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Twinned dichlorobis(2,6-dichloropyrazine-N^4)zinc(II)

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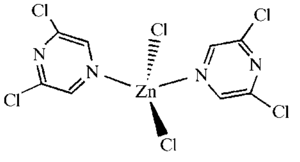
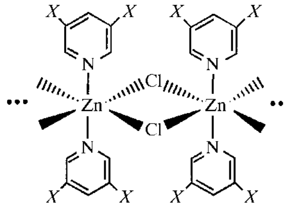
For crystals of the title compound, $[ZnCl_2(C_4H_2Cl_2N_2)_2]$, metric considerations suggest a monoclinic unit cell. However, the symmetry of the diffraction pattern shows the crystals to be triclinic, with very similar lattice constants *a* and *b*, and α and β. All crystals examined were twinned. The discrepancy between the reliability indices for merging in the monoclinic lattice metric symmetry and the triclinic crystal symmetry constitutes an indicator for the volume ratio between the components. The asymmetric unit contains three independent molecules. At the molecular level, the compound shows a distorted tetrahedral coordination around one Zn atom.

Comment

Our interest in intermolecular interactions recently prompted us to synthesize and study the first one-dimensional chain polymers of the type $[Zn(\mu\text{-}Cl)_2py_2]_\infty$, (II) (py is 3,5-dichloropyridine or 3,5-dibromopyridine; Hu & Englert, 2001). 2,6-Dichloropyrazine, the ligand involved in the present study, was expected to have similar steric requirements to the 3,5-dihalopyridines. Furthermore, coordination of a metal should only occur in the 4- and not in the 1-position. Despite these similarities between the dihalopyridine and dihalopyrazine ligands, reaction of zinc dichloride with the latter does not result in the formation of a chain polymer, but gives the title tetrahedral mononuclear complex, (I), underlining the rare nature of the above-mentioned type of coordination polymers.



(I)



X = Cl or Br
(II)

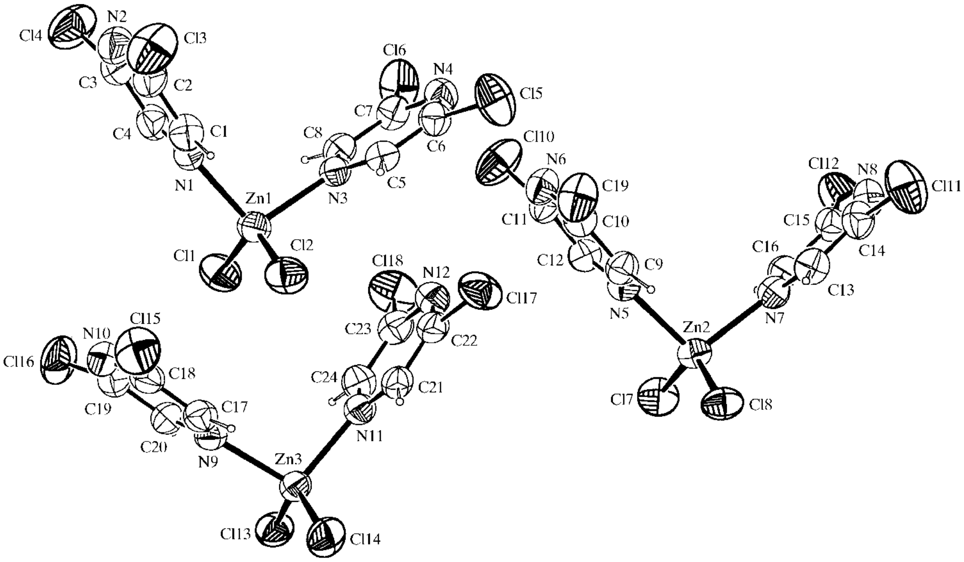


Figure 1
The molecular view of (I) showing the three independent molecules. Displacement ellipsoids are at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

We studied five crystals of (I) by X-ray diffraction and obtained four data sets of comparable accuracy; the intensity data from the fifth sample proved to be less satisfactory in terms of internal consistency and will not be reported. All crystals were twinned. A metrically possible transformation to a monoclinic centred cell is incompatible with the symmetry of the diffraction pattern. The twinning can be classified as metric merohedry (Nespolo & Ferraris, 2000) with monoclinic lattice metric symmetry (LMS). Metric merohedry means that all reflections of the twin components will overlap. In other words, the reciprocal lattice of the twin mimics that of a single crystal and, in the limiting case of a very small twin component, twinning might be completely overlooked. In the present case, the twin law interchanges *a* and *b* according to the matrix (010, 100, 001). Internal agreement factors (R_{int}) for merging the intensity data under the LMS differ strongly between independent data sets and we wish to point out that this variation represents a warning sign for merohedral twinning. A synopsis of R_{int}, obtained under both the triclinic crystal symmetry and the monoclinic LMS, and the volume ratio between the twin components, is provided in Table 1. The discrepancy between R_{int} for merging in the LMS and the crystal symmetry may serve as an indicator for the volume ratio between the twin individuals. In the following discussion, in Table 2 and in the supplementary material), numerical values and their s.u.'s refer to the data set with the smallest contribution of a second individual.

