# [2,6-Bis(2-pyridylamino)pyridine]dichloro-cadmium(II)

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In the title complex, $[CdCl_2(C_{15}H_{13}N_5)]$ or $[CdCl_2(tpdaH_2)]$ ($tpdaH_2$ is tripyridyldiamine), the geometry at the five-coordinate Cd atom is distorted tetragonal pyramidal, with two Cl atoms and the three pyridine N atoms of the tripyridyldiamine molecule. The ligand ($tpdaH_2$) adopts an all-*anti* form. The observed Cd—N bond lengths are 2.2958 (19), 2.3254 (19) and 2.3067 (19) Å, slightly shorter than those in the Cd^{2+} complex with di-2-pyridylamine (dpa).

Comment

Transition metal complexes containing a polypyridylamine ligand are of interest to chemists because of their novel structures and special properties. The polypyridyl ligand, with its good σ electron-donating and π electron-withdrawing properties, is a popular chelating ligand used in modern coordination chemistry (Jing *et al.*, 2000). Metal chain complexes are mostly used in the fundamental study of metal–metal interactions (Yang *et al.*, 1997; Cotton *et al.*, 1998) and investigated for their potential application as molecular metal wires. Previously, a series of polynuclear metal chain complexes have been successfully synthesized and character-ized (Sheu *et al.*, 1996; Shieh *et al.*, 1997; Chang *et al.*, 1999; Peng *et al.*, 2000). Recently, we extended these studies by synthesizing some new transition metal complexes having metal atoms with larger atomic radii. We designed the reaction of the cadmium(II) ion with tripyridyldiamine ($tpdaH_2$) using earlier methods (Sheu *et al.*, 1996; Shieh *et al.*, 1997) and attempted to synthesize Cd—Cd metal chain complexes. The result shows that the synthesis of polynuclear metal chain complexes of cadmium is very difficult under these conditions, and only the mononuclear complex was obtained.

(I)
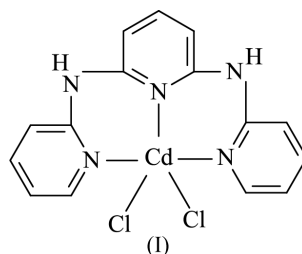
As shown in Fig. 1, the title complex, (I), is a neutral mol-ecule and the geometry of the Cd atom is distorted tetragonal pyramidal, with two Cl atoms and three N atoms from pyridine rings; this structure is similar to others found in the literature (Zhou *et al.*, 2000; Bian *et al.*, 2003). Atom Cl1 is located at the apex of the pyramid, and atoms N1, N3, N5 and Cl2 lie at the four corners of the tetragonal pyramidal base, with a
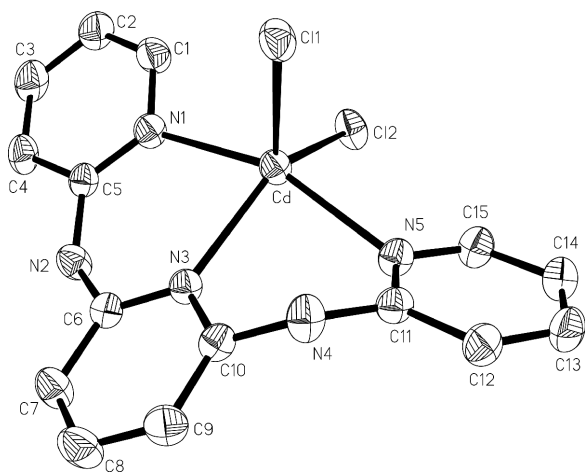
Figure 1
Molecular structure of the title compound. Displacement ellipsoids are shown at the 35% probability level and H atoms have been omitted.
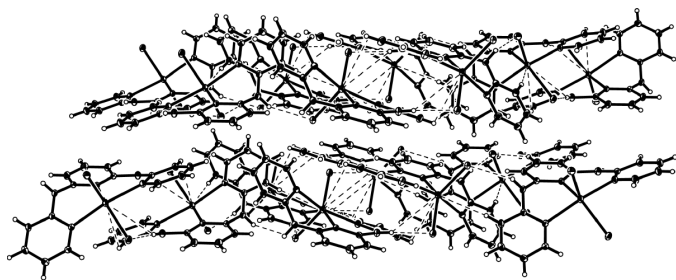
Figure 2
The packing diagram of the title compound. Displacement ellipsoids are shown at the 15% probability level. Dashed lines indicate hydrogen bonds.

