β-Dichloro-(2-pyridinaldazine)zinc(II)

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Abstract. $Zn(C_{12}H_{10}N_4)Cl_2$, monoclinic, $P2_1/n$; $a = 8.677$ (7), $b = 14.582$ (16), $c = 10.822$ (9) Å, $\beta = 90.50$ (5)°, $Z = 4$, $D_x = 1.681$ (5), $D_m = 1.685$ (7) g cm^{-3}. The $C_{12}H_{10}N_4$ ligand (PAA) is shown to act as a tridentate chelate with Zn in a five-coordinate complex. The Zn coordination is mid-way between trigonal bipyramidal and a square pyramidal configuration. Two atoms in the azine bridge are disordered.

Introduction. The crystals used in this study were kindly supplied by Dr Wilmer J. Stratton. Intensities and cell dimensions were measured on an automated Picker FACS I diffractometer with an orange tabular crystal of dimensions $0.16 \times 0.12 \times 0.06$ mm. Systematic absences $h0l$, $h + l \neq 2n$ and $0k0$, $k \neq 2n$ confirm the space group $P2_1/n$. Data were collected to a maximum 2θ value of $45°$ with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å, $\theta-2\theta$ scan, scan-width $= 2.0°$,

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Fig. 1. Bond distances for [Cl₂(PAA)Zn(II)]. The e.s.d.'s for the bond distances are approximately as follows: for Zn–Cl, 0·005 Å; for Zn–N, 0·02 Å; for type L–L, 0·03 Å (L=N,C); for bonds involving N(4) and N(5), 0·07 Å. The dashed bonds to N(4) and N(5) indicate a bonding scheme connecting the alternate azine N sites.

scan speed $1°$ min^{-1}). 20 s background counts were taken at both ends of the scan range. 1809 unique reflections were measured, of which 961 with $I > 2\sigma(I)$ were used in subsequent refinement. Corrections for Lorentz and polarization effects were applied, but no absorption correction was made ($\mu = 22.3$ cm^{-1}). Three reference reflections, which were monitored throughout the data collection, showed no significant changes in intensity.

The heavy-atom method was used to locate the position of the Zn and Cl atoms. A subsequent Fourier map revealed the positions of the C and N atoms. The structure was refined by a full-matrix least-squares program (*FXLS*: van Remoortere & Boer, 1967) with weights based on experimental counting statistics. A Fourier map calculated after the isotropic refinement of the heavy atoms showed the N(2) peak to be extended along a line perpendicular to the N(2)–Zn bond and in the plane of the ligand. A second peak between N(3) and C(1) suggested the disorder model shown in Fig. 1. A refinement of the population parameters for N(2–5) with invariant thermal parameters ($B = 6.0$) yielded occupancies of 0·6, 0·5, 0·4, 0·4, respectively. In an alternate approach to determining occupancies for the disordered nitrogens, the isotropic thermal parameters on N(2–5) were refined for several different values of the occupancy of these positions. The population of N(4) was assumed equal to N(5) and the total population of the four sites to be 2·0. The refinement with the occupancy of N(4) and N(5) equal to 0·4 and of N(2) and N(3) equal to 0·6 resulted in nearly equal thermal parameters for the N(2), N(4) pair and for the N(3), N(5) pair. The population parameters were fixed at these values in subsequent refinement.

Continued refinement (*SF*1–4: Shiono, 1969; *ORFLS*: Busing, Martin & Levy, 1962) on the coordinates of all atoms and anisotropic thermal parameters of all atoms except N(2–5), which were given isotropic thermal parameters, led to a convential R of 0·156 for all reflections, 0·074 omitting reflections with $I < 2\sigma(I)$, and a weighted R on this restricted data set of 0·075. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1968). A series of difference Fourier maps focusing on the azine bridge region of the molecule were examined, but did not lead to any essential improvement in the disorder model. While the peaks corresponding to positions N(2) and N(3) were significantly higher than for N(4) and N(5), further effort to determine the
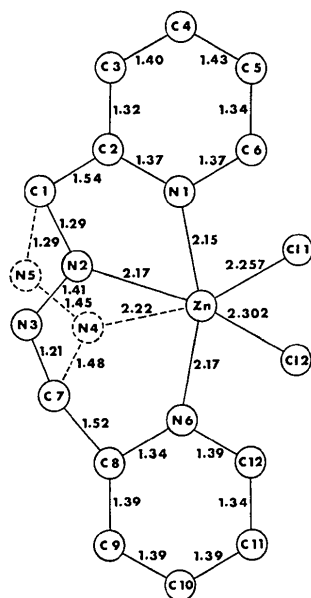
relative occupancies of these azine N positions seemed unwarranted. Only a few difference peaks could be assigned to H positions, hence no H atoms were included in the model. The final positional and thermal parameters are given in Table 1.*

