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(1,5-Dimethyl-6-oxo-1,2,4,5-tetrazinan-3-yl)-imidazolium chloride

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
Some non-H atoms missing
Disorder in solvent or counterion
R factor = 0.040
wR factor = 0.106
Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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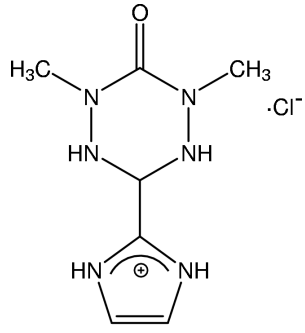
In the cation of the title compound, $C_7H_{13}N_6O^+\cdot Cl^-$, the presence of an sp^3-hybridized C atom at the point of attachment of the imidazolyl substituent leads to a conformation for the tetrazane ring that is intermediate between a screw boat and an envelope. The crystal structure of (I) consists of a three-dimensional network of N—H···O and N—H···Cl hydrogen-bonded cations and anions that is perforated by channels filled with disordered methanol solvent molecules.

Comment

Heterocycle-substituted verdazyl radicals have received considerable attention because of their interesting magnetic properties and chelating ability (Hicks *et al.*, 2001; Barclay *et al.*, 2001; Brook *et al.*, 1997, 2000). Both the free verdazyl molecules and transition-metal complexes containing coordinated verdazyl ligands are potential supramolecular building blocks for molecular magnetic materials. We recently synthesized two new heterocycle-containing verdazyl ligands, 1,5-dimethyl-3-(1-methyl-3-pyrazolyl)-6-oxoverdazyl (Meprv; Wu *et al.*, 2003) and 1,5-dimethyl-3-(2-imidazolyl)-6-oxoverdazyl (imv; during our studies, an abstract describing imv was communicated; Brook *et al.*, 2001). The hydrogenated precursor to imv was isolated in the form of its hydrochloride salt, imvH$_3$HCl, (I), and its crystal structure is presented here.



(I)

As shown in Fig. 1, the imvH$_4^+$ cation of (I) consists of an oxotetrazane ring with an imadazol-2-yl substituent attached at C3. The sp^2- and sp^3-hybridized C atoms at either end of the tetrazane ring influence the coordination geometries of the neighbouring N atoms: N1 and N5, adjacent to C6, have essentially planar geometries, while N2 and N4, adjacent to C3, have pyramidal geometries (Table 1 and Fig. 2). With calculated puckering parameters of Q = 0.431 (2) Å, θ = 62.4 (2)° and φ = 103.7 (3)°, the conformation of the tetrazane ring is between that of a screw boat and that of an envelope (ideal values θ = 67.5° and φ = 90°, and θ = 54.7° and φ = 120°,

