

**(1,5-Dimethyl-6-oxo-1,2,4,5-tetrazinan-3-yl)-imidazolium chloride****Allison M. Mills,<sup>a,\*†</sup> Jian-Zhong Wu,<sup>b,§</sup> Elisabeth Bouwman,<sup>b</sup> Jan Reedijk<sup>b</sup> and Anthony L. Spek<sup>a</sup>**

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**Key indicators**

Single-crystal X-ray study  
 $T = 150\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
Some non-H atoms missing  
Disorder in solvent or counterion  
 $R$  factor = 0.040  
 $wR$  factor = 0.106  
Data-to-parameter ratio = 18.4

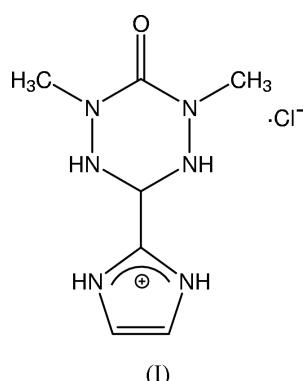
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the cation of the title compound,  $\text{C}_7\text{H}_{13}\text{N}_6\text{O}^+\cdot\text{Cl}^-$ , 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  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen-bonded cations and anions that is perforated by channels filled with disordered methanol solvent molecules.

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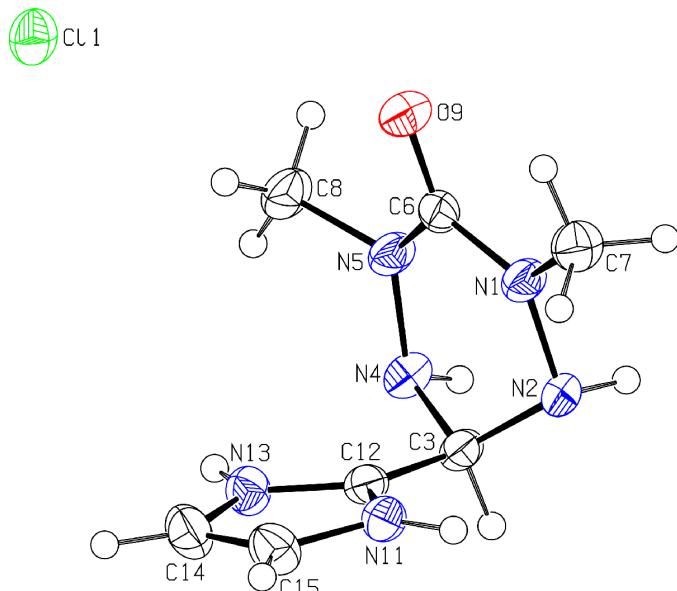
**Comment**

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,  $\text{imvH}_3\text{HCl}$ , (I), and its crystal structure is presented here.

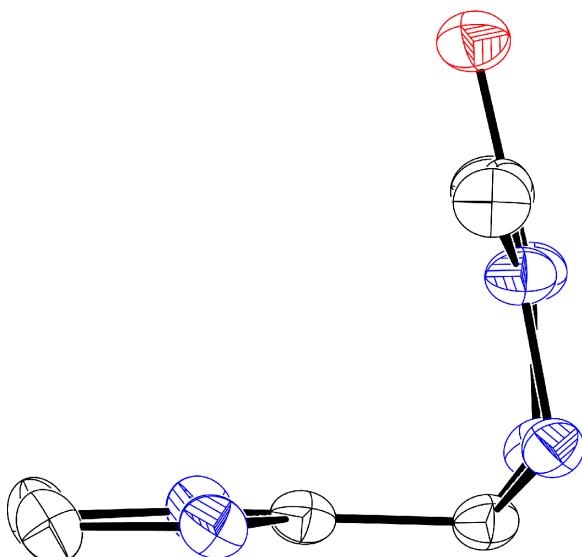


(I)

As shown in Fig. 1, the  $\text{imvH}_3^+$  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  $Q = 0.431(2)\text{ \AA}$ ,  $\theta = 62.4(2)^\circ$  and  $\varphi = 103.7(3)^\circ$ , the conformation of the tetrazane ring is between that of a screw boat and that of an envelope (ideal values  $\theta = 67.5^\circ$  and  $\varphi = 90^\circ$ , and  $\theta = 54.7^\circ$  and  $\varphi = 120^\circ$ ,

