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Hexaaquazinc(II) dichloride bis(hexamethylenetetramine) tetrahydrate

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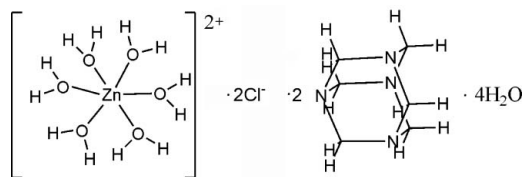
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{N}-\text{C}) = 0.004$ Å; R factor = 0.038; wR factor = 0.113; data-to-parameter ratio = 17.1.

The title compound, $[\text{Zn}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 4\text{H}_2\text{O}$, has been prepared under mild hydrothermal conditions. The Zn^{II} atom, located on a centre of symmetry, is coordinated by six water molecules in a distorted octahedral coordination geometry. The hexamethylenetetramine molecule is not coordinated to Zn^{II} but links the Zn complexes *via* three $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds. The remaining N atom of the hexamethylenetetramine molecule is hydrogen-bonded to a solvent water molecule. In the crystal structure, intermolecular $\text{O}-\text{H} \cdots \text{O}$, $\text{O}-\text{H} \cdots \text{N}$ and $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bonds link the components into a three-dimensional network.

Related literature

For related compounds, see: Zhang *et al.* (2000).

Experimental

Crystal data

 $[\text{Zn}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 4\text{H}_2\text{O}$ $M_r = 596.84$ Triclinic, $P\bar{1}$ $a = 9.345$ (3) Å $b = 9.4176$ (15) Å $c = 9.4535$ (15) Å $\alpha = 119.521$ (1)° $\beta = 94.218$ (2)° $\gamma = 100.969$ (2)° $V = 697.0$ (3) Å³ $Z = 1$ Mo $K\alpha$ radiation $\mu = 1.13$ mm⁻¹ $T = 291$ (2) K $0.36 \times 0.29 \times 0.15$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\text{min}} = 0.690$, $T_{\text{max}} = 0.849$

5184 measured reflections

2576 independent reflections

2466 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.018$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.038$ $wR(F^2) = 0.113$ $S = 1.05$

2576 reflections

151 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.51$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.68$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1W} \cdots \text{N3}$	0.82	2.05	2.827 (3)	158
$\text{O1}-\text{H2W} \cdots \text{O5}^{\text{i}}$	0.83	1.94	2.743 (3)	162
$\text{O2}-\text{H3W} \cdots \text{N2}^{\text{ii}}$	0.83	1.99	2.804 (3)	167
$\text{O2}-\text{H4W} \cdots \text{O4}^{\text{ii}}$	0.84	1.90	2.711 (3)	165
$\text{O3}-\text{H5W} \cdots \text{Cl1}$	0.82	2.55	3.197 (2)	137
$\text{O3}-\text{H6W} \cdots \text{N1}^{\text{iii}}$	0.83	2.01	2.813 (3)	165
$\text{O4}-\text{H7W} \cdots \text{Cl1}$	0.83	2.36	3.175 (2)	168
$\text{O4}-\text{H8W} \cdots \text{N4}^{\text{iv}}$	0.84	2.00	2.835 (3)	174
$\text{O5}-\text{H9W} \cdots \text{Cl1}$	0.83	2.43	3.255 (3)	168
$\text{O5}-\text{H10W} \cdots \text{Cl1}^{\text{v}}$	0.83	2.38	3.213 (3)	175

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; 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: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2186).

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supplementary materials

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Hexaaquazinc(II) dichloride bis(hexamethylenetetramine) tetrahydrate

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Comment

The asymmetric unit (Fig.1) consists of one half of hexaaqua Zn^{II} octahedron, one chloride ion, one uncoordinated neutral hexamethylenetetramine and two molecules of water of crystallization. The hexamethylenetetramine molecule is linked to the $[Zn(H_2O)_6]^{2+}$ via three O—H \cdots N hydrogen bonds, while atom N3 of hexamethylenetetramine is hydrogen-bonded to O5 of the solvent water molecule. The Cl^- anions link to the $[Zn(H_2O)_6]^{2+}$ and water of crystallization via O—H \cdots Cl hydrogen bonding. Hydrogen bonding of these anionic and cationic frameworks results in the formation of a three-dimensional network (Table 1, Fig. 2).