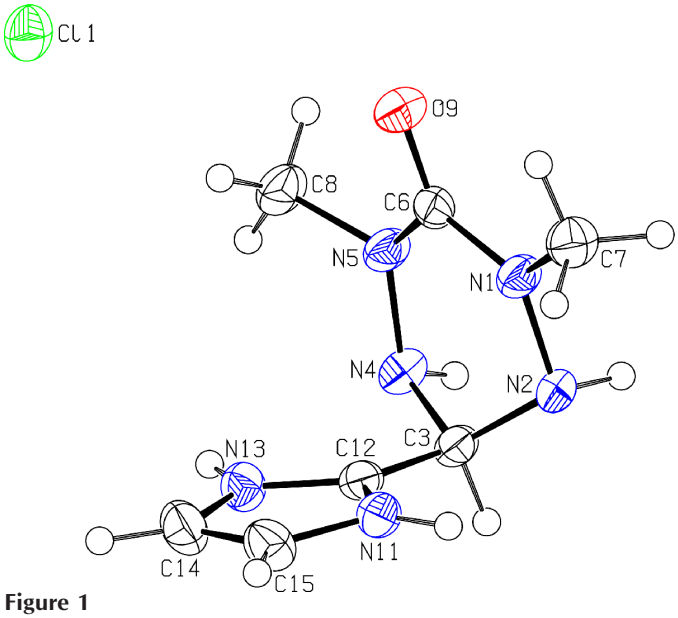


Figure 1
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

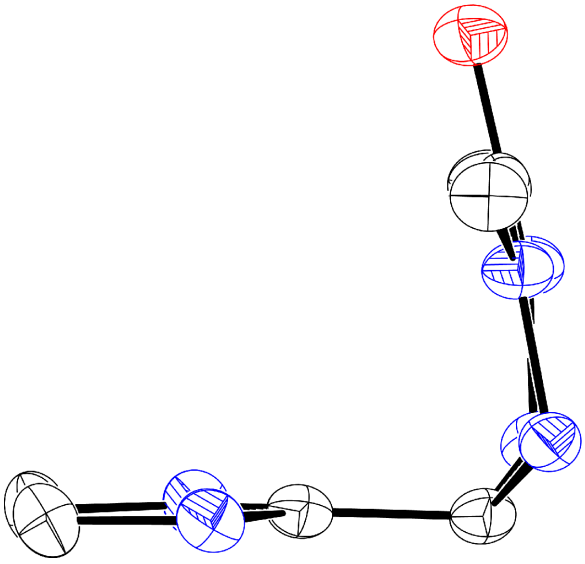


Figure 2
A side view of the cation of (I), showing the slightly puckered conformation of the tetrazane ring. Displacement ellipsoids are drawn at the 50% probability level. Ellipsoids outlined in red, blue and black correspond to O, N and C atoms, respectively. H atoms have been omitted for clarity.

respectively; Cremer & Pople, 1975). The imidazolyl substituent occupies the axial ring position; thus, the two rings are nearly perpendicular, with a dihedral angle of 89.17 (11)° between the least-squares planes. A similar chair-like molecular structure was reported for neutral 1,5-dimethyl-3-(3-pyrazolyl)-6-oxotetrazane ($prvH_3$; Wu *et al.*, 2003). In (I), the cation as a whole has approximate C_s symmetry, since both imidazolyl N atoms are protonated.

In the crystal structure of (I), intermolecular N2—H2···O9^{i} interactions involving one amide group and the carboxyl O atom of the tetrazane rings link the $imvH_4^+$ cations into $C(5)$ chains that propagate in the [001] direction [Table 2; symmetry code: (i) $\frac{1}{3}-x+y, \frac{2}{3}-x, z-\frac{1}{3}$]. The cations are arranged in infinite spirals about the threefold screw axes, with the imidazole rings pointing outwards. Hydrogen bonding between the three remaining NH groups of the cation and the chloride anion [N4—H4···Cl1^{i}, N11—H11···Cl1^{ii} and N13—H13···Cl1^{iii}; symmetry codes: (ii) $x-y, x, -z$; (iii) $x-y, x, 1-z$] assembles the spiral chains into a three-dimensional network, as shown in Fig. 3. Channels lined by the hydrophobic ends of the imidazole rings perforate the network along [0,0,z], [$\frac{1}{3},\frac{2}{3},z$] and [$\frac{2}{3},\frac{1}{3},z$]; these are filled by highly disordered methanol solvent molecules, approximately 14.5 per unit cell. It is conceivable that the methanol molecules are arranged in hydrogen-bonded chains within the hydrophobic channels, and that the extensive solvent disorder arises from the lack of strong interactions between the two substructures.

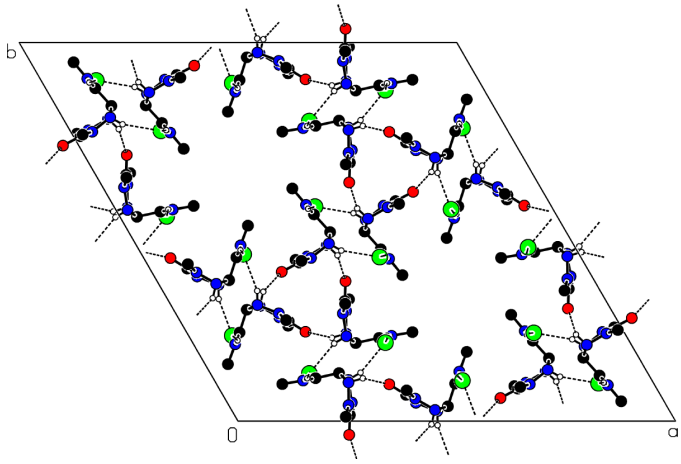


Figure 3
A view down [001] of the crystal structure of (I), showing the three-dimensional network of hydrogen-bonded $imvH_4^+$ cations and Cl^- anions. Channels filled with disordered methanol solvent molecules perforate the network along [0,0,z], [$\frac{1}{3},\frac{2}{3},z$] and [$\frac{2}{3},\frac{1}{3},z$]. Large green circles correspond to Cl atoms; medium red, blue and black circles to O, N and C atoms, respectively; small open circles to H atoms. H atoms not involved in hydrogen bonding have been omitted for clarity.

