organic papers

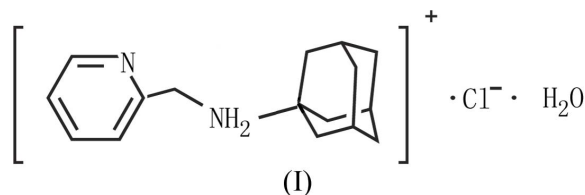## N-(2-Pyridylmethyl)adamantane-1-ammonium chloride monohydrate

Yun-Qian Zhang, Xin Xiao, Qian-Jiang Zhu, Sai-Feng Xue and Zhu Tao*

Institute of Applied Chemistry, Guizhou University, Guiyang, 550025, People's Republic of China

Correspondence e-mail: gzutao@263.net

Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean σ(C–C) = 0.002 Å

R factor = 0.041

wR factor = 0.131

Data-to-parameter ratio = 21.5

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

In the crystal structure of the title compound, $C_{16}H_{23}N_2^+\cdot Cl^-\cdot H_2O$, the molecules and ions are linked through N—H···Cl, O—H···Cl, O—H···N and N—H···O hydrogen bonds. In addition, π–π stacking between pyridine rings leads to a tail-to-tail arrangement.

Comment

Recently, a relatively new family of macrocyclic compounds, the cucurbit[n]urils ((Freeman et al., 1981; Day & Arnold, 2000; Day et al., 2002; Kim et al., 2000) and their derivatives (Zhao et al.,2001; Isobe et al., 2002; Jon et al., 2003; Day et al., 2003) or analogues (Lagona, Fettinger & Isaacs, 2005; Wagner et al., 2005), have been studied extensively in molecular recognition, host–guest chemistry and supramolecular chemistry, and summarized in a number of reviews (Lagona, Mukhopadhyay et al., 2005; Lee et al., 2003; Gerasko et al., 2002). In the present report, we introduced a guest with two units that could each interact with various cucurbit[n]urils, namely N-(2-pyridylmethyl)adamatane-1-amine.


(I)

In the crystal structure of the title compound, (I), water molecule OW1 forms hydrogen bonds with the amine nitrogen on the pyridyl, N1, the protonated amine nitrogen N2 of an adjacent cation and the counter-ion Cl1 (see Table 1 and
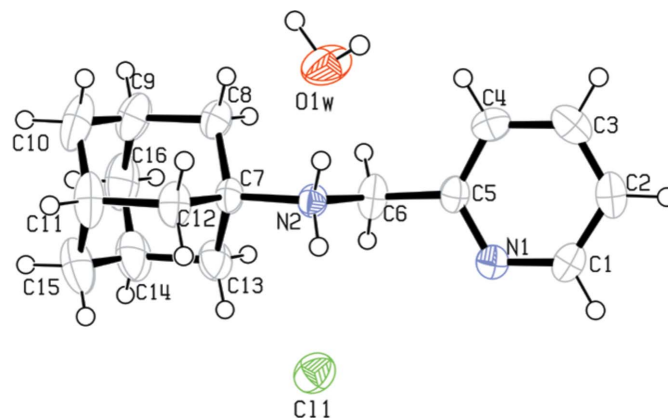
Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
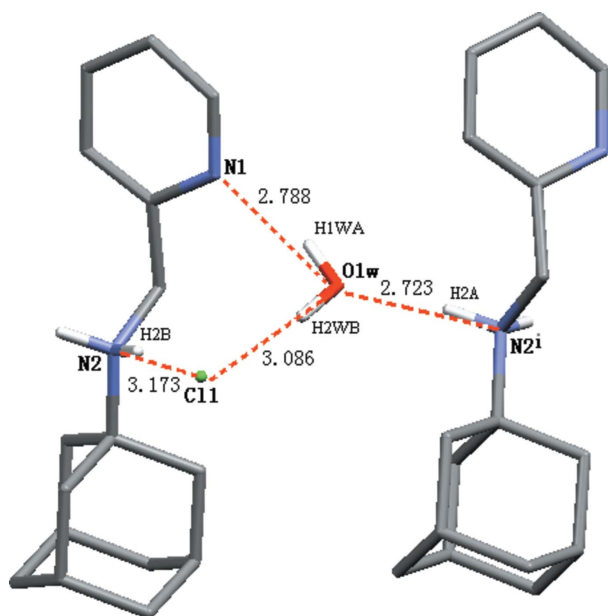
Figure 2
The hydrogen-bonding scheme. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted. [Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z$.]
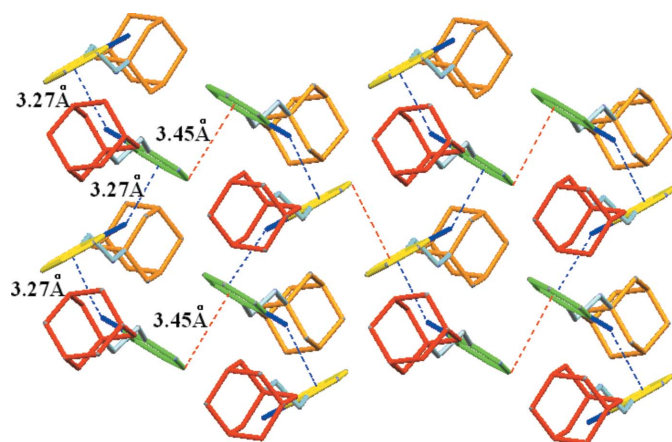
Figure 3
Packing diagram of (I). π–π Stacking and C—H$\cdots\pi$ interactions are shown as red and blue dashed lines, respectively. H atoms have been omitted for clarity.

