Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Dichloro(di-2-pyridylamine)zinc(II): a redetermination at 110 K

Martin Lutz,[a]* Anthony L. Spek,[a] Pieter C. A. Bruijnincx,[b] Robertus J. M. Klein Gebbink[b] and Gerard van Koten[b]

[a]Bijvoet Centre for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and [b]Debye Institute, Organic Chemistry and Catalysis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Correspondence e-mail: m.lutz@chem.uu.nl

Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.001 Å
R factor = 0.020
wR factor = 0.047
Data-to-parameter ratio = 27.6

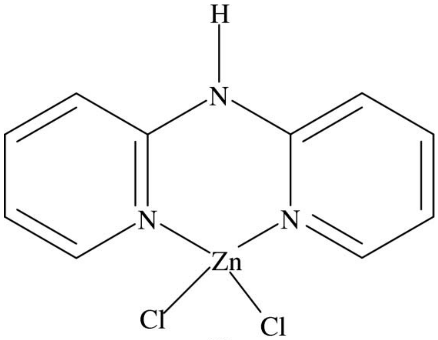
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, [$ZnCl_2(C_{10}H_9N_3)$], has been investigated at 110 K. In contrast with the previously published room-temperature structure [Ho *et al.* (1999). *J. Chem. Soc. Dalton Trans.* pp. 1581–1586], the amine N atom is found to have a symmetrical planar environment. The two independent Zn—Cl distances are significantly different, but the difference of 0.0414 (3) Å is within the range found in other tetrahedral $ZnCl_2$ complexes.

Received 11 August 2005
Accepted 15 August 2005
Online 20 August 2005

Comment

The crystal structure of dichloro[bis(2-pyridyl)amine]zinc(II), (I), has been published by Ho *et al.* (1999) with a distorted non-planar geometry at the amine N atom, expressed by C—N—H angles of 106 (2) and 117 (2)° and a rather long N—H distance of 1.12 (4) Å. In order to determine more precisely the environment of the amine N atom, we re-determined the structure at low temperature. All H atoms could be located in the difference Fourier map and were refined freely with isotropic displacement parameters. The amine N atom has a symmetrical planar geometry, with C—N—H angles of 114.1 (12) and 112.2 (11)° and an angle sum of 360.0°, and an N—H distance of 0.827 (17) Å (Fig. 1).



(I)

The molecule of (I) has an approximate mirror symmetry with an r.m.s. deviation of 0.064 Å (Pilati & Forni, 1998). The N—H group, the Zn atom and the Cl ligands are located on the local mirror plane. Thus, the ligand is not completely flat but shows an interplanar angle of 5.96 (5)° between the two pyridine rings. The central six-membered chelate ring, containing the Zn atom, three N atoms and atoms C5 and C6, is puckered. A conformational analysis (Cremer & Pople, 1975) shows that this ring has an envelope conformation (Evans & Boeyens, 1989), with the Zn atom 0.1436 (3) Å

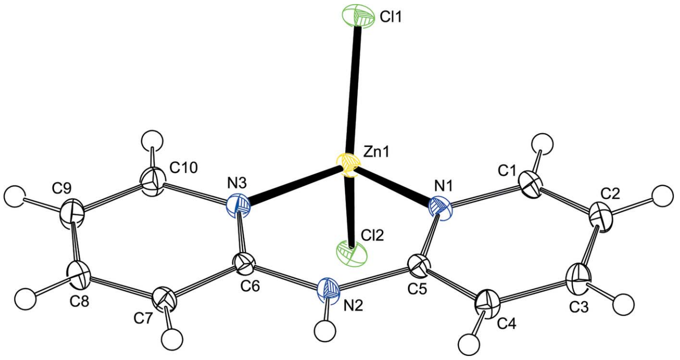


Figure 1
Displacement ellipsoid plot of (I). Ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

