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# Hexaaquazinc(II) bis[trichloro(3,7-dihydro-1,3,7-trimethyl-1*H*-purine-2,6-dione-$\kappa N^9$)-zincate(II)] dihydrate

**Zhi-Min Jin,[a]* Li Li,[a] Mao-Lin Hu,[b] Hao Su[a] and Cheng-Xiang Tong[a]**

[a]College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China, and [b]Department of Chemistry, Wenzhou Normal College, Wenzhou, Zhejiang 325003, People's Republic of China

Correspondence e-mail: zimichem@sina.com

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The title compound, $[Zn(H_2O)_6][ZnCl_3(C_8H_{10}N_4O_2)]_2\cdot 2H_2O$, consists of two disordered water molecules, one hexahydrated $Zn^{II}$ cation and two $[Zn^{II}Cl_3(caffeine)]^-$ anions, which are arranged around an inversion center. The coordination around the hexahydrated $Zn^{II}$ cation is octahedral. This cation is linked with $[Zn^{II}Cl_3(caffeine)]^-$ anions and water molecules *via* O—H···O hydrogen bonds. Moreover, O—H···O and O—H···Cl hydrogen bonds are co-operative in building up two-dimensional bilayers in which hexahydrated $Zn^{II}$ cations are sandwiched between two layers of $[Zn^{II}Cl_3(caffeine)]^-$ anions, which are anti-parallel to each other.

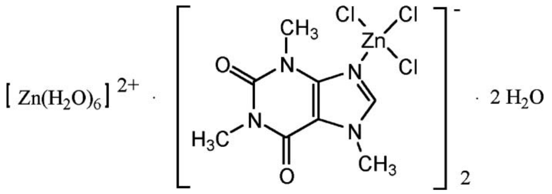
**Key indicators**

Single-crystal X-ray study
*T* = 298 K
Mean *σ*(C–C) = 0.003 Å
Disorder in solvent or counterion
*R* factor = 0.027
*wR* factor = 0.070
Data-to-parameter ratio = 13.9

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

## Comment

Caffeine has been found to inhibit postreplication repair of both ultraviolet and chemically induced damage in DNA (Roberts, 1978, 1981), and its influence on both animal and vegetable cell behavior in normal and abnormal situations is under continuous investigation. Caffeine coordination complexes of divalent metal ions remains an active area of research (Bandoli *et al.*, 1976; Bushnell *et al.*, 1983; Cramer *et al.*, 1981; Crowston *et al.*, 1986; Goodgame *et al.*, 1984; Melnik *et al.*, 1998). We report here a new compound, (I), in which caffeine (Caf) is coordinated with zinc(II).



(I)

The title compound consists of two disordered water molecules, one hexahydrated $Zn^{II}$ cation and two $[ZnCl_3(Caf)]^-$ anions which are built up by coordination of a caffeine molecule on a $[ZnCl_3]^-$ anion (Fig. 1). The Zn—O distances range from 2.0684 (19) to 2.1101 (19) Å. The hexahydrated $Zn^{II}$ ion is located at an inversion center and the coordination around the metal ion is roughly octahedral, with slight elongation along one direction (Table 1). The hexahydrated $Zn^{II}$ cation is linked with the $[ZnCl_3(Caf)]^-$ anion and to the disordered water molecule *via* O—H···O hydrogen bonds (Table 1).

The structure of the $[ZnCl_3(Caf)]^-$ anion is stablized by intramolecular C—H···O and C—H···Cl (Table 1) hydrogen bonds (Steiner & Desiraju, 1998). The three Zn—Cl bond distances [2.2435 (6), 2.2497 (7) and 2.2707 (7) Å] are longer than those typically observed for dichlorozinc(II) compounds

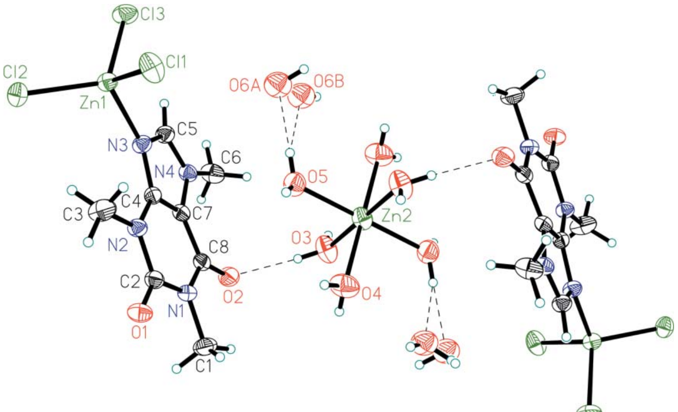


**Figure 1**
The asymmetric unit and symmetry-related moieties of (I), showing the atom labels and 35% probability displacement ellipsoids. Atoms O6*A* and O6*B* are two components, with occupancies of 0.78 and 0.22, respectively, of a disordered water molecule. Unlabeled atoms are related by the symmetry code $(-x, -y, 1 - z)$. Hydrogen bonds are illustrated as dashed lines.

