\bar{2}$) by translation along the *a* axis (Fig. 3*b*).

The ribbons are linked into a three-dimensional structure through a number of O—H···O, N—H···O and C—H···O hydrogen bonds (Table 2, entries 4–8) mediated by the anionic chains. The main agent is the N—H···O hydrogen bond (entry 4 in Table 2) and the way in which it acts is shown in detail in Fig. 4(*a*); the three components shown therein (the anionic chain and two AripH$^+$ cations) appear parallel to the projection plane but at different heights, *X* being in the plane, while *Y* and *Z* lie below/above by approximately half of an *a* translation. Thus, the AripH$^+$ ribbons are diagonally 'pierced' by the anionic chains, which generates the three-dimensional network shown in Fig. 4(*b*).

The N—H···O hydrogen bond between the amide groups of adjacent AripH$^+$ cations (Table 2, third entry), which is characteristic of most of the reported Arip variants, is quite interesting. In all the Arip structures where this interaction exists, it produces one of two well defined supramolecular synthons, *viz.* either a *C*(4) catemer or a centrosymmetric diamide $R_2^2(8)$ ring (Bernstein *et al.*, 1995). The former synthon (Figs. 5*b* and 5*c*) appears in structures crystallizing in

space groups with translation symmetry elements (2_1 axis, glide planes) translating along a short unit-cell dimension, and which serves for the 'threading' of the chain. The second (more frequent) synthon generates centrosymmetric dimers (Fig. 5a) and usually occurs in Arip variants crystallizing in the space group $P\bar{1}$.

In (II) and (III), the N—H···O hydrogen bond connecting adjacent groups gives rise to two only slightly different synthons, leading to almost identical $C(4)$ substructures differing by the presence, in structure (II) [or its absence in structure (III)], of a secondary C—H···O interaction (Figs. 5b and 5c). The resulting catemers are related by quite different translation symmetry operations, viz. the $Pbca$ a-glide plane in (II) and the $P2_1/c$ 2_1-axis in (III). The title salt (I) crystallizes in the space group $P\bar{1}$, with no translation elements, and presents the usual $R_2^2(8)$ hydrogen-bonded ring (Fig. 5a).

Thus, all three known Arip$^+$ salts, viz. (I), (II) and (III), adhere to this empirical rule linking symmetry and synthon character. However, the reasons for a given salt 'choosing' one or the other are for the moment unclear, and the speculation regarding the possible pre-eminence of the patterns found in (II) and (III), made in some of our previous discussions (Freire et al., 2012b), now seems unsupported. Further work on the subject is in progress.

Experimental

Aripiprazole (1.5×10^{-4} mol, 67 mg) was dissolved in a boiling mixture of methanol (5 ml) and acetone (0.5 ml). When dissolution was considered complete, an excess of oxalic acid was added and the resulting solution was left to cool slowly. Very good quality crystals of (I) in the form of colourless prisms appeared within a few hours and were used as obtained without further recrystallization.

Crystal data

$2C_{23}H_{28}Cl_2N_3O_2{}^+ \cdot C_2O_4{}^{2-} \cdot C_2H_2O_4$	$\gamma = 109.767\,(8)°$
$M_r = 1076.82$	$V = 1288.2\,(2)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.9609\,(7)$ Å	Mo $K\alpha$ radiation
$b = 11.2732\,(9)$ Å	$\mu = 0.30$ mm^{-1}
$c = 15.8323\,(11)$ Å	$T = 294$ K
$\alpha = 101.794\,(6)°$	$0.60 \times 0.15 \times 0.08$ mm
$\beta = 95.410\,(7)°$	

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer	16111 measured reflections
	6079 independent reflections
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)	3903 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.058$
$T_{min} = 0.95$, $T_{max} = 0.98$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.160$	
$S = 1.04$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
6079 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}
337 parameters	
3 restraints	

All H atoms were initially found in difference Fourier maps. H atoms bonded to heteroatoms were refined isotropically, with N—H

Table 1
Comparison of selected torsion angles (°) for (I), (II) and (III).