Fig. 2). In addition, the protonated amine nitrogen N2 forms a further hydrogen bond with Cl1.

Layers are formed with cations packing in a tail-to-tail manner (Fig. 3, pyridine units in yellow and green), such that the adamantaneamine units (in red and orange) are far away from each other. The driving force for this self-assembled structure can be attributed to π–π stacking and C—H$\cdots\pi$ interactions (Lin *et al.*, 2003; Tao *et al.*, 2003, 2004) between the aromatic pyridyl rings in the title compound. π–π Stacking occurs between adjacent pyridine rings of the same colour (green to green or yellow to yellow); the distance (red dashed lines) between two rings is about 3.27 Å (Fig. 3). The C—H$\cdots\pi$ interaction occurs between adjacent pyridine rings of

different colours, for example, the carbon with the blue proton on a green pyridine ring points to the top of an adjacent yellow pyridine ring; the C—H$\cdots\pi$ distance (blue dashed lines) is about 3.45 Å. Thus, the crystal structure of the title compound is built up through a combination of hydrogen bonds, π–π stacking and C—H$\cdots\pi$ interactions.

Experimental

A solution of 2-pyridinecarbaldehyde (1.5 ml, 8.92 mmol) in CHCl$_3$ (10 ml) was added to a stirred solution of 1-adamantaneamine (1.41 g, 8.92 mmol) in CHCl$_3$ (40 ml) on an ice bath over a period of 10 min. MgSO$_4$ (1 g) was then added to the mixture. The MgSO$_4$ was removed by filtration after 1.5 h, and the solvent was removed by evaporation, yielding a solid material, which was dissolved in ethanol (20 ml). To this stirred solution, a solution of NaBH$_4$ (0.678 g) inethanol (20 ml) was added dropwise at 273 K for 2 h and then filtered. The filtrate was neutralized with HCl to pH 6–7 and filtered again. Concentrated HCl (10 ml) was added to the filtrate containing (I), which was left to stand in a cool room overnight. 1.5 g of colourless crystals were collected, in a yield of 62%.

