Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

catena-Poly[[dichlorozinc(II)]-μ-cyanoguanidine]

Lyndsey K. Ritche and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail: w.harrison@abdn.ac.uk

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(N–C) = 0.004 Å
R factor = 0.026
wR factor = 0.071
Data-to-parameter ratio = 31.5

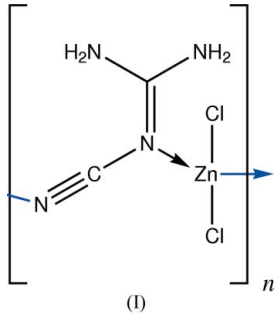
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 22 January 2007
Accepted 23 January 2007

The one-dimensional title compound, $[ZnCl_2(C_2H_4N_4)]_n$, contains $ZnCl_2N_2$ tetraheda linked by *N*,*N*-bridging cyanoguanidine molecules. A network of N—H···Cl hydrogen bonds help to establish the crystal packing.

Comment

The title compound, (I) (Fig. 1), is a one-dimensional coordination polymer containing cyanoguanidine molecules, Zn^{2+} ions and Cl^- ions. The Zn^{2+} cation is tetrahedrally coordinated by two terminal Cl^- ions and two cyanoguanidine molecules (Table 1), one bonded through the cyanide atom N4 and one from the imine atom N3. The C1—N3—C2 bond angle in (I) is 116.22 (15)°, compared with the corresponding angle of 118.38 (2)° in the free ligand (Hirshfeld & Hope, 1980). The C1—N3 [1.370 (2) Å] and C2—N3 [1.308 (3) Å] bond lengths in (I) indicate that the conventional Lewis structure shown in the chemical scheme (C1═N3 a formal double bond and C2—N3 a formal single bond) is only a very approximate representation of the actual electron distribution in the molecule (Hughes, 1940; Hirshfeld & Hope, 1980).



(I)

The connectivity of the building units in (I) results in a polymeric chain of stoichiometry $Zn(C_2H_4N_4)Cl_2$ (Fig. 2), which propagates in the polar [001] direction. The chain conformation is reinforced by an intra-chain N1—H2···Cl1 hydrogen bond. Further N—H···Cl bonds cross-link the polymeric strands (Table 2). Atom H1 has no nearby Cl^- ions but possibly forms a weak bifurcated N—H···(Cl,Cl) interaction (bond angle sum for H1 = 359°).

Two polymorphs of the molecular compound $Zn(C_2H_4N_4)_2Cl_2$ have been reported by Pickardt & Kuhn (1995) and Fowkes & Harrison (2005). These both contain $ZnCl_2N_2$ tetrahedra, with the two cyanoguanidine molecules both bonding through their cyanide N atoms. Other compounds with the stoichiometry of the title compound, $M(C_2H_4N_4)X_2$ (M is a divalent metal cation and X is a halide) include $Hg(C_2H_4N_4)Cl_2$ and $Cd(C_2H_4N_4)Br_2$ (Pickardt &

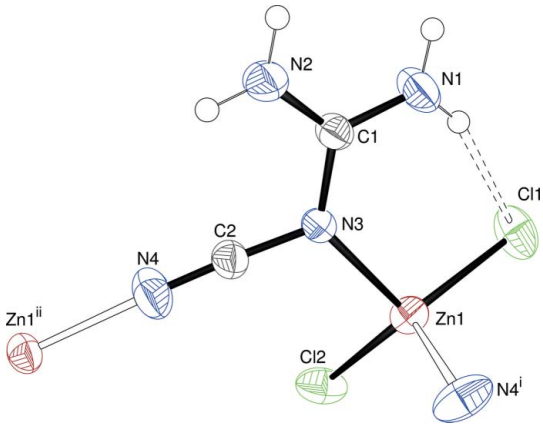


Figure 1
The asymmetric unit of (I), expanded to show the polymeric connectivity (open bonds) of the chain. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius. The intra-chain hydrogen bond is indicated by a double-dashed line. [Symmetry codes: (i) $1-x, -y, z-\frac{1}{2}$, (ii) $1-x, -y, z+\frac{1}{2}$.]

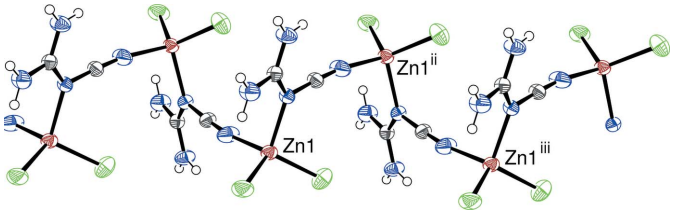


Figure 2
Part of an [001] polymeric chain in (I). [Symmetry codes: (ii) $1-x, -y, z+\frac{1}{2}$, (iii) $x, y, z+1$.]