**Figure 1**

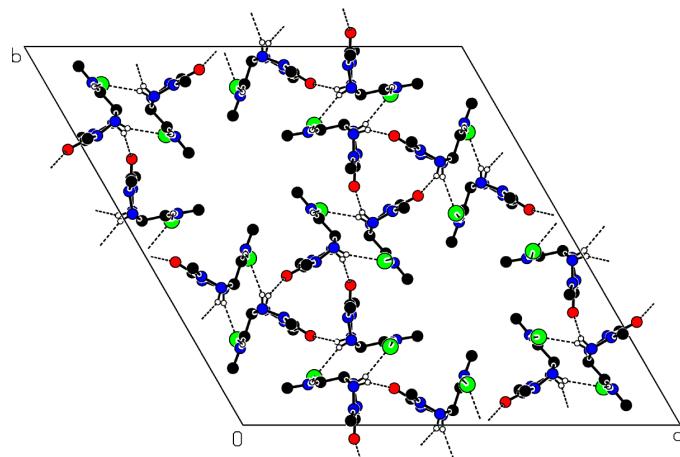
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

**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) $^{\circ}$  between the least-squares planes. A similar chair-like molecular structure was reported for neutral 1,5-dimethyl-3-(3-pyrazolyl)-6-oxotetrazane (prvH<sub>3</sub>; Wu *et al.*, 2003). In (I), the cation as a whole has approximate *C<sub>s</sub>* symmetry, since both imidazolyl N atoms are protonated.

In the crystal structure of (I), intermolecular N2—H2···O9<sup>i</sup> interactions involving one amide group and the carboxyl O

**Figure 3**

A view down [001] of the crystal structure of (I), showing the three-dimensional network of hydrogen-bonded imvH<sub>4</sub><sup>+</sup> cations and Cl<sup>-</sup> 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.

atom of the tetrazane rings link the imvH<sub>4</sub><sup>+</sup> 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<sup>i</sup>, N11—H11···Cl1<sup>ii</sup> and N13—H13···Cl1<sup>iii</sup>; 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.

## 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%). <sup>1</sup>H NMR (DMSO-*d*<sup>6</sup>):  $\delta$  7.62 (*s*, 2H, 4',5'-H), 6.64 (*s*, *br*, NH), 5.58 (*s*, 1H, 3-H), 2.97 (*s*, 6H, CH<sub>3</sub>).

## Crystal data

$C_7H_{13}N_6O^+\cdot Cl^-$   
 $M_r = 232.68$   
Trigonal,  $R\bar{3}$   
 $a = 27.3044(5)\text{ \AA}$   
 $c = 8.3804(2)\text{ \AA}$   
 $V = 5410.79(19)\text{ \AA}^3$   
 $Z = 18$   
 $D_x = 1.285\text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
Cell parameters from 18411 reflections  
 $\theta = 1.0\text{--}27.5^\circ$   
 $\mu = 0.31\text{ mm}^{-1}$   
 $T = 150(2)\text{ K}$   
Block, colourless  
 $0.42 \times 0.24 \times 0.21\text{ mm}$

## Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: none  
18411 measured reflections  
2757 independent reflections  
2083 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -35 \rightarrow 34$   
 $k = -23 \rightarrow 35$   
 $l = -10 \rightarrow 10$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.106$   
 $S = 1.06$   
2757 reflections  
150 parameters  
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 3.583P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\text{max}} = 0.001$$

$$\Delta\rho_{\text{max}} = 0.25\text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.33\text{ e \AA}^{-3}$$

The crystal structure of (I) contains channels along  $[0,0,z]$ ,  $[\frac{1}{3},\frac{2}{3},z]$  and  $[\frac{2}{3},\frac{1}{3},z]$  ( $712.9\text{ \AA}^3$  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  $C-H = 0.95\text{--}1.00\text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{C})$ . 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)  $\text{\AA}$  and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ .

Data collection: COLLECT (Nonius, 1998); cell refinement: HKL2000 (Otwinowski & Minor, 1997); data reduction: HKL2000; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

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 ( $\text{\AA}$ ,  $^\circ$ ).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}2-\text{H}2\cdots\text{O}9^i$	0.933 (14)	2.118 (17)	2.8857 (19)	138.7 (16)
$\text{N}4-\text{H}4\cdots\text{Cl}1^i$	0.889 (14)	2.495 (16)	3.3170 (15)	154.2 (17)
$\text{N}11-\text{H}11\cdots\text{Cl}1^{ii}$	0.849 (15)	2.335 (15)	3.1636 (15)	165.2 (19)
$\text{N}13-\text{H}13\cdots\text{Cl}1^{iii}$	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)  $x-y, x, 1-z$ .

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