Experimental

All the reagents were of AR grade and used without further purification. $C_6H_{12}N_4$ (1.401 g, 10 mmol) were dissolved in 50 mL H_2O solution, then the resultant solution was added in 10 mL double-distilled water containing $ZnCl_2$ (0.273 g, 2 mmol). The resulting solution was heated at 423 K for 96 h. After cooling to room temperature, block crystals were obtained in a yield up to 21.1%.

Refinement

H atoms bonded to O atoms were located in a difference map and included in their 'as found' positions with $U_{iso}(H) = 1.5U_{eq}(O)$. Other H atoms were positioned geometrically with C—H = 0.97 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. All H atoms were treated as riding.

Figures

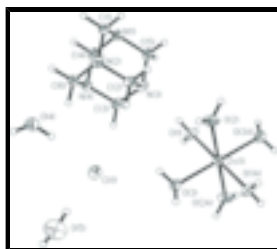


Fig. 1. Plot of an asymmetric unit with the 30% probability ellipsoids.

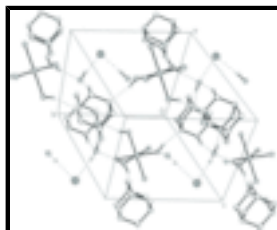


Fig. 2. Three-dimensional network of hydrogen-bonding pattern with the motif $R_4^4(16)$ linking the cationic moieties with hexamine which are in turn interwoven with anionic moieties via water molecules.

Hexaaquazinc(II) dichloride bis(hexamethylenetetramine) tetrahydrate

Crystal data

$[\text{Zn}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 4\text{H}_2\text{O}$	$Z = 1$
$M_r = 596.84$	$F_{000} = 316$
Triclinic, $P\bar{1}$	$D_x = 1.422 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 9.345 (3) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 9.4176 (15) \text{ \AA}$	Cell parameters from 2143 reflections
$c = 9.4535 (15) \text{ \AA}$	$\theta = 2.5\text{--}25.5^\circ$
$\alpha = 119.5210 (10)^\circ$	$\mu = 1.13 \text{ mm}^{-1}$
$\beta = 94.218 (2)^\circ$	$T = 291 (2) \text{ K}$
$\gamma = 100.969 (2)^\circ$	Block, colorless
$V = 697.0 (3) \text{ \AA}^3$	$0.36 \times 0.29 \times 0.15 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	2576 independent reflections
Radiation source: fine-focus sealed tube	2466 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.018$
Detector resolution: 0 pixels mm^{-1}	$\theta_{\text{max}} = 25.5^\circ$
$T = 291(2) \text{ K}$	$\theta_{\text{min}} = 2.5^\circ$
φ and ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$k = -11 \rightarrow 11$
$T_{\text{min}} = 0.690$, $T_{\text{max}} = 0.849$	$l = -11 \rightarrow 11$
5184 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.113$	$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.6988P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
2576 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
151 parameters	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.67 \text{ e \AA}^{-3}$
	Extinction correction: none

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.5000	0.0000	0.0000	0.02942 (16)
Cl1	0.18939 (10)	0.17479 (10)	0.43496 (10)	0.0530 (2)
O1	0.3835 (2)	0.1347 (2)	-0.0573 (2)	0.0385 (5)
H1W	0.3888	0.2257	0.0269	0.058*
H2W	0.3035	0.0961	-0.1235	0.058*
O2	0.6192 (2)	0.2238 (2)	0.1987 (2)	0.0445 (5)
H3W	0.6176	0.2521	0.2964	0.067*
H4W	0.6833	0.2949	0.1930	0.067*
O3	0.3580 (2)	-0.0281 (3)	0.1463 (3)	0.0449 (5)
H5W	0.3405	0.0629	0.2078	0.067*
H6W	0.3658	-0.0839	0.1907	0.067*
O4	0.1961 (2)	0.5028 (3)	0.7778 (3)	0.0453 (5)
H7W	0.2082	0.4201	0.6931	0.068*
H8W	0.1053	0.4939	0.7784	0.068*
O5	0.1487 (3)	0.0521 (4)	0.7002 (4)	0.0734 (8)
H9W	0.1699	0.0950	0.6431	0.110*
H10W	0.0600	-0.0024	0.6715	0.110*
N1	0.3345 (3)	0.7407 (3)	0.2554 (3)	0.0330 (5)
N2	0.3362 (3)	0.6543 (3)	0.4602 (3)	0.0333 (5)
N3	0.3418 (3)	0.4524 (3)	0.1728 (3)	0.0321 (5)
N4	0.1152 (2)	0.5427 (3)	0.2441 (3)	0.0340 (5)
C1	0.3865 (3)	0.7935 (3)	0.4289 (3)	0.0356 (6)
H1A	0.3492	0.8886	0.5010	0.043*
H1B	0.4942	0.8302	0.4552	0.043*
C2	0.3944 (3)	0.5116 (3)	0.3488 (3)	0.0342 (6)
H2A	0.3628	0.4191	0.3677	0.041*
H2B	0.5022	0.5466	0.3743	0.041*
C3	0.1782 (3)	0.4021 (3)	0.1376 (3)	0.0381 (6)
H3A	0.1440	0.3088	0.1546	0.046*
H3B	0.1422	0.3632	0.0223	0.046*
C4	0.1706 (3)	0.6838 (4)	0.2176 (4)	0.0375 (6)
H4A	0.1348	0.6480	0.1032	0.045*
H4B	0.1311	0.7778	0.2876	0.045*