Kuhn, 1996). The mercury compound contains *N*,*N*-bonded cyanoguanidine molecues, as seen here in (I), but the Cl^- ions also act as μ_2 bridges between the irregularly-coordinated Hg^{2+} ions, leading to a layered polymeric network. The cadmium compound features cyanide-N-bonded cyanoguanidine molecules and bridging Br^- ions, leading to one-dimensional chains of distorted tetrahedral CdN_2Br_2 units.

Experimental

An aqueous solution (10 ml) of cyanoguanidine (0.73 *M*) and a methanolic solution (10 ml) of $ZnCl_2$ (0.73 *M*) were mixed at 293 K in a Petri dish, resulting in a colourless mixture. Colourless blocks and slabs of (I) grew over the course of a few days as the water/methanol evaporated at 293 K.

Crystal data

$[ZnCl_2(C_2H_4N_4)]$
M_r = 220.36
Orthorhombic, $Pca2_1$
a = 13.6756 (8) Å
b = 7.3710 (5) Å
c = 7.4200 (5) Å
V = 747.96 (8) Å^3
Z = 4
D_x = 1.957 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 3.92 mm^{-1}
T = 293 (2) K
Slab, colourless
0.51 × 0.49 × 0.09 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.240, T_{max} = 0.720
9597 measured reflections
2612 independent reflections
2481 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 32.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.071
S = 1.05
2612 reflections
83 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0218 (16)
Absolute structure: Flack (1983), with 1163 Friedel pairs
Flack parameter: 0.027 (11)

Table 1
Selected bond lengths (Å).

Zn1—N4^{iv}	1.985 (2)	Zn1—Cl2	2.2238 (7)
Zn1—N3	2.0887 (14)	Zn1—Cl1	2.2252 (7)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1^{v}	0.86	2.92	3.6437 (18)	144
N1—H1···Cl2^{vi}	0.86	2.92	3.389 (2)	116
N1—H2···Cl1	0.86	2.48	3.3050 (18)	161
N2—H3···Cl1^{v}	0.86	2.42	3.262 (2)	166
N2—H4···Cl2^{vii}	0.86	2.50	3.289 (2)	153

Symmetry codes: (v) $x+\frac{1}{2}, -y+1, z$; (vi) $-x+1, -y+1, z-\frac{1}{2}$; (vii) $x+\frac{1}{2}, -y, z$.

H atoms were placed in idealized locations, with N—H = 0.86 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(N)$.

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

References

Bruker (1999). *SMART* (Version 5.624), *SAINT-Plus* (Version 6.02a) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fowkes, A. & Harrison, W. T. A. (2005). *Acta Cryst.* E**61**, m2021–m2022.
Hirshfeld, F. L. & Hope, H. (1980). *Acta Cryst.* B**36**, 406–415.
Hughes, E. W. (1940). *J. Am. Chem. Soc.* **62**, 1258–1267.
Pickardt, J. & Kuhn, B. (1995). *Z. Kristallogr.* **210**, 901–901.
Pickardt, J. & Kuhn, B. (1996). *Z. Naturforsch. Teil B*, **51**, 1701–1706.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supporting information

Acta Cryst. (2007). E**63**, m617–m618 [https://doi.org/10.1107/S1600536807003807]

catena-Poly[[dichlorozinc(II)]-μ-cyanoguanidine]