Experimental

1,1′-Dimethyl carbonic dihydrazide was first prepared from triphosgene (4.2 g, 14 mmol) and methylhydrazine (9.18 ml, 168 mmol) according to the literature method, with the exception that toluene, rather than benzene, was used as solvent (Barr *et al.*, 1999). The reaction mixture was filtered and evaporated. The product, 1,1′-dimethyl carbonic dihydrazide, was not isolated, but dissolved in methanol (50 ml) and washed with hexane to remove the excess methylhydrazine. To the methanolic solution was added dropwise a hot (323 K) methanol solution (80 ml) of imidazole-2-carboxaldehyde (1.5 g, 14 mmol). The mixture was then refluxed for 24 h. The solvent was removed under reduced pressure. Acetone was used to induce precipitation, and to transfer and wash the white product (yield 1.67 g). A second crop (0.52 g) containing crystals suitable for X-ray diffraction was obtained from the filtrate upon standing (total yield 2.19 g, 8.7 mmol, 62%). ^{1}H NMR (DMSO-d^6): δ 7.62 (*s*, 2H, 4′,5′-H), 6.64 (*s*, *br*, NH), 5.58 (*s*, 1H, 3-H), 2.97 (*s*, 6H, CH_3).

Crystal data

$C_7H_{13}N_6O^+\cdot Cl^-$	Mo $K\alpha$ radiation
M_r = 232.68	Cell parameters from 18411 reflections
Trigonal, $R\overline{3}$	θ = 1.0–27.5°
a = 27.3044 (5) Å	μ = 0.31 mm^{-1}
c = 8.3804 (2) Å	T = 150 (2) K
V = 5410.79 (19) Å^3	Block, colourless
Z = 18	0.42 × 0.24 × 0.21 mm
D_x = 1.285 Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.049
φ and ω scans	θ_{max} = 27.5°
Absorption correction: none	$h = -35 \rightarrow 34$
18411 measured reflections	$k = -23 \rightarrow 35$
2757 independent reflections	$l = -10 \rightarrow 10$
2083 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 3.583P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.040	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.106	$\Delta\rho_{max}$ = 0.25 e Å^{-3}
S = 1.06	$\Delta\rho_{min}$ = −0.33 e Å^{-3}
2757 reflections	
150 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.4244 (19)	C6—N1	1.359 (2)
N1—C7	1.449 (2)	C6—O9	1.240 (2)
N2—C3	1.452 (2)	N11—C12	1.327 (2)
C3—N4	1.449 (2)	C12—N13	1.330 (2)
C3—C12	1.495 (2)	N13—C14	1.385 (2)
N4—N5	1.433 (2)	C14—C15	1.344 (3)
N5—C6	1.361 (2)	C15—N11	1.378 (2)
N5—C8	1.460 (2)		
C6—N1—N2	122.58 (14)	N5—C6—N1	117.76 (15)
C6—N1—C7	122.49 (15)	N5—C6—O9	121.05 (15)
N2—N1—C7	114.81 (13)	N1—C6—O9	121.19 (16)
N1—N2—C3	108.98 (12)	C15—N11—C12	109.49 (15)
N2—C3—N4	115.22 (14)	N11—C12—N13	107.47 (16)
N2—C3—C12	108.26 (14)	N11—C12—C3	126.71 (16)
N4—C3—C12	109.38 (14)	N13—C12—C3	125.76 (16)
C3—N4—N5	110.73 (13)	C12—N13—C14	109.44 (15)
N4—N5—C6	123.47 (13)	N13—C14—C15	106.44 (16)
N4—N5—C8	113.53 (13)	C14—C15—N11	107.15 (16)
C6—N5—C8	119.28 (14)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O9^{i}	0.933 (14)	2.118 (17)	2.8857 (19)	138.7 (16)
N4—H4···Cl1^{i}	0.889 (14)	2.495 (16)	3.3170 (15)	154.2 (17)
N11—H11···Cl1^{ii}	0.849 (15)	2.335 (15)	3.1636 (15)	165.2 (19)
N13—H13···Cl1^{iii}	0.836 (15)	2.384 (16)	3.1817 (16)	159.7 (18)

Symmetry codes: (i) $\frac{1}{3} - x + y, \frac{2}{3} - x, z - \frac{1}{3}$; (ii) $x - y, x, -z$; (iii) $x - y, x, 1 - z$.

The crystal structure of (I) contains channels along [0,0,z], [$\frac{1}{3},\frac{2}{3},z$] and [$\frac{2}{3},\frac{1}{3},z$] (712.9 Å^3 per unit cell) that are filled with highly disordered methanol solvent molecules. Attempts to model the methanol molecules using partially occupied sites were unsatisfactory. Since the disorder could not be resolved, *PLATON*/*SQUEEZE* was used to ascertain the solvent contribution to the structure factors (262 electrons per unit cell; van der Sluis & Spek, 1990; Spek, 2003). The solvent contribution is not included in the derived crystal data. H atoms bound to carbon were placed in idealized positions and allowed to ride on their C atoms, with C—H = 0.95–1.00 Å and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C). The methyl H atoms were allowed to rotate freely about their C—C bonds. The positions of the H atoms bound to nitrogen were refined, with the N—H distances restrained to 0.88 (2) or 0.91 (2) Å and with U_{iso}(H) = 1.2U_{eq}(N).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL*2000 (Otwinowski & Minor, 1997); data reduction: *HKL*2000; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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