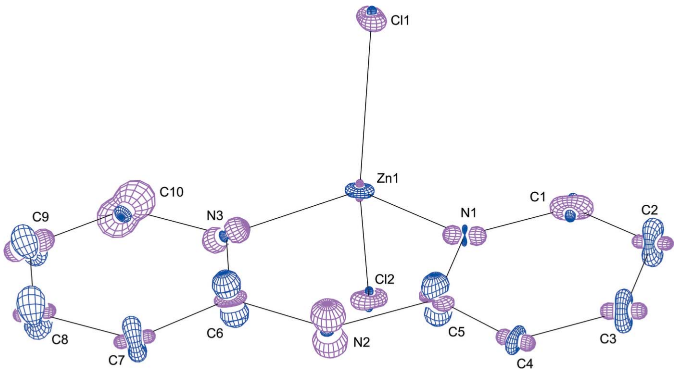


Figure 2
PEANUT plot (Hummel *et al.*, 1990), showing the difference between the measured displacement parameters and the parameters obtained by a rigid-body refinement using the program *THMA11* (Schomaker & Trueblood, 1998). A scale factor of 6.15 was used for the root-mean-square surfaces. Blue lines indicate positive differences and purple lines negative ones. The largest difference is found for atom N2 (see text).

above the plane. A closer inspection of the anisotropic displacement parameters indicates that the amine atom N2 has the largest anisotropicity and moves perpendicular to the plane. This can also be seen in the difference between the measured displacement ellipsoids and the ellipsoids from a rigid-body model (Fig. 2). The puckering of the central chelate ring is thus not considered to be static.

The crystal structure of (I) is isostructural with the corresponding Co^{II} complex, (II) (Cotton *et al.*, 1998). The Zn—N distances of 2.0202 (8) and 2.0280 (8) Å in (I) are very similar to the Co—N distances of 1.998 (3) and 2.008 (3) Å in (II). Correspondingly, the C—N—C angles of the amine group, 133.67 (8)° in (I) and 133.7 (3)° in (II), are the same. This amine angle is larger than the angle at the keto group of 126.1 (2)° in the corresponding dipyridylketone ZnCl$_2$ complex (Katsoulakou *et al.*, 2002), which shows a similar envelope conformation of the central chelate ring.

The *M*—Cl distances in (I) differ from each other by 0.0414 (3) Å. Such a difference is not unusual in tetrahedral zinc complexes. In (II), this difference is only 0.022 (1) Å. This might be an effect of the different measurement temperatures of 110 K for (I) and 213 K for (II), but a real difference between Zn and Co cannot be excluded. In both cases, the Cl atom of the longer bond is the acceptor of hydrogen bonds.

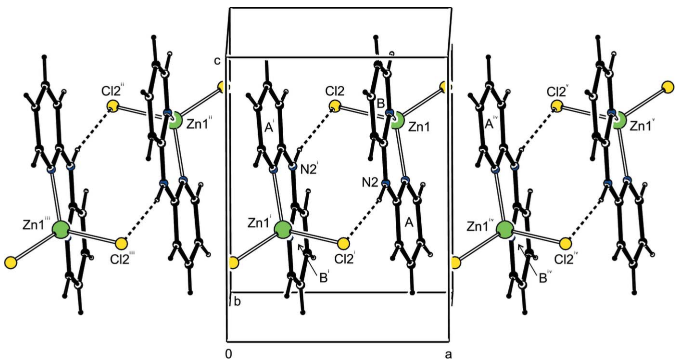


Figure 3
Formation of dimers by N—H···Cl hydrogen bonding. π–π stacking within the dimers and between the dimers forms a one-dimensional rod in the crystallographic *a* direction. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x - 1, y, z$; (iii) $-x, 1 - y, 1 - z$; (iv) $2 - x, 1 - y, 1 - z$; (v) $x + 1, y, z$.]

A centrosymmetric dimer is formed *via* intermolecular hydrogen bonding, with the amine group as donor and atom Cl2 as acceptor. Within this dimer, there are additional π–π interactions between the pyridine rings, with a distance of about 3.48 Å between ring *A* (N1/C1–C5) and ring B^{i} [N3/C6–C10; symmetry code: (i) $1 - x, 1 - y, 1 - z$] of the second molecule in the dimer (and *vice versa*). A similar distance is found between the dimers, with a distance of approximately 3.45 Å between ring *A* and ring B^{iv} [symmetry code: (iv) $2 - x, 1 - y, 1 - z$]. These π–π interactions result in the formation of a rod-like arrangement in the direction of the crystallographic *a* axis (Fig. 3). Different rods are connected by weak intermolecular C—H···Cl interactions between atoms C9 and Cl2 (Table 2).