The asymmetric unit of (I) contains three independent molecules (Fig. 1). They are similar not only in terms of bond lengths and angles, but also with respect to the dihedral angles subtended by the planes through the pyrazine ligands [87.40 (18), 87.39 (18) and 89.64 (18)°]. A packing diagram is shown in Fig. 2. No particularly short intermolecular interactions occur, the shortest Cl···Cl distance being *ca* 3.39 Å.

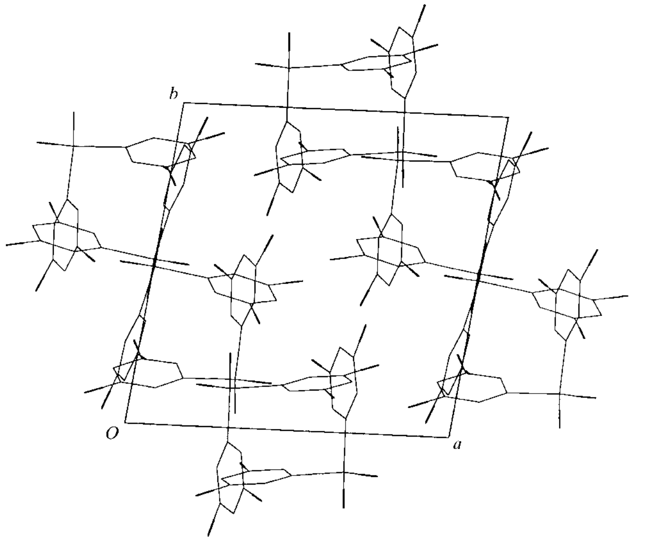


Figure 2
A packing diagram for (I), viewed along the *c* axis.

Experimental

Colourless crystals of (I) were grown by slow evaporation from a solution of $ZnCl_2$ and 2,6-Cl_2-pyrazine (1:2) in ethanol under a flow of nitrogen.

Crystal data

$[ZnCl_2(C_4H_2Cl_2N_2)_2]$
$M_r = 434.22$
Triclinic, $P\bar{1}$
$a = 12.4478\ (7)$ Å
$b = 12.4880\ (8)$ Å
$c = 15.6692\ (9)$ Å
$\alpha = 75.954\ (1)^\circ$
$\beta = 76.134\ (1)^\circ$
$\gamma = 79.438\ (1)^\circ$
$V = 2273.7\ (2)$ Å^3
$Z = 6$
$D_x = 1.903$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 31 443 reflections
$\theta = 1.4$–28.3°
$\mu = 2.67$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.36 × 0.30 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.398$, $T_{max} = 0.587$
31 443 measured reflections
11 257 independent reflections
6480 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 28.3^\circ$
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.077$
$S = 0.81$
11 257 reflections
515 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Internal agreement factors (R_{int}) – a hint for twinning.

Data set	R_{int}(LMS)	R_{int}(crystal)	Volume fraction of 2nd twin individual
1	0.343	0.046	0.1016 (4)
2	0.154	0.061	0.3673 (8)
3	0.075	0.047	0.4765 (8)
4	0.067	0.048	0.4974 (9)

Table 2
Selected geometric parameters (Å, °).

Zn1—N1	2.084 (3)	Zn1—Cl1	2.1833 (11)
Zn1—N3	2.084 (3)	Zn1—Cl2	2.1905 (11)
Zn2—N5	2.094 (3)	Zn2—Cl7	2.1757 (10)
Zn2—N7	2.086 (3)	Zn2—Cl8	2.1894 (10)
Zn3—N9	2.085 (3)	Zn3—Cl13	2.1924 (10)
Zn3—N11	2.095 (3)	Zn3—Cl14	2.1764 (11)
N1—Zn1—N3	101.30 (11)	Cl1—Zn1—Cl2	127.86 (5)
N5—Zn2—N7	101.26 (11)	Cl7—Zn2—Cl8	127.53 (4)
N9—Zn3—N11	101.53 (11)	Cl13—Zn3—Cl14	127.47 (4)

All H atoms were introduced in idealized positions and included as riding (C—H = 0.98 Å), with $U_{iso}(H) = 1.3U_{eq}$(non-H).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1164). Services for accessing these data are described at the back of the journal.

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