



New refinement of the crystal structure of $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ at 100 K

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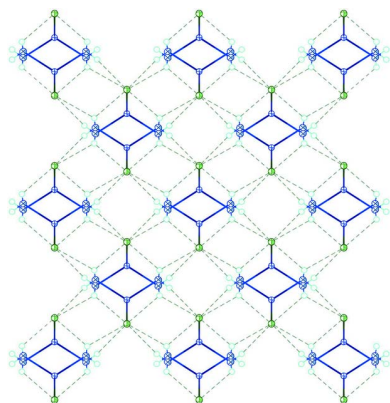
The crystal structure of $[\text{ZnCl}_2(\text{NH}_3)_2]$, diamminedichloridozinc, was re-investigated at low temperature, revealing the positions of the hydrogen atoms and thus a deeper insight into the hydrogen-bonding scheme in the crystal packing. In comparison with previous crystal structure determinations [MacGillavry & Bijvoet (1936). *Z. Kristallogr.* **94**, 249–255; Yamaguchi & Lindqvist (1981). *Acta Chem. Scand.* **35**, 727–728], an improved precision of the structural parameters was achieved. In the crystal, tetrahedral $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$ units (point-group symmetry $mm2$) are linked through $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds into a three-dimensional network.

1. Chemical context

$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ is found in discharged zinc–air batteries. It is formed by dissolution of the zinc electrode in an ZnCl_2 – NH_4Cl electrolyte. At high Zn^{2+} concentrations, the cations subsequently undergo complex formation with NH_3 and Cl^- (Clark *et al.*, 2017). Moreover, in the last century, $\text{Zn}(\text{NH}_3)_n\text{Cl}_2$ phases with $n = 0.167$ –6 have been intensively investigated since these materials appear to be by-products of hydro-cracking of heavy-oil fractions. The monoammine salt with $n = 1$ and the diammine salt with $n = 2$ are the most studied members in this family. Thermal stability, thermomechanical and thermogravimetric behaviour are well documented for these systems (Gardner *et al.*, 1989).

The crystal-structure model of $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ was to this day incomplete, lacking the positions of hydrogen atoms. The crystal structure of $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ was originally determined by MacGillavry & Bijvoet (1936) without refinement of atomic positions [COD number ID 1010197; ICSD number 26136; PDF4 number 01-074-0506]. This incompleteness was rather normal considering the X-ray techniques and measurement conditions at that time. An improved structure model was obtained decades later from a room-temperature data set collected on a four-circle diffractometer by Yamaguchi & Lindqvist (1981), however without hydrogen-atom positions [PDF4 number 04-015-4717]. One more record of this phase in PDF4 [number 00-024-1435] can be found, however with a very limited X-ray powder diffraction pattern range from 5 – $63^\circ/2\theta$, which is unsuitable for Rietveld refinement.

Large single crystals of $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ were obtained as a side product of a chemical vapour transport (CVT) reaction, which allowed the reinvestigation of the crystal structure at low temperature with a particular focus on determination of the H-atom positions.



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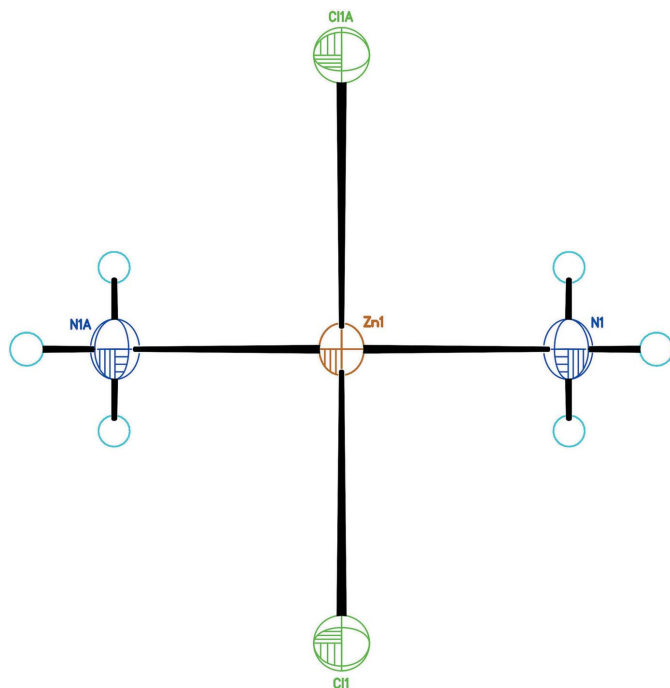


Figure 1
The tetrahedral $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$ group. H atoms (cyan circles) are plotted with arbitrary size. [Symmetry code: (A) $1 - x, \frac{1}{2} - y, z$].