Discussion. An extended study by Wilmer Stratton and co-workers of metal chelate compounds containing tetrafunctional azine ligands has shown this system of ligands to be quite unusual in the variability of chelation (Stratton, 1970; and references therein). One such ligand, 2-pyridinaldazine (PAA) forms at least four types of compounds with zinc(II) salts: $[Zn_2(PAA)_3]X_4$, $[Zn(PAA)_2]X_2$, α-$[Zn(PAA)X_2]$ and β-$[Zn(PAA)X_2]$ (Stratton & Hansma, 1975). A variety of chemical and physical evidence indicates that the α 1:1 compounds are tetrahedral with simple bidentate coordination, whereas the β 1:1 compounds are apparently five-coordinate with tridentate coordination of the ligand. The present study was undertaken in order to verify the latter structure for β-$[Zn(PAA)Cl_2]$.

The bond distances and the atom labeling scheme for β-dichloro-(2-pyridinaldazine)zinc(II) are shown in Fig. 1 and the bond angles are given in Table 2. The molecular geometry is illustrated in Fig. 2. No intermolecular contacts shorter than the sum of van der Waals radii were found.

The disorder, which is evidenced by the alternate positions for N(2) and N(3) [labeled N(4) and N(5) in Fig. 1], could be understood as a static packing dis-

* The structure factor tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31189 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

order, in which approximately 40% of the molecules are rotated about the pseudo twofold axis roughly bisecting the Cl(1)–Zn–Cl(2) angle. This model would assume the molecules to have an electrostatic field of nearly $mm2$ symmetry, which would allow packing of the molecules in two orientations of approximately the same energy. The disorder might also be accounted for by a dynamic rotation of the C(1), N(2), N(3), C(7) group about the C(1)–C(2) and C(7)–C(8) single bonds with N(3) replacing N(2) as the atom coordinated to Zn. The X-ray data alone are insufficient to discriminate between these two models. Either of these would achieve the interchange of the five- and six-membered chelate rings. However, most of the atoms would be nearly superimposed on their previous position with only N(2) and N(3) being shifted by appreciable
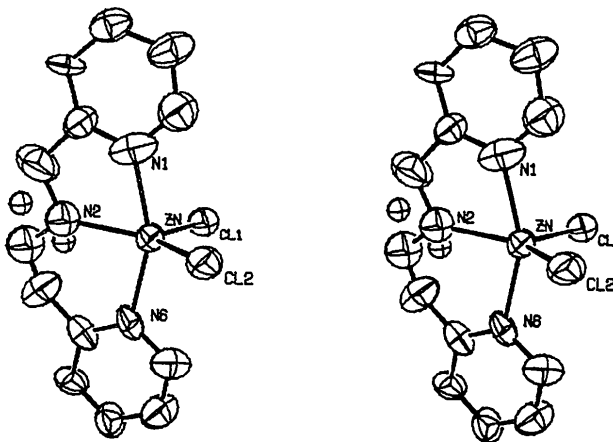

Fig. 2. A stereographic drawing of the molecule showing the thermal ellipsoids at 50% probability for all atoms, except N(4) and N(5).