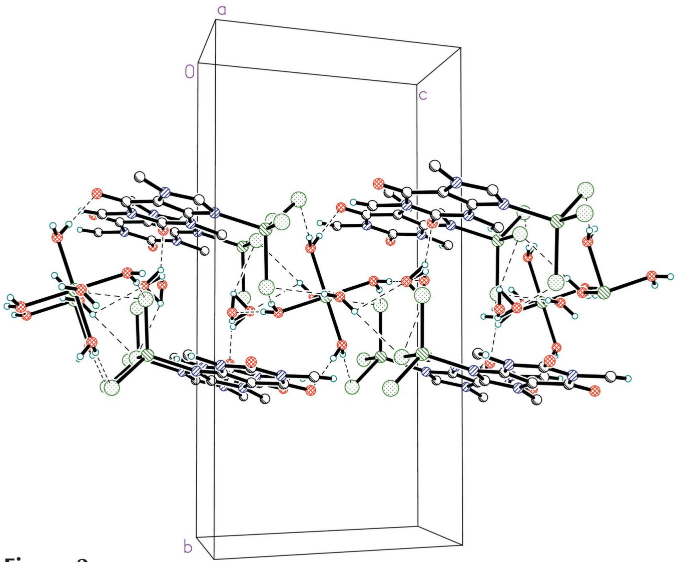


**Figure 2**
A stereoview of the packing. Hydrogen bonds are depicted by dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

(Matthew & Palenik, 1971), but they are comparable to those of [$Zn^{II}Cl_3$(thiamine)] (Bencini & Borghi, 1987). The Zn—N distance [2.0495 (18) Å] is similar to those reported for other Zn complexes (Cires-Mejias *et al.*, 2004; Ghosh & Bharadwaj, 1997), and N3—C4 [1.371 (3) Å] is longer than in *trans*-[$PtCl_2$(caffeine)$_2$]·$H_2O$ (Crowston *et al.*, 1986). The C4—N3—C5 angle [103.63 (18)°] is normal compared with those of other caffeine ligands (Bandoli *et al.*, 1976; Crowston *et al.*, 1986; Romero-Molina *et al.*, 1986; Goodgame *et al.*, 1984), but smaller than that of caffeine [107.8 (3)°; Crowston *et al.*, 1986; Parvez & Fervez, 1994].

Molecules of (I) are connected by O—H···O and O—H···Cl hydrogen bonds (Table 1) to form two-dimensional bilayers (Fig. 2) parallel to the (010) plane. The hexahydrated $Zn^{II}$ cations are sandwiched between two layers of [$ZnCl_3$(Caf)]$^-$ anions which are anti-parallel to each other. The whole structure is established by translation of the bilayer mirroring image on the (010) plane. There are no interactions between neighboring bilayers.

## Experimental

Caffeine and $ZnCl_2$ in a 1:3 molar ratio were mixed and dissolved in sufficient water by heating to a temperature where a clear solution resulted. Crystals of (I) were formed by gradual evaporation of water over a period of one week at 293 K. IR (KBr, cm$^{-1}$): 3582 (*br*), 3096, 1707 (*s*), 1665 (*s*), 1605, 1549 (*s*), 1514, 1461, 1412, 1362, 1317, 1281, 1225, 1175, 1037, 980, 896, 763, 748, 618, 492, 438.

### *Crystal data*

[$Zn(H_2O)_6$][$ZnCl_3(C_8H_{10}N_4O_2)$]$_2$·2$H_2O$
$M_r = 941.40$
Monoclinic, $P2_1/n$
$a = 8.8699$ (6) Å
$b = 19.7245$ (13) Å
$c = 10.8701$ (7) Å
$\beta = 111.508$ (1)°
$V = 1769.3$ (2) Å$^3$
$Z = 2$
$D_x = 1.767$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 890 reflections
$\theta = 2.3$–34.6°
$\mu = 2.53$ mm$^{-1}$
$T = 298$ (2) K
Prism, colorless
0.30 × 0.25 × 0.20 mm

### *Data collection*

Bruker SMART APEX CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.473$, $T_{max} = 0.603$
9304 measured reflections
3178 independent reflections
2841 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25.2°$
$h = -10 \rightarrow 10$
$k = -23 \rightarrow 21$
$l = -13 \rightarrow 9$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.070$
$S = 1.06$
3178 reflections
229 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 0.441P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.29$ e Å$^{-3}$
$\Delta\rho_{min} = -0.30$ e Å$^{-3}$