2. Structural commentary

As shown in Fig. 1, the new structure refinement of $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ (100 K data) confirms the former model by Yamaguchi & Lindqvist (1981). The small shrinkage of the unit cell at low temperature is mainly due to lattice dynamics. However, the bond lengths within the $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ tetrahedron refined from 100 K data are similar to the ones obtained from room-temperature data, but with higher precision. This confirms that the tetrahedron is a very rigid building block of the structure (Fig. 2). Two independent H atoms, one in a general position (H1A) and one on a mirror plane (H1B), bond to the nitrogen atom with refined bond lengths of $\text{N1}-\text{H1A} = 0.825(17) \text{ \AA}$ and $\text{N1}-\text{H1B} = 0.74(4) \text{ \AA}$, respectively. Hydrogen-bonding interactions of weak-to-medium strengths (Table 1) between the NH_3 group

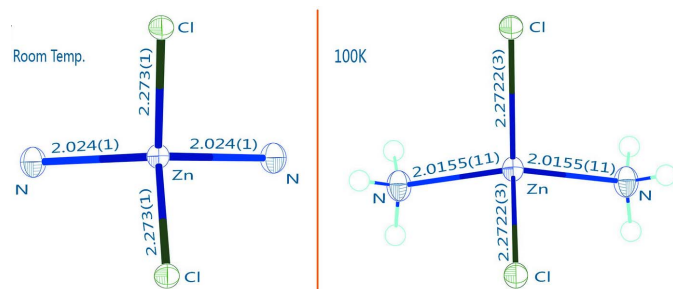


Figure 2
Comparison of the $[\text{ZnN}_2\text{Cl}_2]$ tetrahedra from the room temperature data (left; Yamaguchi & Lindqvist, 1981) and the present 100 K data (right). Bond lengths for the room-temperature data were calculated with *DIAMOND* (Brandenburg, 2006).

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{Cl1}^{\text{i}}$	0.825 (17)	2.806 (18)	3.4552 (9)	137.0 (17)
$\text{N1}-\text{H1A}\cdots\text{Cl1}^{\text{ii}}$	0.825 (17)	2.897 (18)	3.5505 (9)	137.6 (16)
$\text{N1}-\text{H1B}\cdots\text{Cl1}^{\text{iii}}$	0.74 (4)	2.95 (3)	3.5556 (10)	141 (1)
$\text{N1}-\text{H1B}\cdots\text{Cl1}^{\text{iv}}$	0.74 (4)	2.95 (3)	3.5556 (10)	141 (1)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x - \frac{1}{2}, y, -z + \frac{1}{2}$.

and the Cl ligands of adjacent tetrahedra lead to formation of a three-dimensional network, as shown in Fig. 3.

3. Synthesis and crystallization

$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ was obtained during the course of a chemical vapour transport experiment. Prior to use, a silica tube sealed at one end ($\varnothing = 15 \text{ mm}$, wall thickness = 2 mm) was heated under vacuum to 1073 K overnight. Zinc oxide (317 mg) and previously dried ammonium chloride (190 mg) were pressed into pellets and put into the pretreated silica tube. After evacuation to 10^{-6} mbar, the tube was sealed and placed into a horizontal tube furnace. The temperature at the source was slowly heated to 1173 K and maintained at this value for the whole duration of growth. At the low-temperature zone (873 K), a colourless powder mixed with high-quality single crystals of $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ with an irregular morphology was collected after complete cooling to room temperature. Since