Table 1. *Atomic parameters*

Estimated standard deviations of the least significant digits are indicated in parentheses. The mean square atomic vibrations are in $Å^2 \times 10^2$.

	x	y	z	U_{11} (U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	0·5329 (2)	0·3709 (1)	0·7271 (2)	7·0	4·3	6·0	0·3	2·3	0·2
Cl(1)	0·6356 (5)	0·3604 (3)	0·9189 (3)	10·0	5·0	6·7	−0·2	1·3	0·1
Cl(2)	0·2677 (4)	0·3699 (3)	0·7290 (4)	7·1	4·6	9·6	0·3	3·0	−0·8
N(1)	0·546 (2)	0·5170 (8)	0·702 (1)	9·6	5·3	10·4	−1·5	−3·2	1·3
N(2)*	0·697 (3)	0·399 (1)	0·581 (2)	7·0					
N(3)	0·811 (3)	0·347 (2)	0·521 (2)	9·0					
N(4)	0·716 (6)	0·358 (3)	0·586 (4)	9·0					
N(5)	0·822 (5)	0·418 (3)	0·522 (4)	10·0					
N(6)	0·552 (1)	0·2271 (8)	0·675 (1)	5·4	7·2	5·0	1·3	1·2	−1·8
C(1)	0·746 (2)	0·491 (1)	0·548 (2)	15·0	7·2	8·8	3·1	−1·0	−1·7
C(2)	0·643 (2)	0·558 (1)	0·620 (1)	10·8	5·7	5·9	−2·5	0·2	0·6
C(3)	0·653 (2)	0·6474 (8)	0·600 (1)	11·9	2·1	8·2	0·7	1·3	−0·9
C(4)	0·558 (2)	0·7044 (9)	0·671 (1)	7·2	4·8	6·9	−1·0	−2·4	0·7
C(5)	0·453 (2)	0·666 (1)	0·759 (2)	5·7	6·0	11·4	−1·5	−0·7	1·4
C(6)	0·456 (2)	0·575 (1)	0·771 (2)	7·3	7·2	10·0	0·6	1·3	0·4
C(7)	0·771 (2)	0·269 (1)	0·539 (2)	9·4	8·6	11·0	−2·4	0·1	2·4
C(8)	0·662 (2)	0·200 (1)	0·597 (1)	6·8	7·7	4·8	1·4	−0·7	−1·7
C(9)	0·690 (2)	0·1082 (9)	0·569 (1)	8·4	4·0	7·1	1·4	−0·4	−1·1
C(10)	0·595 (2)	0·045 (1)	0·628 (1)	6·8	8·4	6·8	0·2	1·3	−1·2
C(11)	0·483 (2)	0·075 (1)	0·710 (2)	6·3	5·6	12·2	0·3	2·1	0·5
C(12)	0·456 (2)	0·164 (1)	0·731 (2)	7·3	6·1	9·7	−0·6	−0·7	−1·1

* The occupancy of positions N(2) and N(3) is 0·6 and for N(4) and N(5) the occupancy is 0·4.

Table 2. *Bond angles*

Cl(1)–Zn—Cl(2)	112·2 (2)	N(5)—N(4)—C(7)	99·0 (3)
Cl(1)–Zn—N(1)	99·3 (4)	N(4)—N(5)—C(1)	94·0 (3)
Cl(1)–Zn—N(2)	115·3 (7)	Zn—N(6)—C(8)	120·5 (9)
Cl(1)–Zn—N(4)	110·0 (1)	Zn—N(6)—C(12)	119·0 (1)
Cl(1)–Zn—N(6)	98·2 (3)	C(8)—N(6)—C(12)	120·0 (1)
Cl(2)–Zn—N(1)	93·6 (4)	N(2)—C(1)—C(2)	107·0 (2)
Cl(2)–Zn—N(2)	131·9 (7)	N(5)—C(1)—C(2)	160·0 (2)
Cl(2)–Zn—N(4)	137·0 (1)	N(1)—C(2)—C(1)	114·0 (1)
Cl(2)–Zn—N(6)	94·2 (4)	N(1)—C(2)—C(3)	125·0 (2)
N(1)–Zn—N(2)	71·8 (7)	C(1)—C(2)—C(3)	120·0 (2)
N(1)–Zn—N(4)	88·0 (1)	C(2)—C(3)—C(4)	117·0 (1)
N(1)–Zn—N(6)	156·5 (5)	C(3)—C(4)—C(5)	121·0 (1)
N(2)–Zn—N(6)	86·5 (7)	C(4)—C(5)—C(6)	116·0 (1)
N(4)–Zn—N(6)	71·0 (1)	N(1)—C(6)—C(5)	124·0 (2)
Zn—N(1)–C(2)	123·0 (1)	N(3)—C(7)—C(8)	150·0 (2)
Zn—N(1)–C(6)	120·0 (1)	N(4)—C(7)—C(8)	103·0 (2)
C(2)–N(1)–C(6)	116·0 (1)	N(6)—C(8)—C(7)	121·0 (1)
Zn—N(2)–N(3)	134·0 (2)	N(6)—C(8)—C(9)	123·0 (1)
Zn—N(2)–C(1)	123·0 (2)	C(7)—C(8)—C(9)	116·0 (1)
N(3)–N(2)–C(1)	100·0 (2)	C(8)—C(9)—C(10)	115·0 (1)
N(2)–N(3)–C(7)	103·0 (2)	C(9)—C(10)—C(11)	120·0 (1)
Zn—N(4)–N(5)	137·0 (3)	C(10)—C(11)—C(12)	122·0 (2)
Zn—N(4)–C(7)	123·0 (2)	N(6)—C(12)—C(11)	118·0 (1)