	(I) (this work)	(II) (Freire et al., 2012a)	(III) (Freire et al., 2012b)
C2—N2—C5—C6	74.3 (2)	161.37 (17)	160.4 (2)
C2—N2—C5—C10	−104.9 (2)	−15.3 (2)	−15.5 (4)
C3—N2—C5—C6	−158.83 (19)	−67.8 (2)	−66.6 (3)
C3—N2—C5—C10	21.9 (3)	115.59 (17)	117.6 (2)
C1—N1—C11—C12	69.2 (2)	152.38 (14)	157.6 (2)
C4—N1—C11—C12	−167.23 (19)	−84.54 (17)	−79.0 (3)
N1—C11—C12—C13	163.53 (19)	−169.64 (14)	−172.7 (2)
C11—C12—C13—C14	−170.8 (2)	−69.0 (2)	−71.0 (3)
C15—O2—C14—C13	−77.1 (3)	−172.12 (14)	−167.47 (19)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2B···Cl1	0.97	2.62	3.224 (2)	120
O1A—H1A···O1B	0.86 (1)	1.71 (1)	2.561 (2)	174 (3)
N3—H3N···O1^{i}	0.86 (1)	2.01 (1)	2.866 (3)	173 (3)
N1—H1N···O2B	0.85 (1)	1.90 (1)	2.730 (2)	164 (2)
C1—H1C···O2B^{ii}	0.97	2.49	3.272 (2)	137
C2—H2A···O2B	0.97	2.48	3.197 (3)	131
C11—H11B···O2A^{iii}	0.97	2.41	3.368 (3)	171
C13—H13B···O2A^{iv}	0.97	2.43	3.262 (3)	143

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

and O—H bond-length restraints of 0.85 (1) Å. All other H atoms were placed in geometrically optimized positions, with C—H = 0.93 (aromatic) or 0.97 Å (methylene) and with U_{iso}(H) = $1.2U_{eq}$(C).

Data collection: CrysAlis PRO (Oxford Diffraction, 2009); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

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supplementary materials

Aripiprazole salts. III. Bis(aripiprazolium) oxalate–oxalic acid (1/1)

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Bis(4-(2,3-dichlorophenyl)-1-{4-[(2-oxo-1,2,3,4-tetrahydroquinolin-7- yl)oxy]butyl}piperazin-1-ium); oxalate; oxalic acid

Crystal data

$2C_{23}H_{28}Cl_2N_3O_2{}^+ \cdot C_2O_4{}^{2-} \cdot C_2H_2O_4$	$Z = 1$
$M_r = 1076.82$	$F(000) = 564$
Triclinic, $P\bar{1}$	$D_x = 1.388$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.9609 (7)$ Å	Cell parameters from 3032 reflections
$b = 11.2732 (9)$ Å	$\theta = 3.8–29.1°$
$c = 15.8323 (11)$ Å	$\mu = 0.30$ mm^{-1}
$\alpha = 101.794 (6)°$	$T = 294$ K
$\beta = 95.410 (7)°$	Plate, colourless
$\gamma = 109.767 (8)°$	$0.60 \times 0.15 \times 0.08$ mm
$V = 1288.2 (2)$ Å^3	

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer	16111 measured reflections
Radiation source: fine-focus sealed tube	6079 independent reflections
Graphite monochromator	3903 reflections with $I > 2\sigma(I)$
ω scans, thick slices	$R_{int} = 0.058$
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	$\theta_{max} = 29.2°$, $\theta_{min} = 3.7°$
	$h = -10\rightarrow10$
	$k = -15\rightarrow15$
$T_{min} = 0.95$, $T_{max} = 0.98$	$l = 0\rightarrow21$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.057$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.160$	
$S = 1.04$	H atoms treated by a mixture of independent and constrained refinement
6079 reflections	
337 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 0.0853P]$
3 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.32$ e Å^{-3}
	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