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{ZnCl}_2(\text{NH}_3)_2]$
M_r	170.34
Crystal system, space group	Orthorhombic, <i>Imma</i>
Temperature (K)	100
a, b, c (\AA)	7.7077 (2), 8.0226 (2), 8.4526 (3)
V (\AA^3)	522.67 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.56
Crystal size (mm)	$0.26 \times 0.18 \times 0.16$
Data collection	
Diffractometer	Rigaku SuperNOVA
Absorption correction	Analytical (<i>CrysAlis PRO</i> ; Rigaku OD, 2019)
$T_{\text{min}}, T_{\text{max}}$	0.277, 0.454
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2303, 708, 678
R_{int}	0.017
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.833
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.015, 0.036, 1.04
No. of reflections	708
No. of parameters	25
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.50, -0.55

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

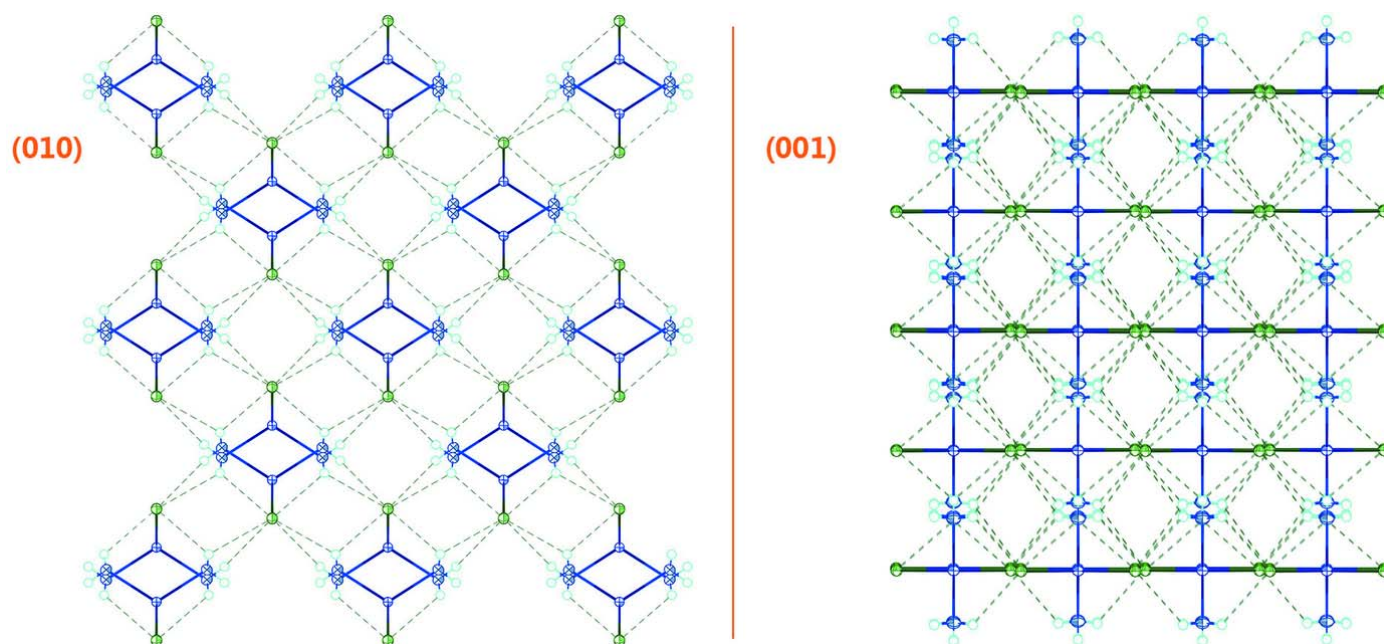


Figure 3
Packing view along the b axis (left) and the c axis (right), showing $N-H\cdots Cl$ interactions between adjacent $[Zn(NH_3)_2Cl_2]$ tetrahedra.

the thermal stability of $Zn(NH_3)_2Cl_2$ is limited as it already decomposes at 463 K (Gardner *et al.*, 1989), it is very likely that $Zn(NH_3)_2Cl_2$ crystallized at the very end of the cooling process.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Unlike the two previous refinements in space group $Imam$, the unit cell was chosen to be in the standard setting ($Imma$) for space group No. 74. Three reflections (020, 002, 004) affected by the incident beam-stop were omitted. The two H atoms were refined freely.