amounts. The slight misalignment of the remaining nearly coincident atoms has been absorbed into the thermal parameters and is displayed by large standard deviations in atomic positions. In some cases, bond distances and angles calculated from centers of thermal ellipsoids, which in fact represent two displaced atomic positions, are somewhat inaccurate. This is especially true for bonds and angles involving atoms C(1) and C(7) in the azine bridge.

Of the several possible geometric isomers for the PAA ligand (Stratton, Rettig & Drury, 1969; Stratton & Hansma, 1975), the one found here is the *cis-trans* form, which is the only isomer conducive to tridentate chelation. The bond distances and angles for the PAA ligand are generally those expected to within the accuracy of the disorder model. The six atoms of each pyridyl ring have a root-mean-square displacement of 0·01 Å from the least-squares plane defined by those atoms. These two planes form a dihedral angle of 8°, which is composed of a twist about the N(1)–N(6) axis, plus a slight bend of the N(1), C(2–6) ring toward the Cl(2) side of the molecule. The Zn atom is in the N(1), C(2–6) plane, but displaced a perpendicular distance of 0·23 Å from the N(6), C(8–12) plane toward the Cl(1) side of the molecule.

The coordination about the Zn atom is similar to that found for terpyridylzinc chloride (Einstein & Penfold, 1966; Corbridge & Cox, 1956), which has been interpreted both as a distortion from trigonal bipyramidal coordination and as a distorted square pyramid (Gerloch, 1966). It has recently been suggested (Muetterties & Guggenberger, 1974) that the precise intermediate shape of a five-atom polyhedron can be most usefully described in terms of the three dihedral angles about the edges connecting the equatorial atoms in the trigonal bipyramidal limiting case. As the coordination polyhedron is converted to square pyramidal, one of

the dihedral angles would go to zero as the two adjacent triangular faces become the square base and the other two equatorial edges become edges connecting the apex of the square pryamid to the base corners. Hence, for the ideal trigonal bipyramid, the shape determining dihedral angles e_3, e_1 and e_2 are all equal to 53·1°, while for the ideal tetragonal pyramid $e_3 = 0·0°$, and $e_1 = e_2 = 75·7°$. When atom coordinates are adjusted to give equal Zn–Cl and Zn–N distances the shape determining dihedral angles for the present compound are $e_3 = 30°$, $e_1 = 55°$ and $e_2 = 76°$, where e_3, e_1 and e_2 are the angles between the normals to planes, which meet at edges N(2)–Cl(2), N(2)–Cl(1) and Cl(1)–Cl(2), respectively; while for the terpyridylzinc chloride these dihedral angles are $e_3 = 15°$, $e_1 = 57°$, and $e_2 = 84°$. The inequality of e_1 and e_2 shows that neither of these structures lies on the Berry (1960) rearrangement path which retains C_{2v} symmetry throughout the interconversion of the two idealized polyhedra. While many ML_5-type complexes observe this constraint, the steric requirements of the ligands account for its violation in these cases. The mode of distortion in these two Zn complexes appears to be similar, with the terpyridyl complex approaching the square pyramidal conformation, while the PAA complex lies approximately midway between the two ideal polyhedra.

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