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

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

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.24705 (8)	0.54881 (6)	0.79059 (5)	0.0672 (2)
Cl2	0.30443 (12)	0.80669 (8)	0.92693 (5)	0.0900 (3)
O1	0.7228 (2)	−0.50763 (17)	−0.01832 (12)	0.0692 (5)
O2	0.4837 (2)	−0.01643 (16)	0.21786 (11)	0.0608 (5)
N1	0.6067 (2)	0.33562 (15)	0.59188 (10)	0.0342 (4)
H1N	0.687 (2)	0.3920 (18)	0.5745 (14)	0.052 (7)*
N2	0.5850 (2)	0.51519 (16)	0.74493 (11)	0.0403 (4)
N3	0.6600 (3)	−0.35294 (19)	0.07242 (13)	0.0512 (5)
H3N	0.5451 (16)	−0.390 (3)	0.0532 (18)	0.082 (9)*
C1	0.4556 (3)	0.3858 (2)	0.59495 (13)	0.0406 (5)
H1B	0.3560	0.3270	0.6146	0.049*
H1C	0.4118	0.3896	0.5366	0.049*
C2	0.5193 (3)	0.51949 (19)	0.65630 (13)	0.0408 (5)
H2A	0.6161	0.5791	0.6356	0.049*
H2B	0.4201	0.5511	0.6575	0.049*
C3	0.7385 (3)	0.4717 (2)	0.74336 (14)	0.0485 (5)
H3A	0.7836	0.4700	0.8020	0.058*
H3B	0.8359	0.5320	0.7234	0.058*
C4	0.6791 (3)	0.3365 (2)	0.68233 (14)	0.0470 (5)
H4A	0.7815	0.3084	0.6811	0.056*
H4B	0.5862	0.2756	0.7042	0.056*
C5	0.6137 (3)	0.6317 (2)	0.80828 (14)	0.0435 (5)
C6	0.4646 (3)	0.6587 (2)	0.83523 (14)	0.0478 (5)
C7	0.4896 (4)	0.7729 (2)	0.89606 (15)	0.0570 (6)
C8	0.6596 (4)	0.8628 (3)	0.93203 (17)	0.0690 (8)
H8	0.6752	0.9393	0.9731	0.083*
C9	0.8076 (4)	0.8375 (3)	0.90613 (18)	0.0720 (8)
H9	0.9239	0.8978	0.9299	0.086*
C10	0.7856 (3)	0.7247 (2)	0.84598 (16)	0.0586 (6)
H10	0.8875	0.7098	0.8299	0.070*
C11	0.5517 (3)	0.20455 (18)	0.52984 (13)	0.0394 (5)
H11A	0.4421	0.1461	0.5430	0.047*
H11B	0.6464	0.1698	0.5382	0.047*
C12	0.5183 (3)	0.20936 (19)	0.43575 (13)	0.0441 (5)
H12A	0.6125	0.2846	0.4268	0.053*
H12B	0.4029	0.2192	0.4229	0.053*
C13	0.5163 (3)	0.0868 (2)	0.37300 (14)	0.0506 (6)
H13A	0.6230	0.0689	0.3914	0.061*
H13B	0.4101	0.0133	0.3748	0.061*
C14	0.5133 (4)	0.1022 (2)	0.28102 (15)	0.0548 (6)