Experimental

The synthesis and crystallization of (I) were performed according to the literature method of Ho *et al.* (1999).

Crystal data

[ZnCl$_2$(C$_{10}$H$_9$N$_3$)]
M_r = 307.47
Triclinic, $P\overline{1}$
a = 7.34630 (18) Å
b = 8.58832 (18) Å
c = 9.4140 (2) Å
α = 74.888 (2)°
β = 89.897 (1)°
γ = 85.238 (1)°
V = 571.31 (2) Å^3
Z = 2
D_x = 1.787 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 16716 reflections
θ = 2.2–35.0°
μ = 2.59 mm^{-1}
T = 110 (2) K
Plate, colourless
0.27 × 0.24 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.51, T_{max} = 0.81
26436 measured reflections
4993 independent reflections
4516 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 35.0°
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$

m1814 Lutz *et al.* • [ZnCl$_2$(C$_{10}$H$_9$N$_3$)] *Acta Cryst.* (2005). E**61**, m1813–m1815

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.047$
$S = 1.06$
4993 reflections
181 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 0.2075P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.0202 (8)	Zn1—Cl2	2.2502 (3)
Zn1—N3	2.0280 (8)	N2—C6	1.3835 (12)
Zn1—Cl1	2.2088 (2)	N2—C5	1.3862 (11)
N1—Zn1—N3	93.19 (3)	Cl1—Zn1—Cl2	112.465 (10)
N1—Zn1—Cl1	113.77 (2)	C6—N2—C5	133.67 (8)
N3—Zn1—Cl1	116.57 (2)	C6—N2—H2*N*	114.1 (12)
N1—Zn1—Cl2	112.13 (2)	C5—N2—H2*N*	112.2 (11)
N3—Zn1—Cl2	107.20 (2)		
N3—Zn1—N1—C5	15.55 (8)	C6—N2—C5—N1	−6.30 (16)
N1—Zn1—N3—C6	−15.39 (8)	Zn1—N3—C6—N2	7.96 (12)
Zn1—N1—C5—N2	−8.33 (12)	C5—N2—C6—N3	6.47 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···Cl2^{i}	0.83 (2)	2.45 (2)	3.2563 (8)	166 (2)
C9—H9···Cl2^{iv}	0.95 (2)	2.81 (2)	3.6803 (10)	154 (1)

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

The X-ray intensities were obtained with two different exposure times and rotation angles of 1°. 363 φ and 770 ω scans were measured with an exposure time of 40 s per frame, and 364 φ scans with an exposure time of 8 s per frame. All benzene H atoms were refined freely with isotropic displacement parameters, in order to demonstrate that the outcome of the free refinement of H2N is reliable.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *PEAKREF* (Schreurs, 2005); data reduction: *EVALCCD* (Duisenberg *et al.* 2003); method used to solve structure: coordinates taken from literature (Ho *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

This work was supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW–NWO).

References

Cotton, F. A., Daniels, L. M., Jordan, G. T. IV & Murillo, C. A. (1998). *Polyhedron*, **17**, 589–597.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Evans, G. G. & Boeyens, J. A. (1989). *Acta Cryst.* B**45**, 581–590.
Ho, K.-Y., Yu, W.-Y., Cheung, K.-K. & Che, C.-M. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1581–1586.
Hummel, W., Hauser, J. & Bürgi, H. B. (1990). *J. Mol. Graphics*, **8**, 214–220.
Katsoulakou, E., Lalioti, N., Raptopoulou, C. P., Terzis, A., Manessi-Zoupa, E. & Perlepes, S. P. (2002). *Inorg. Chem. Commun.* **5**, 719–723.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Pilati, T. & Forni, A. (1998). *J. Appl. Cryst.* **31**, 503–504.
Schomaker, V. & Trueblood, K. N. (1998). *Acta Cryst.* B**54**, 507–514.
Schreurs, A. M. M. (2005). *PEAKREF*. Utrecht University, The Netherlands.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2002). *SADABS*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Acta Cryst. (2005). E**61**, m1813–m1815 Lutz *et al.* • [$ZnCl_2(C_{10}H_9N_3)$] **m1815**