Crystal data

C$_{16}$H$_{23}$N$_2{}^+$·Cl$^-$·H$_2$O	$Z = 4$
$M_r = 296.83$	$D_x = 1.236$ Mg m^{-3}
Monoclinic, $P2_1/a$	Mo $K\alpha$ radiation
$a = 12.6019$ (6) Å	$\mu = 0.24$ mm^{-1}
$b = 7.1780$ (4) Å	$T = 293$ (2) K
$c = 17.6949$ (9) Å	Prism, colourless
$\beta = 94.783$ (3)°	$0.21 \times 0.18 \times 0.15$ mm
$V = 1595.04$ (14) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	14934 measured reflections
φ and ω scans	3962 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	3072 reflections with $I > 2\sigma(I)$
$T_{min} = 0.952$, $T_{max} = 0.965$	$R_{int} = 0.026$
	$\theta_{max} = 28.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 0.2198P]$
$wR(F^2) = 0.131$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
3962 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
184 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.012 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2A$\cdots$O1W	0.90	1.83	2.7228 (15)	170
N2—H2B$\cdots$Cl1	0.90	2.28	3.1729 (13)	171
O1W—H1WA$\cdots$N1^i	0.86	1.96	2.7885 (16)	162
O1W—H2WB$\cdots$Cl1^i	0.94	2.16	3.0859 (13)	168

Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z$.

Water H atoms were located in a difference Fourier map and refined in their as-found positions relative to the O atoms with U_{iso}(H) = 1.2U_{eq}(O). Other H atoms were placed in calculated

organic papers

positions, with C—H = 0.93–0.98 Å and N—H = 0.90 Å, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Bruker (2002). *SADABS, SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Day, A. I. & Arnold, A. P. (2000). Patent No. WO0068232.
Day, A. I., Arnold, A. P. & Blanch, R. J. (2003). *Molecules*, **8**, 74–84.
Day, A. I., Blanch, R. J., Arnold, A. P., Lorenzo, S., Lewis, G. R. & Dance, I. (2002). *Angew. Chem. Int. Ed.* **41**, 275–277.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Freeman, W. A., Mock, W. L. & Shih, N. Y. (1981). *J. Am. Chem. Soc.* **103**, 7367–7370.
Gerasko, O. A., Samsonenko, D. G. & Fedin, V. P. (2002). *Russ. Chem. Rev.* **71**, 741–760.
Isobe, H., Sato, S. & Nakamura, E. (2002). *Org. Lett.* **4**, 1287–1289.
Jon, S. Y., Selvapalam, N., Oh, D. H., Kang, J. K., Kim, S. Y., Jeon, Y. J., Lee, J. W. & Kim, K. (2003). *J. Am. Chem. Soc.* **125**, 10186–10187.
Kim, J., Jung, I. S., Kim, S.-Y., Lee, E., Kang, J.-K., Sakamoto, S., Yamaguchi, K. & Kim, K. (2000). *J. Am. Chem. Soc.* **122**, 540–541.
Lagona, J., Fettinger, J. C. & Isaacs, L. (2005). *J. Org. Chem.* **70**, 10381–10392.
Lagona, J., Mukhopadhyay, P., Chakrabarti, S. & Isaacs, L. (2005). *Angew. Chem. Int. Ed.* **44**, 4844–4870.
Lee, J. W., Samal, S., Selvapalam, N., Kim, H. J. & Kim, K. (2003). *Acc. Chem. Res.* **36**, 621–630.
Lin, R. G., Tao, Z., Xue, S. F., Zhu, Q. J., Jackson, W. G., Wei, Z. B. & Long, L. S. (2003). *Polyhedron*, **22**, 3467–3474.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Tao, Z., Zhang, G. Y., Luo, X. Q., Xue, S. F., Zhu, Q. J., Jackson, W. G., Wei, Z. B. & Long, L. S. (2004). *Inorg. Chim. Acta*, **357**, 953–964.
Tao, Z., Zhu, Q. J., Jackson, W. G., Zhou, Z. Y. & Zhou, X. G. (2003). *Polyhedron*, **22**, 263–270.
Wagner, B. D., Boland, P. G., Lagona, J. & Isaacs, L. (2005). *J. Phys. Chem. B*, **109**, 7686–7691.
Zhao, J., Kim, H. J., Oh, J., Kim, S. Y., Lee, J. W., Sakamoto, S., Yamaguchi, K. & Kim, K. (2001). *Angew. Chem. Int. Ed.* **40**, 4233–4235.