H14A	0.4181	0.1340	0.2664	0.066*
H14B	0.6279	0.1669	0.2779	0.066*
C15	0.6264 (3)	−0.0600 (2)	0.20975 (15)	0.0501 (5)
C16	0.5807 (3)	−0.1784 (2)	0.14990 (14)	0.0472 (5)
H16	0.4620	−0.2221	0.1200	0.057*
C17	0.7105 (3)	−0.2324 (2)	0.13404 (14)	0.0456 (5)
C18	0.8883 (3)	−0.1695 (2)	0.17826 (16)	0.0543 (6)
C19	0.9316 (3)	−0.0503 (3)	0.23817 (18)	0.0665 (7)
H19	1.0497	−0.0068	0.2688	0.080*
C20	0.8014 (4)	0.0060 (3)	0.25359 (17)	0.0635 (7)
H20	0.8332	0.0868	0.2929	0.076*
C21	0.7780 (3)	−0.4032 (2)	0.03771 (16)	0.0545 (6)
C22	0.9744 (3)	−0.3217 (3)	0.06867 (19)	0.0696 (7)
H22A	1.0136	−0.2658	0.0296	0.083*
H22B	1.0429	−0.3787	0.0648	0.083*
C23	1.0195 (3)	−0.2375 (3)	0.1617 (2)	0.0714 (8)
H23A	1.0163	−0.2914	0.2025	0.086*
H23B	1.1414	−0.1731	0.1719	0.086*
C1A	1.0303 (3)	0.94180 (19)	0.48760 (16)	0.0439 (5)
O1A	0.9369 (2)	0.84251 (14)	0.51231 (14)	0.0642 (5)
H1A	0.976 (4)	0.779 (2)	0.503 (2)	0.099 (11)*
O2A	1.1549 (3)	0.94871 (19)	0.45082 (18)	0.0999 (8)
C1B	0.9590 (3)	0.55404 (18)	0.50263 (14)	0.0388 (5)
O1B	1.0421 (2)	0.64998 (13)	0.47545 (12)	0.0586 (5)
O2B	0.8173 (2)	0.53727 (14)	0.53253 (11)	0.0550 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0512 (4)	0.0691 (4)	0.0832 (5)	0.0232 (3)	0.0261 (3)	0.0152 (3)
Cl2	0.1043 (6)	0.0955 (6)	0.0942 (6)	0.0634 (5)	0.0522 (5)	0.0135 (4)
O1	0.0576 (11)	0.0657 (11)	0.0818 (12)	0.0354 (9)	0.0097 (9)	−0.0075 (9)
O2	0.0550 (10)	0.0633 (10)	0.0602 (10)	0.0296 (9)	0.0138 (8)	−0.0084 (8)
N1	0.0358 (9)	0.0322 (9)	0.0416 (9)	0.0179 (8)	0.0122 (7)	0.0128 (7)
N2	0.0422 (10)	0.0434 (10)	0.0400 (9)	0.0248 (8)	0.0048 (8)	0.0063 (7)
N3	0.0419 (11)	0.0493 (11)	0.0594 (12)	0.0212 (10)	0.0059 (10)	0.0008 (9)
C1	0.0396 (11)	0.0466 (12)	0.0424 (11)	0.0262 (10)	0.0057 (9)	0.0089 (9)
C2	0.0436 (12)	0.0423 (11)	0.0446 (11)	0.0262 (10)	0.0096 (9)	0.0096 (9)
C3	0.0498 (13)	0.0559 (14)	0.0471 (12)	0.0329 (11)	0.0016 (10)	0.0086 (10)
C4	0.0556 (13)	0.0524 (13)	0.0472 (12)	0.0353 (11)	0.0099 (10)	0.0162 (10)
C5	0.0482 (13)	0.0449 (12)	0.0422 (11)	0.0234 (11)	0.0091 (10)	0.0099 (9)
C6	0.0521 (13)	0.0490 (13)	0.0484 (12)	0.0236 (11)	0.0133 (10)	0.0149 (10)
C7	0.0760 (18)	0.0610 (15)	0.0486 (13)	0.0404 (14)	0.0243 (13)	0.0130 (12)
C8	0.092 (2)	0.0558 (16)	0.0534 (15)	0.0339 (16)	0.0063 (15)	−0.0082 (12)
C9	0.0643 (18)	0.0616 (17)	0.0717 (18)	0.0186 (14)	−0.0011 (14)	−0.0088 (13)
C10	0.0527 (15)	0.0593 (15)	0.0577 (15)	0.0241 (12)	0.0035 (12)	−0.0012 (11)
C11	0.0404 (11)	0.0310 (10)	0.0507 (12)	0.0155 (9)	0.0151 (9)	0.0113 (9)
C12	0.0519 (13)	0.0368 (11)	0.0470 (12)	0.0198 (10)	0.0138 (10)	0.0096 (9)
C13	0.0605 (15)	0.0380 (12)	0.0556 (14)	0.0187 (11)	0.0217 (12)	0.0100 (10)
C14	0.0646 (16)	0.0531 (14)	0.0513 (14)	0.0269 (12)	0.0189 (12)	0.0100 (11)