maximum deviation from the mean plane of these basal atoms (N1, N3, N5 and Cl2) of 0.2380 (3) Å for N3. The lengths of the two Cd—Cl bonds are 2.5298 (6) and 2.4691 (6) Å, both within normal ranges (Tao *et al.*, 2002). The Cd—N bond lengths are 2.2958 (19), 2.3254 (19) and 2.3067 (19) Å, and are slightly shorter than those in the Cd^{II}–di-2-pyridylamine (dpa) complex (Zhu *et al.*, 2001). Selected bond distances and angles are listed in Table 1. To the best of our knowledge, five-coordinate Cd^{II} is found in only about 5% of cadmium complexes (Wang *et al.*, 2003; Sigel & Martin, 1994). The tripyridyldiamine is a tridentate chelating ligand in this structure, and it exhibits an all-*anti* conformation. The three pyridine rings are not coplanar, and the dihedral angles between the planes of the central pyridine ring and the others are 15.6 (5) and 34.1 (3)°.

The molecular stacking is evident from the packing diagram (Fig. 2). The complex molecules overlap each other, forming layers linked by van der Waals forces. A closer inspection of the crystal structure reveals the presence of intermolecular hydrogen bonds between adjacent Cl atoms and amine N atoms of the tpdaH$_2$ ligand in the same layer, which play an important role in the assembly of the crystal structure. The main hydrogen bonds are listed in Table 2.

Experimental

Tripyridyldiamine (0.415 g), CdCl$_2$·2H$_2$O (0.74 g) and naphthalene (9.72 g) were placed in an Erlemeyer flask. The system was put under vacuum for 10 min and always kept under nitrogen. The mixture was heated for 10 min until boiling, and then anhydrous *tert*-butyl alcohol (8 ml) was added with an injector and the mixture was kept boiling for 1 h. A mixture of potassium *tert*-butoxide (0.5 g) and anhydrous *tert*-butyl alcohol (5 ml) was then injected, with continued heating for 4 h. The mixture was washed with *n*-hexane, and the solid was recrystallized from acetonitrile/diethyl ether. Light-yellow single crystals were obtained after 3 d.

Crystal data

[CdCl$_2$(C$_{15}$H$_{13}$N$_5$)]	$D_x = 1.823$ Mg m^{-3}
$M_r = 446.60$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6805
$a = 7.7545$ (2) Å	reflections
$b = 23.8945$ (6) Å	$\theta = 2.5–27.5°$
$c = 9.4462$ (2) Å	$\mu = 1.68$ mm^{-1}
$\beta = 111.644$ (1)°	$T = 295$ (2) K
$V = 1626.88$ (7) Å^3	Plate, light yellow
$Z = 4$	$0.40 \times 0.40 \times 0.05$ mm

Data collection

Bruker SMART CCD area detector diffractometer	3733 independent reflections
	3041 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.023$
Absorption correction: multi-scan (North *et al.*, 1968)	$\theta_{max} = 27.5°$
	$h = -10 \rightarrow 10$
$T_{min} = 0.523$, $T_{max} = 0.920$	$k = -28 \rightarrow 31$
14 214 measured reflections	$l = -12 \rightarrow 10$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2]$
$wR(F^2) = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
3733 reflections	$\Delta\rho_{max} = 0.46$ e Å^{-3}
208 parameters	$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd—N1	2.2958 (19)	Cd—Cl1	2.4691 (6)
Cd—N5	2.3067 (19)	Cd—Cl2	2.5298 (6)
Cd—N3	2.3254 (19)		
N1—Cd—N5	158.84 (7)	N5—Cd—Cl1	100.01 (5)
N1—Cd—N3	82.90 (7)	N3—Cd—Cl1	105.69 (5)
N5—Cd—N3	83.57 (7)	N1—Cd—Cl2	88.43 (5)
N1—Cd—Cl1	99.27 (5)	Cl1—Cd—Cl2	114.43 (2)

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
N2—H2A$\cdots$Cl2^i	0.86	2.44	3.303 (3)	170
N4—H4A$\cdots$Cl1^{ii}	0.86	2.59	3.294 (6)	139
C15—H15A$\cdots$Cl2	0.93	2.73	3.408 (2)	131

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

H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.93 Å, and refined in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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