supplementary materials

C5	0.3925 (3)	0.5955 (4)	0.1482 (3)	0.0353 (6)
H5A	0.3595	0.5592	0.0331	0.042*
H5B	0.5003	0.6306	0.1729	0.042*
C6	0.1728 (3)	0.5995 (4)	0.4186 (3)	0.0369 (6)
H6A	0.1333	0.6925	0.4910	0.044*
H6B	0.1386	0.5076	0.4377	0.044*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0395 (3)	0.0233 (2)	0.0250 (2)	0.00991 (17)	0.00711 (17)	0.01148 (18)
Cl1	0.0591 (5)	0.0399 (4)	0.0534 (5)	0.0135 (3)	0.0246 (4)	0.0173 (4)
O1	0.0604 (11)	0.0278 (9)	0.0329 (10)	0.0192 (8)	-0.0009 (8)	0.0105 (8)
O2	0.0710 (13)	0.0280 (10)	0.0220 (9)	-0.0076 (9)	0.0009 (9)	0.0081 (8)
O3	0.0675 (14)	0.0422 (11)	0.0548 (12)	0.0327 (10)	0.0401 (11)	0.0367 (10)
O4	0.0398 (11)	0.0386 (11)	0.0417 (11)	0.0003 (9)	0.0055 (9)	0.0130 (9)
O5	0.0604 (16)	0.086 (2)	0.0720 (18)	0.0027 (14)	-0.0156 (13)	0.0485 (16)
N1	0.0423 (12)	0.0298 (11)	0.0371 (12)	0.0160 (10)	0.0161 (10)	0.0214 (10)
N2	0.0426 (12)	0.0285 (11)	0.0242 (10)	0.0036 (9)	0.0050 (9)	0.0125 (9)
N3	0.0407 (12)	0.0255 (11)	0.0275 (11)	0.0144 (9)	0.0046 (9)	0.0102 (9)
N4	0.0345 (11)	0.0289 (11)	0.0335 (11)	0.0088 (9)	0.0063 (9)	0.0124 (9)
C1	0.0433 (15)	0.0221 (12)	0.0348 (14)	0.0048 (10)	0.0100 (11)	0.0110 (11)
C2	0.0432 (15)	0.0284 (13)	0.0326 (13)	0.0090 (11)	0.0007 (11)	0.0178 (11)
C3	0.0417 (15)	0.0264 (13)	0.0327 (14)	0.0086 (11)	-0.0005 (11)	0.0066 (11)
C4	0.0443 (15)	0.0376 (15)	0.0404 (15)	0.0219 (12)	0.0136 (12)	0.0226 (12)
C5	0.0452 (15)	0.0399 (15)	0.0314 (13)	0.0217 (12)	0.0167 (11)	0.0214 (12)
C6	0.0427 (15)	0.0337 (14)	0.0326 (14)	0.0055 (11)	0.0128 (11)	0.0167 (11)

Geometric parameters (\AA , $^\circ$)