C15	0.0442 (13)	0.0518 (13)	0.0489 (13)	0.0145 (11)	0.0135 (10)	0.0038 (10)
C16	0.0410 (12)	0.0523 (13)	0.0453 (12)	0.0172 (10)	0.0107 (10)	0.0044 (10)
C17	0.0478 (13)	0.0458 (12)	0.0409 (12)	0.0177 (11)	0.0064 (10)	0.0058 (9)
C18	0.0421 (13)	0.0564 (14)	0.0598 (14)	0.0154 (11)	0.0073 (11)	0.0100 (11)
C19	0.0422 (14)	0.0678 (17)	0.0682 (17)	0.0075 (13)	−0.0001 (12)	−0.0023 (13)
C20	0.0578 (16)	0.0569 (15)	0.0650 (16)	0.0162 (13)	0.0170 (13)	−0.0027 (12)
C21	0.0509 (14)	0.0568 (15)	0.0621 (15)	0.0294 (12)	0.0118 (12)	0.0109 (12)
C22	0.0489 (15)	0.0772 (18)	0.091 (2)	0.0356 (14)	0.0186 (14)	0.0141 (15)
C23	0.0435 (14)	0.0716 (17)	0.098 (2)	0.0260 (13)	0.0051 (14)	0.0135 (16)
C1A	0.0302 (10)	0.0331 (11)	0.0743 (15)	0.0154 (9)	0.0122 (10)	0.0186 (10)
O1A	0.0530 (10)	0.0318 (8)	0.1244 (16)	0.0217 (8)	0.0391 (10)	0.0339 (9)
O2A	0.0898 (14)	0.0666 (12)	0.200 (3)	0.0566 (11)	0.0992 (16)	0.0747 (14)
C1B	0.0319 (10)	0.0292 (10)	0.0599 (13)	0.0146 (9)	0.0116 (10)	0.0137 (9)
O1B	0.0490 (9)	0.0370 (8)	0.1116 (14)	0.0253 (7)	0.0367 (9)	0.0386 (9)
O2B	0.0483 (9)	0.0413 (8)	0.0963 (13)	0.0279 (7)	0.0361 (9)	0.0322 (8)

Geometric parameters (Å, º)