Lyndsey K. Ritche and William T. A. Harrison

***catena*-Poly[[dichlorozinc(II)]-μ-cyanoguanidine]**

Crystal data

$[ZnCl_2(C_2H_4N_4)]$
$M_r = 220.36$
Orthorhombic, $Pca2_1$
Hall symbol: P 2c -2ac
$a = 13.6756$ (8) Å
$b = 7.3710$ (5) Å
$c = 7.4200$ (5) Å
$V = 747.96$ (8) Å^3
$Z = 4$
$F(000) = 432$
$D_x = 1.957$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6450 reflections
$\theta = 2.8$–$32.5°$
$\mu = 3.92$ mm^{-1}
$T = 293$ K
Slab, colourless
0.51 × 0.49 × 0.09 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 1999)
$T_{min} = 0.240$, $T_{max} = 0.720$
9597 measured reflections
2612 independent reflections
2481 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 32.5°$, $\theta_{min} = 2.8°$
$h = -20 \rightarrow 20$
$k = -10 \rightarrow 11$
$l = -11 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.071$
$S = 1.05$
2612 reflections
83 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0218 (16)
Absolute structure: Flack (1983), with 1163 Friedel pairs
Absolute structure parameter: 0.027 (11)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.424511 (14)	0.23356 (3)	0.72398 (5)	0.02943 (8)
Cl1	0.40928 (4)	0.51909 (9)	0.63074 (11)	0.04953 (16)
Cl2	0.33515 (4)	0.15972 (8)	0.96339 (10)	0.04576 (14)
C1	0.65364 (13)	0.2735 (2)	0.7454 (3)	0.0276 (4)
C2	0.58011 (11)	0.0556 (3)	0.9148 (3)	0.0307 (4)
N1	0.64494 (13)	0.4213 (3)	0.6480 (3)	0.0420 (4)
H1	0.6963	0.4784	0.6126	0.050*
H2	0.5879	0.4611	0.6196	0.050*
N2	0.74078 (13)	0.2115 (3)	0.7896 (3)	0.0390 (4)
H3	0.7924	0.2680	0.7545	0.047*
H4	0.7460	0.1146	0.8534	0.047*
N3	0.56986 (10)	0.1852 (2)	0.7959 (2)	0.0265 (3)
N4	0.58423 (12)	−0.0587 (4)	1.0211 (4)	0.0471 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02959 (11)	0.02627 (11)	0.03243 (13)	0.00409 (6)	−0.00139 (11)	−0.00518 (13)
Cl1	0.0527 (3)	0.0378 (3)	0.0581 (4)	0.0195 (2)	0.0104 (3)	0.0144 (3)
Cl2	0.0439 (2)	0.0449 (3)	0.0484 (3)	−0.0134 (2)	0.0135 (2)	−0.0086 (3)
C1	0.0270 (7)	0.0267 (7)	0.0291 (11)	−0.0018 (5)	0.0025 (6)	0.0031 (7)
C2	0.0255 (7)	0.0336 (10)	0.0330 (10)	−0.0001 (6)	0.0009 (6)	0.0073 (8)
N1	0.0390 (8)	0.0353 (9)	0.0515 (12)	0.0006 (7)	0.0059 (8)	0.0180 (9)
N2	0.0247 (7)	0.0397 (9)	0.0525 (12)	−0.0014 (7)	−0.0001 (7)	0.0112 (8)
N3	0.0253 (6)	0.0253 (7)	0.0290 (8)	−0.0018 (5)	−0.0008 (5)	0.0043 (6)
N4	0.0321 (8)	0.0528 (13)	0.0563 (15)	0.0059 (7)	0.0077 (7)	0.0275 (11)

Geometric parameters (Å, º)

Zn1—N4^{i}	1.985 (2)	C2—N4	1.156 (3)
Zn1—N3	2.0887 (14)	C2—N3	1.308 (3)
Zn1—Cl2	2.2238 (7)	N1—H1	0.8600
Zn1—Cl1	2.2252 (7)	N1—H2	0.8600
C1—N1	1.313 (3)	N2—H3	0.8600
C1—N2	1.318 (3)	N2—H4	0.8600
C1—N3	1.370 (2)	N4—Zn1^{ii}	1.985 (2)

N4^{i}—Zn1—N3	98.07 (7)	C1—N1—H1	120.0
N4^{i}—Zn1—Cl2	114.44 (8)	C1—N1—H2	120.0
N3—Zn1—Cl2	106.09 (5)	H1—N1—H2	120.0
N4^{i}—Zn1—Cl1	111.87 (9)	C1—N2—H3	120.0
N3—Zn1—Cl1	109.26 (5)	C1—N2—H4	120.0
Cl2—Zn1—Cl1	115.37 (3)	H3—N2—H4	120.0
N1—C1—N2	120.42 (18)	C2—N3—C1	116.22 (15)
N1—C1—N3	117.97 (17)	C2—N3—Zn1	113.50 (11)
N2—C1—N3	121.60 (18)	C1—N3—Zn1	130.18 (14)
N4—C2—N3	176.63 (17)	C2—N4—Zn1^{ii}	171.1 (2)
N1—C1—N3—C2	−169.9 (2)	Cl2—Zn1—N3—C2	29.17 (17)
N2—C1—N3—C2	11.4 (3)	Cl1—Zn1—N3—C2	154.14 (16)
N1—C1—N3—Zn1	6.2 (3)	N4^{i}—Zn1—N3—C1	94.6 (2)
N2—C1—N3—Zn1	−172.58 (18)	Cl2—Zn1—N3—C1	−146.97 (18)
N4^{i}—Zn1—N3—C2	−89.24 (19)	Cl1—Zn1—N3—C1	−22.0 (2)

Symmetry codes: (i) −*x*+1, −*y*, *z*−1/2; (ii) −*x*+1, −*y*, *z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1^{iii}	0.86	2.92	3.6437 (18)	144
N1—H1···Cl2^{iv}	0.86	2.92	3.389 (2)	116
N1—H2···Cl1	0.86	2.48	3.3050 (18)	161
N2—H3···Cl1^{iii}	0.86	2.42	3.262 (2)	166
N2—H4···Cl2^{v}	0.86	2.50	3.289 (2)	153

Symmetry codes: (iii) *x*+1/2, −*y*+1, *z*; (iv) −*x*+1, −*y*+1, *z*−1/2; (v) *x*+1/2, −*y*, *z*.