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Diamminedichloridozinc

Crystal data

$[\text{ZnCl}_2(\text{NH}_3)_2]$

$M_r = 170.34$

Orthorhombic, *Imma*

$a = 7.7077$ (2) Å

$b = 8.0226$ (2) Å

$c = 8.4526$ (3) Å

$V = 522.67$ (3) Å³

$Z = 4$

$F(000) = 336$

$D_x = 2.165$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1597 reflections

$\theta = 3.6\text{--}37.4^\circ$

$\mu = 5.56$ mm⁻¹

$T = 100$ K

Irregular, colourless

$0.26 \times 0.18 \times 0.16$ mm

Data collection

Rigaku SuperNOVA
diffractometer

Radiation source: micro-focus sealed X-ray tube

ω scans

Absorption correction: analytical
(*CrysAlis PRO*; Rigaku OD, 2019)

$T_{\min} = 0.277$, $T_{\max} = 0.454$

2303 measured reflections

708 independent reflections

678 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 36.3^\circ$, $\theta_{\min} = 3.5^\circ$

$h = -12 \rightarrow 8$

$k = -13 \rightarrow 12$

$l = -12 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.015$

$wR(F^2) = 0.036$

$S = 1.04$

708 reflections

25 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0188P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.50$ e Å⁻³

$\Delta\rho_{\min} = -0.55$ e Å⁻³

Extinction correction: SHELXL2018
(Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0043 (6)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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	0.500000	0.250000	0.61168 (2)	0.01163 (6)
Cl1	0.500000	0.47954 (3)	0.76915 (3)	0.01375 (6)
N1	0.28237 (15)	0.250000	0.47949 (13)	0.01603 (17)
H1A	0.274 (3)	0.3281 (19)	0.416 (2)	0.045 (4)*
H1B	0.206 (5)	0.250000	0.533 (4)	0.090 (11)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01002 (9)	0.01352 (9)	0.01134 (9)	0.000	0.000	0.000
Cl1	0.01288 (11)	0.01346 (11)	0.01490 (11)	0.000	0.000	-0.00253 (7)
N1	0.0136 (4)	0.0211 (4)	0.0134 (4)	0.000	-0.0016 (3)	0.000

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

Zn1—Cl1 ⁱ	2.2722 (3)	N1—H1A ⁱⁱ	0.825 (17)
Zn1—Cl1	2.2722 (3)	N1—H1A	0.825 (17)
Zn1—N1 ⁱ	2.0155 (11)	N1—H1B	0.74 (4)
Zn1—N1	2.0155 (11)		
Cl1 ⁱ —Zn1—Cl1	108.282 (14)	Zn1—N1—H1A ⁱⁱ	115.0 (13)
N1—Zn1—Cl1	108.951 (17)	Zn1—N1—H1A	115.0 (13)
N1 ⁱ —Zn1—Cl1 ⁱ	108.951 (17)	Zn1—N1—H1B	109 (3)
N1—Zn1—Cl1 ⁱ	108.951 (17)	H1A—N1—H1A ⁱⁱ	99 (2)
N1 ⁱ —Zn1—Cl1	108.950 (17)	H1A—N1—H1B	109 (2)
N1 ⁱ —Zn1—N1	112.66 (7)	H1B—N1—H1A ⁱⁱ	109 (2)

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

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots Cl1 ⁱⁱⁱ	0.825 (17)	2.806 (18)	3.4552 (9)	137.0 (17)
N1—H1A \cdots Cl1 ^{iv}	0.825 (17)	2.897 (18)	3.5505 (9)	137.6 (16)
N1—H1B \cdots Cl1 ^v	0.74 (4)	2.95 (3)	3.5556 (10)	141 (1)
N1—H1B \cdots Cl1 ^{vi}	0.74 (4)	2.95 (3)	3.5556 (10)	141 (1)

Symmetry codes: (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1/2, -y+1, z-1/2$; (v) $-x+1/2, -y+1/2, -z+3/2$; (vi) $x-1/2, y, -z+3/2$.