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O5—H5*WA*···O6*A* | 0.84 (3) | 1.88 (1) | 2.725 (4) | 177 (3) |
| O5—H5*WA*···O6*B* | 0.84 (3) | 1.78 (2) | 2.569 (11) | 154 (2) |
| O5—H5*WB*···Cl1$^{i}$ | 0.84 (3) | 2.36 (1) | 3.176 (2) | 162 (2) |
| O3—H3*WA*···O2 | 0.84 (3) | 1.96 (3) | 2.803 (2) | 176 (3) |
| O3—H3*WB*···Cl2$^{ii}$ | 0.85 (3) | 2.28 (3) | 3.1037 (19) | 167 (3) |
| O4—H4*WA*···Cl1$^{i}$ | 0.84 (3) | 2.39 (2) | 3.180 (2) | 156 (3) |
| O4—H4*WB*···Cl3$^{iii}$ | 0.84 (3) | 2.60 (1) | 3.430 (2) | 173 (3) |
| O6*A*—H6*A*1···O1$^{iv}$ | 0.85 | 2.00 | 2.838 (3) | 170 |
| O6*A*—H6*A*2···Cl3$^{v}$ | 0.85 | 2.57 | 3.388 (3) | 161 |
| O6*B*—H6*B*1···O1$^{iv}$ | 0.85 | 2.32 | 2.821 (9) | 118 |
| C1—H1*B*···O2 | 0.96 | 2.30 | 2.736 (3) | 107 |
| C3—H3*B*···O1 | 0.96 | 2.27 | 2.703 (3) | 106 |

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

H atoms of water molecules were located in difference Fourier maps, and incorporated in the refinement with $U_{iso}$(H) = 1.2–1.5$U_{eq}$(O). Other H atoms were placed in calculated positions and

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allowed to ride on their parent atoms at distances of 0.93 (C5—H5) and 0.96 Å (methyl), with $U_{\rm iso}$(H) = 1.2–1.5$U_{\rm eq}$(C). A water molecule is disordered over two sites, O6*A* and O6*B*, with occupancies of 0.78 and 0.22, respectively.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

## References

Bandoli, G., Cingibiagini, M., Clemente, D. A. & Rizzardi, G. (1976). *Inorg. Chim. Acta*, **20**, 71–78.

Bencini, A. & Borghi, E. (1987). *Inorg. Chim. Acta*, **135**, 85–91.

Bruker (2000). *SMART* (Version 5.618), *SADABS* (Version 2.05), *SAINT* (Version 6.02a) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Bushnell, G. W., Densmore, R. J., Dixon, K. R. & Ralfs, A. C. (1983). *Can. J. Chem.* **61**, 1132–1141.

Cires-Mejias, C., Tanase, S., Reedijk, J., Gonzalez-Vilchez, F., Vilaplana, R., Mills, A. M., Kooijman, H. & Spek, A. L. (2004). *Inorg. Chim. Acta*, **357**, 1494–1498.

Cramer, R. E., Ho, D. M., van Doorne, W., Ibers, J. A., Norton, T. & Kashiwagi, M. (1981). *Inorg. Chem.* **20**, 2457–2461.

Crowston, E. H., Goodgame, D. M. L., Hayman, P. B., Slawin, A. M. Z. & Williams, D. J. (1986). *Inorg. Chim. Acta*, **122**, 161–168.

Ghosh, P. & Bharadwaj, P. K. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2673–2683.

Goodgame, D. M. L., Hayman, P. B., Riley, R. T. & Williams, D. J. (1984). *Inorg. Chim. Acta*, **91**, 89–93.

Matthew, M. & Palenik, G. J. (1971). *Inorg. Chim. Acta*, **5**, 349–353.

Melnik, M., Koman, M. & Glowiak, T. (1998). *Polyhedron*, **17**, 1767–1771.

Parvez, M. & Fervez, G. (1994). *Acta Cryst.* C**50**, 1303–1305.

Roberts, J. J. (1978). *Adv. Rad. Biol.* **7**, 211–213.

Roberts, J. J. (1981). *Adv. Inorg. Biochem.* **3**, 273–275.

Romero-Molina, M. A., Colacio-Rodriguez, E., Ruiz-Sanchez, J. & Salas-Peregrin, J. M. (1986). *Inorg. Chim. Acta*, **123**, 133–136.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. Versions 97-1. University of Göttingen, Germany.

Steiner, T. & Desiraju, G. R. (1998). *Chem. Commun.* pp. 891–892.

*Acta Cryst.* (2005). E**61**, m1849–m1851 Jin *et al.* • $[Zn(H_2O)_6][ZnCl_3(C_8H_{10}N_4O_2)]_2 \cdot 2H_2O$ **m1851**