Zn1—O2 ⁱ	2.0269 (18)	N2—C2	1.476 (3)
Zn1—O2	2.0269 (18)	N2—C1	1.481 (3)
Zn1—O1	2.0507 (17)	N3—C3	1.472 (4)
Zn1—O1 ⁱ	2.0507 (17)	N3—C5	1.476 (3)
Zn1—O3 ⁱ	2.0595 (18)	N3—C2	1.477 (3)
Zn1—O3	2.0595 (18)	N4—C4	1.477 (4)
O1—H1W	0.8223	N4—C3	1.478 (3)
O1—H2W	0.8281	N4—C6	1.479 (4)
O2—H3W	0.8279	C1—H1A	0.9700
O2—H4W	0.8360	C1—H1B	0.9700
O3—H5W	0.8221	C2—H2A	0.9700
O3—H6W	0.8267	C2—H2B	0.9700
O4—H7W	0.8326	C3—H3A	0.9700
O4—H8W	0.8374	C3—H3B	0.9700
O5—H9W	0.8338	C4—H4A	0.9700
O5—H10W	0.8316	C4—H4B	0.9700
N1—C1	1.470 (4)	C5—H5A	0.9700
N1—C4	1.476 (4)	C5—H5B	0.9700

N1—C5	1.479 (3)	C6—H6A	0.9700
N2—C6	1.471 (4)	C6—H6B	0.9700
O2 ⁱ —Zn1—O2	180.00 (11)	C3—N4—C6	107.8 (2)
O2 ⁱ —Zn1—O1	92.66 (8)	N1—C1—N2	111.7 (2)
O2—Zn1—O1	87.34 (8)	N1—C1—H1A	109.3
O2 ⁱ —Zn1—O1 ⁱ	87.34 (8)	N2—C1—H1A	109.3
O2—Zn1—O1 ⁱ	92.66 (8)	N1—C1—H1B	109.3
O1—Zn1—O1 ⁱ	180.00 (12)	N2—C1—H1B	109.3
O2 ⁱ —Zn1—O3 ⁱ	89.59 (9)	H1A—C1—H1B	107.9
O2—Zn1—O3 ⁱ	90.41 (9)	N2—C2—N3	111.6 (2)
O1—Zn1—O3 ⁱ	86.57 (8)	N2—C2—H2A	109.3
O1 ⁱ —Zn1—O3 ⁱ	93.43 (8)	N3—C2—H2A	109.3
O2 ⁱ —Zn1—O3	90.41 (9)	N2—C2—H2B	109.3
O2—Zn1—O3	89.59 (9)	N3—C2—H2B	109.3
O1—Zn1—O3	93.43 (8)	H2A—C2—H2B	108.0
O1 ⁱ —Zn1—O3	86.57 (8)	N3—C3—N4	112.2 (2)
O3 ⁱ —Zn1—O3	180.00 (19)	N3—C3—H3A	109.2
Zn1—O1—H1W	109.5	N4—C3—H3A	109.2
Zn1—O1—H2W	126.6	N3—C3—H3B	109.2
H1W—O1—H2W	113.2	N4—C3—H3B	109.2
Zn1—O2—H3W	124.5	H3A—C3—H3B	107.9
Zn1—O2—H4W	124.2	N1—C4—N4	112.2 (2)
H3W—O2—H4W	111.0	N1—C4—H4A	109.2
Zn1—O3—H5W	109.6	N4—C4—H4A	109.2
Zn1—O3—H6W	123.5	N1—C4—H4B	109.2
H5W—O3—H6W	113.5	N4—C4—H4B	109.2
H7W—O4—H8W	110.1	H4A—C4—H4B	107.9
H9W—O5—H10W	111.5	N3—C5—N1	111.7 (2)
C1—N1—C4	108.4 (2)	N3—C5—H5A	109.3
C1—N1—C5	108.2 (2)	N1—C5—H5A	109.3
C4—N1—C5	108.3 (2)	N3—C5—H5B	109.3
C6—N2—C2	108.5 (2)	N1—C5—H5B	109.3
C6—N2—C1	108.5 (2)	H5A—C5—H5B	108.0
C2—N2—C1	108.0 (2)	N2—C6—N4	112.0 (2)
C3—N3—C5	108.7 (2)	N2—C6—H6A	109.2
C3—N3—C2	108.4 (2)	N4—C6—H6A	109.2
C5—N3—C2	107.9 (2)	N2—C6—H6B	109.2
C4—N4—C3	108.0 (2)	N4—C6—H6B	109.2
C4—N4—C6	108.1 (2)	H6A—C6—H6B	107.9
C4—N1—C1—N2	58.4 (3)	C1—N1—C4—N4	-58.6 (3)
C5—N1—C1—N2	-58.8 (3)	C5—N1—C4—N4	58.6 (3)
C6—N2—C1—N1	-58.6 (3)	C3—N4—C4—N1	-58.3 (3)
C2—N2—C1—N1	58.9 (3)	C6—N4—C4—N1	58.1 (3)
C6—N2—C2—N3	58.3 (3)	C3—N3—C5—N1	58.1 (3)
C1—N2—C2—N3	-59.1 (3)	C2—N3—C5—N1	-59.2 (3)
C3—N3—C2—N2	-58.2 (3)	C1—N1—C5—N3	59.2 (3)

