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

Received 22 January 2007
Accepted 23 January 2007

Key indicators

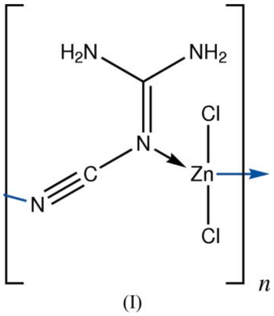
Single-crystal X-ray study
T = 293 K
Mean σ(N–C) = 0.004 Å
R factor = 0.026
wR factor = 0.071
Data-to-parameter ratio = 31.5

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

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 &

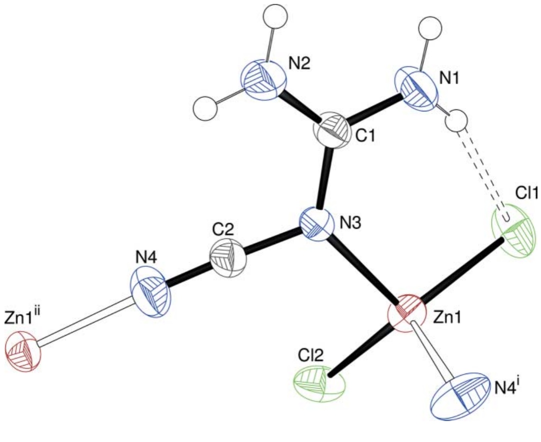


Figure 1
The asymmetric unit of (I), expanded to show the polymeric connectivity (open bonds) of the chain. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius. The intra-chain hydrogen bond is indicated by a double-dashed line. [Symmetry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

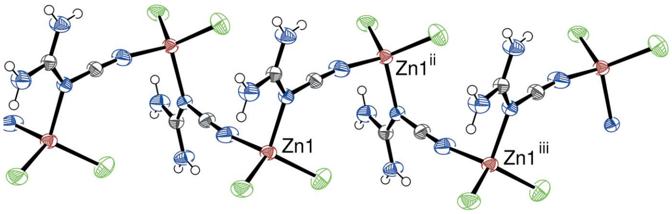


Figure 2
Part of an [001] polymeric chain in (I). [Symmetry codes: (ii) $1 - x, -y, z + \frac{1}{2}$, (iii) $x, y, z + 1$.]

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
$\mu = 3.92$ 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 $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 32.5°$

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, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots Cl1^{v}$	0.86	2.92	3.6437 (18)	144
$N1-H1\cdots Cl2^{vi}$	0.86	2.92	3.389 (2)	116
$N1-H2\cdots Cl1$	0.86	2.48	3.3050 (18)	161
$N2-H3\cdots Cl1^{v}$	0.86	2.42	3.262 (2)	166
$N2-H4\cdots Cl2^{vii}$	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.