Cl1—C6	1.730 (2)	C11—C12	1.504 (3)
Cl2—C7	1.731 (3)	C11—H11A	0.9700
O1—C21	1.231 (3)	C11—H11B	0.9700
O2—C15	1.388 (3)	C12—C13	1.522 (3)
O2—C14	1.428 (3)	C12—H12A	0.9700
N1—C4	1.489 (3)	C12—H12B	0.9700
N1—C11	1.493 (2)	C13—C14	1.500 (3)
N1—C1	1.493 (2)	C13—H13A	0.9700
N1—H1N	0.848 (9)	C13—H13B	0.9700
N2—C5	1.414 (3)	C14—H14A	0.9700
N2—C3	1.464 (2)	C14—H14B	0.9700
N2—C2	1.467 (2)	C15—C20	1.372 (3)
N3—C21	1.354 (3)	C15—C16	1.379 (3)
N3—C17	1.405 (3)	C16—C17	1.383 (3)
N3—H3N	0.862 (10)	C16—H16	0.9300
C1—C2	1.504 (3)	C17—C18	1.388 (3)
C1—H1B	0.9700	C18—C19	1.388 (3)
C1—H1C	0.9700	C18—C23	1.503 (3)
C2—H2A	0.9700	C19—C20	1.402 (4)
C2—H2B	0.9700	C19—H19	0.9300
C3—C4	1.518 (3)	C20—H20	0.9300
C3—H3A	0.9700	C21—C22	1.493 (3)
C3—H3B	0.9700	C22—C23	1.516 (4)
C4—H4A	0.9700	C22—H22A	0.9700
C4—H4B	0.9700	C22—H22B	0.9700
C5—C10	1.395 (3)	C23—H23A	0.9700
C5—C6	1.404 (3)	C23—H23B	0.9700
C6—C7	1.381 (3)	C1A—O2A	1.186 (3)
C7—C8	1.369 (4)	C1A—O1A	1.277 (2)
C8—C9	1.381 (4)	C1A—C1A^i	1.536 (4)
C8—H8	0.9300	O1A—H1A	0.858 (10)
C9—C10	1.370 (3)	C1B—O2B	1.235 (2)

C9—H9	0.9300	C1B—O1B	1.246 (2)
C10—H10	0.9300	C1B—C1B[ii]	1.557 (4)
C15—O2—C14	118.99 (18)	H11A—C11—H11B	107.9
C4—N1—C11	112.11 (14)	C11—C12—C13	111.76 (16)
C4—N1—C1	109.18 (15)	C11—C12—H12A	109.3
C11—N1—C1	112.60 (15)	C13—C12—H12A	109.3
C4—N1—H1N	108.5 (15)	C11—C12—H12B	109.3
C11—N1—H1N	110.5 (16)	C13—C12—H12B	109.3
C1—N1—H1N	103.5 (16)	H12A—C12—H12B	107.9
C5—N2—C3	115.85 (16)	C14—C13—C12	110.97 (17)
C5—N2—C2	112.34 (15)	C14—C13—H13A	109.4
C3—N2—C2	109.44 (15)	C12—C13—H13A	109.4
C21—N3—C17	124.7 (2)	C14—C13—H13B	109.4
C21—N3—H3N	121 (2)	C12—C13—H13B	109.4
C17—N3—H3N	114 (2)	H13A—C13—H13B	108.0
N1—C1—C2	110.49 (16)	O2—C14—C13	112.98 (18)
N1—C1—H1B	109.6	O2—C14—H14A	109.0
C2—C1—H1B	109.6	C13—C14—H14A	109.0
N1—C1—H1C	109.6	O2—C14—H14B	109.0
C2—C1—H1C	109.6	C13—C14—H14B	109.0
H1B—C1—H1C	108.1	H14A—C14—H14B	107.8
N2—C2—C1	110.14 (15)	C20—C15—C16	120.3 (2)
N2—C2—H2A	109.6	C20—C15—O2	125.5 (2)
C1—C2—H2A	109.6	C16—C15—O2	114.16 (19)
N2—C2—H2B	109.6	C15—C16—C17	120.3 (2)
C1—C2—H2B	109.6	C15—C16—H16	119.8
H2A—C2—H2B	108.1	C17—C16—H16	119.8
N2—C3—C4	109.74 (17)	C16—C17—C18	121.0 (2)
N2—C3—H3A	109.7	C16—C17—N3	119.0 (2)
C4—C3—H3A	109.7	C18—C17—N3	120.0 (2)
N2—C3—H3B	109.7	C19—C18—C17	117.8 (2)
C4—C3—H3B	109.7	C19—C18—C23	124.0 (2)
H3A—C3—H3B	108.2	C17—C18—C23	118.1 (2)
N1—C4—C3	110.95 (16)	C18—C19—C20	121.5 (2)
N1—C4—H4A	109.4	C18—C19—H19	119.2
C3—C4—H4A	109.4	C20—C19—H19	119.2
N1—C4—H4B	109.4	C15—C20—C19	119.0 (2)
C3—C4—H4B	109.4	C15—C20—H20	120.5
H4A—C4—H4B	108.0	C19—C20—H20	120.5
C10—C5—C6	116.9 (2)	O1—C21—N3	120.7 (2)
C10—C5—N2	123.28 (19)	O1—C21—C22	123.3 (2)
C6—C5—N2	119.78 (19)	N3—C21—C22	115.9 (2)
C7—C6—C5	120.7 (2)	C21—C22—C23	114.5 (2)
C7—C6—Cl1	119.64 (19)	C21—C22—H22A	108.6
C5—C6—Cl1	119.63 (17)	C23—C22—H22A	108.6
C8—C7—C6	121.2 (2)	C21—C22—H22B	108.6
C8—C7—Cl2	118.48 (19)	C23—C22—H22B	108.6
C6—C7—Cl2	120.3 (2)	H22A—C22—H22B	107.6