supplementary materials

C5—N3—C2—N2	59.4 (3)	C4—N1—C5—N3	-58.1 (3)
C5—N3—C3—N4	-58.3 (3)	C2—N2—C6—N4	-58.8 (3)
C2—N3—C3—N4	58.7 (3)	C1—N2—C6—N4	58.4 (3)
C4—N4—C3—N3	58.0 (3)	C4—N4—C6—N2	-58.0 (3)
C6—N4—C3—N3	-58.6 (3)	C3—N4—C6—N2	58.5 (3)

Symmetry codes: (i) $-x+1, -y, -z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1W \cdots N3	0.82	2.05	2.827 (3)	158
O1—H2W \cdots O5 ⁱⁱ	0.83	1.94	2.743 (3)	162
O2—H3W \cdots N2 ⁱⁱⁱ	0.83	1.99	2.804 (3)	167
O2—H4W \cdots O4 ⁱⁱⁱ	0.84	1.90	2.711 (3)	165
O3—H5W \cdots C11	0.82	2.55	3.197 (2)	137
O3—H6W \cdots N1 ^{iv}	0.83	2.01	2.813 (3)	165
O4—H7W \cdots C11	0.83	2.36	3.175 (2)	168
O4—H8W \cdots N4 ^v	0.84	2.00	2.835 (3)	174
O5—H9W \cdots C11	0.83	2.43	3.255 (3)	168
O5—H10W \cdots C11 ^{vi}	0.83	2.38	3.213 (3)	175

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

Fig. 1

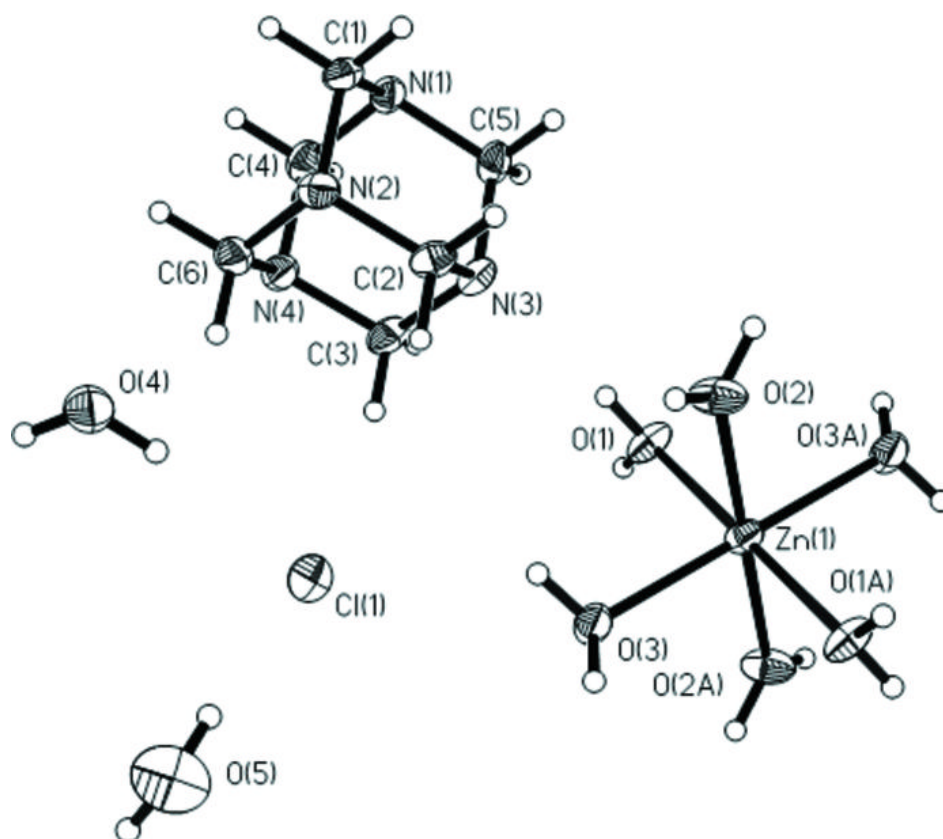


Fig. 2

