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Zinc cyanamide, $Zn(CN_2)$

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Single crystals of the title compound have been grown by annealing microcrystalline zinc cyanamide at 843 K in silver crucibles. $Zn(CN_2)$ crystallizes as colourless prisms. The crystal structure is composed of corner-linked $ZnN_{4/2}$ tetrahedra. Carbon and nitrogen form $(CN_2)^{2-}$ dumb-bells with the C atom on a twofold axis. Nitrogen is approximately trigonally planar, coordinated by two Zn atoms and one C atom.

Comment

The structural characterization of M^{II}–cyanamides (M^{II} is a transition metal) has up until now been limited to cadmium cyanamide (Dvoinin *et al.*, 1982). Recently, mercury cyanamide has been prepared and its crystal structure determined (Becker & Jansen, 2000). In the course of further structural investigations of crystalline metal cyanamides, we have grown single crystals of $Zn(CN_2)$, which was first described by Grube (Grube & Nitsche, 1914). Nowadays, zinc cyanamide, (I), is a component in non-polluting anticorrosive white pigments (Nagayama *et al.*, 1994).

$$Zn^{2+} \cdot \left[N{=}C{=}N \right]^{2-}$$

(I)

We present here the first structural investigation on $Zn(CN_2)$. In the title compound, zinc is tetrahedrally coordinated by N atoms, with bond lengths of 1.985 (2) and 2.035 (2) Å. Nitrogen is surrounded in an approximately trigonally planar manner by two Zn^{2+} cations and one C atom. The ZnN_4 tetrahedra share corners while the C atoms are each situated between two N atoms to form slightly bent $(CN_2)^{2-}$ dumb-bells [N—C—N 176.3 (3)°] (Fig. 1). The cyanamide dumb-bells are surrounded by four Zn atoms, which are arranged in a staggered conformation (Fig. 2). Although the corner-linked ZnN_4 tetrahedra are similar to the silicon dioxide polymorphs, there is no topological relationship to any of them; the ZnN_4 tetrahedra form Zn_4N_4 rings which have no precedence in SiO_2 structures. The ZnN_4 tetrahedra form chains along the (111) direction with every second ZnN_4 unit being twisted counterclockwise (rotation angle 81.5°). With regard to zinc and nitrogen, the structure can be related to the high pressure polymorph of Willemite (Zn_2SiO_4–II; Marumo & Syono, 1970), with nitrogen being substituted for oxygen. The sites of the tetrahedrally coordinated Si atoms are empty in the structure of $Zn(CN_2)$. The position of carbon in zinc cyanamide can be reproduced by shifting silicon in Zn_2SiO_4–II towards the edges of its coordination polyhedron, thus forming dumb-bells.

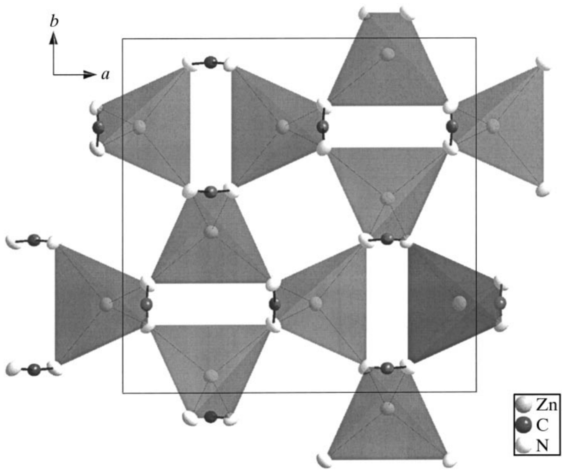

Figure 1
View of the crystal structure of $Zn(CN_2)$. The ZnN_4 building units have been shown as polyhedra.

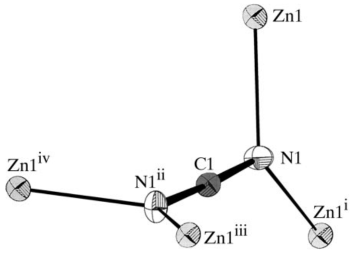

Figure 2
View of the staggered conformation of the anion of $Zn(CN_2)$ and the cations. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $1-y, x-1, -z$; (ii) $\frac{3}{2}-x, y, \frac{3}{4}-z$; (iii) $1-y, x-1, 1-z$; (iv) $\frac{3}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$.]

Experimental

$Zn(CN_2)$ was precipitated from aqueous solutions of $ZnSO_4$ and $Na_2(CN_2)$ (in a 1:1 molar ratio). The precipitate was washed several times with distilled water and dried *in vacuo* at 10^{-3} mbar (1 bar = 10^5 Pa). The resulting powder was compacted. The pellet obtained was placed in a silver crucible, sealed in a glass tube under argon and heated to 843 K over a period of 70 h. It was held at this temperature for 150 h. After slow cooling to room temperature ($6\ K\ h^{-1}$), crystals suitable for single-crystal investigation were obtained.

Crystal data

$Zn(CN_2)$
$M_r = 105.40$
Tetragonal, $I\bar{4}2d$
$a = 8.8047\ (2)$ Å
$c = 5.4329\ (2)$ Å
$V = 421.17\ (2)$ Å^3
$Z = 8$
$D_x = 3.324\ Mg\ m^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 557 reflections
$\theta = 4.41–37.55°$
$\mu = 11.227\ mm^{-1}$
$T = 293\ (2)$ K
Prism, colourless
0.06 × 0.04 × 0.04 mm

Data collection

Bruker AXS SMART CCD diffractometer	$R_{\rm int} = 0.075$
ω scans	$\theta_{\rm max} = 37.51°$
4078 measured reflections	$h = -15 \rightarrow 15$
557 independent reflections	$k = -14 \rightarrow 15$
509 reflections with $I > 2\sigma(I)$	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0262P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$(\Delta/\sigma)_{\rm max} < 0.001$
$wR(F^2) = 0.053$	$\Delta\rho_{\rm max} = 0.75$ e Å^{-3}
$S = 1.007$	$\Delta\rho_{\rm min} = -0.66$ e Å^{-3}
557 reflections	Absolute structure: Flack (1983)
20 parameters	Flack parameter = 0.09 (4)

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1010). Services for accessing these data are described at the back of the journal.

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