C7—C8—C9	118.6 (2)	C18—C23—C22	111.5 (2)
C7—C8—H8	120.7	C18—C23—H23A	109.3
C9—C8—H8	120.7	C22—C23—H23A	109.3
C10—C9—C8	121.0 (3)	C18—C23—H23B	109.3
C10—C9—H9	119.5	C22—C23—H23B	109.3
C8—C9—H9	119.5	H23A—C23—H23B	108.0
C9—C10—C5	121.5 (2)	O2A—C1A—O1A	125.28 (19)
C9—C10—H10	119.3	O2A—C1A—C1A^i	121.3 (2)
C5—C10—H10	119.3	O1A—C1A—C1A^i	113.4 (2)
N1—C11—C12	112.24 (14)	C1A—O1A—H1A	114 (2)
N1—C11—H11A	109.2	O2B—C1B—O1B	125.62 (17)
C12—C11—H11A	109.2	O2B—C1B—C1B^{ii}	117.6 (2)
N1—C11—H11B	109.2	O1B—C1B—C1B^{ii}	116.7 (2)
C12—C11—H11B	109.2		

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

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C2—H2B⋯Cl1	0.97	2.62	3.224 (2)	120
O1A—H1A⋯O1B	0.86 (1)	1.71 (1)	2.561 (2)	174 (3)
N3—H3N⋯O1^{iii}	0.86 (1)	2.01 (1)	2.866 (3)	173 (3)
N1—H1N⋯O2B	0.85 (1)	1.90 (1)	2.730 (2)	164 (2)
C1—H1C⋯O2B^{iv}	0.97	2.49	3.272 (2)	137
C2—H2A⋯O2B	0.97	2.48	3.197 (3)	131
C11—H11B⋯O2A^{ii}	0.97	2.41	3.368 (3)	171
C13—H13B⋯O2A^{v}	0.97	2.43	3.262 (3)	143

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

Table 1. Comparison of selected torsion angles (°) for (I), (II) and (III)

Torsion angle	(I) (this work)	(II) (Freire *et al.*, 2012*a*)	(III) (Freire *et al.*, 2012*b*)
C2—N2—C5—C6	74.3 (2)	161.37 (17)	160.4 (2)
C2—N2—C5—C10	-104.9 (2)	-15.3 (2)	-15.5 (4)
C3—N2—C5—C6	-158.83 (19)	-67.8 (2)	-66.6 (3)
C3—N2—C5—C10	21.9 (3)	115.59 (17)	117.6 (2)
C1—N1—C11—C12	69.2 (2)	152.38 (14)	157.6 (2)
C4—N1—C11—C12	-167.23 (19)	-84.54 (17)	-79.0 (3)
N1—C11—C12—C13	163.53 (19)	-169.64 (14)	-172.7 (2)
C11—C12—C13—C14	-170.8 (2)	-69.0 (2)	-71.0 (3)
C15—O2—C14—C13	-77.1 (3)	-172.12 (14)	-167.47 (19)