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# [2,6-Bis(2-pyridylamino)pyridine]dinitratocadmium monohydrate

**Xiao-Niu Fang, Xin-Fa Li and Xi-Rui Zeng***

Department of Chemistry, JingGangShan College, 343009 Ji'an, Jiangxi, People's Republic of China

Correspondence e-mail: xiruizeng@jgsu.edu.cn

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**Key indicators**

Single-crystal X-ray study
$T$ = 295 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ factor = 0.026
$wR$ factor = 0.060
Data-to-parameter ratio = 15.6

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

The Cd atom in the title complex, $[Cd(NO_3)_2(C_{15}H_{13}N_5)]\cdot H_2O$ or $[Cd(NO_3)_2(tpdaH_2)]\cdot H_2O$ ($tpdaH_2$ is tripyridyldiamine), has a pentagonal–bipyramidal coordination formed by the tridentate $tpdaH_2$ ligand and two chelate nitrate groups. The $tpdaH_2$ ligand is *mer*-coordinated, with the N atom of the central pyridine ring in the equatorial position [Cd—N = 2.3148 (17) Å] and the N atoms of the peripheral pyridine rings in the axial positions [Cd—N = 2.2345 (19) and 2.2351 (19) Å, and N—Cd—N = 169.39 (6)°]. The remaining four equatorial positions are occupied by the four O atoms of two nitrate groups, one of which has almost equal Cd—O bond lengths [2.431 (2) and 2.4644 (19) Å], whereas the other shows a significant difference between the Cd—O bond lengths [2.441 (2) and 2.603 (2) Å]. The H atoms of both NH groups of the $tpdaH_2$ ligand are involved in hydrogen bonds with water O atoms as acceptors, whereas both water H atoms form hydrogen bonds with the O atoms of one of the nitrate groups. The hydrogen bonds link the molecules of the title complex and solvent molecules into an infinite three-dimensional network.

## Comment

Transition metal complexes with polypyridylamine ligands have attracted considerable interest because of their diverse structures and special optical and electromagnetic properties (Xu *et al.*, 2004). The tripyridyldiamine ligand exhibits $\sigma$-donor and $\pi$-acceptor properties and represents a popular chelating ligand (Jing *et al.*, 2000). Metal chain complexes have mostly been used in fundamental studies of metal–metal interactions (Yang *et al.*, 1997; Cotton *et al.*, 1998) and metal string complexes have been investigated for their potential application as molecular metal wires (Peng *et al.*, 2000). Previously, a series of polynuclear metal chain complexes has been successfully synthesized and characterized (Sheu *et al.*, 1996; Shieh *et al.*, 1997; Chang *et al.*, 1999). We have tried to extend these studies by synthesizing some new transition metal complexes having metal atoms with larger atomic radii. In particular, on the basis of earlier methods (Sheu *et al.*, 1996; Shieh *et al.*, 1997), we attempted to design the synthesis of complexes with Cd metal chains by reaction of the cadmium(II) ion with tripyridyldiamine ($tpdaH_2$). However, the only product that we could isolate in this way happened to be a mononuclear Cd complex; this result shows that the synthetic conditions we used are not suitable for the preparation of metal chains based on Cd—Cd bonds. We report here the synthesis and crystal structure of the title complex, (I), which was crystallized as the monohydrate.

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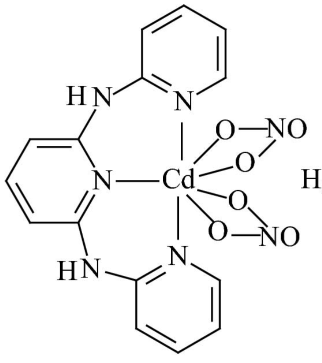

(I)

The Cd1 atom in the title complex has a distorted pentagonal–bipyramidal coordination formed by the tridentate tpda$H_2$ ligand and two chelate nitrate groups (Fig. 1). The tpda$H_2$ ligand is *mer*-coordinated, with the peripheral N1 and N5 atoms in the axial positions [Cd1—N1 = 2.2345 (19) Å, Cd1—N5 = 2.2351 (19) Å and N1—Cd1—N5 = 169.39 (6)°] and the central N3 atom in the equatorial plane of the bipyramid [Cd1—N3 = 2.3148 (17) Å]. The remaining four equatorial positions are occupied by two chelate nitrate groups, one of which has almost equal Cd—O bond lengths [Cd1—O1 = 2.4644 (19) Å and Cd1—O2 = 2.431 (2) Å], whereas the other shows a significant difference in the Cd—O bond lengths [Cd1—O4 = 2.603 (2) Å and Cd1—O5 = 2.441 (2) Å]. Even though the Cd—O distances for chelate nitrate groups are known to exhibit substantial variations (Wang *et al.*, 1999; Nathan & Traina, 2003), the difference in bond-length pattern between the two nitrate groups in the structure of (I) seems surprising, given the identical functions of these two groups within the coordination sphere of atom Cd1. The notable difference between the two nitrate groups in the crystal structure of (I) is that the non-symmetrically coordinated group is more heavily involved in the hydrogen-bond system of the crystal structure (see Table 2).

Atoms O1, O2, O4, O5 and N3 in the equatorial plane of the pentagonal bipyramid are approximately coplanar with the central Cd atom, the maximum deviation from the least-squares plane through all six atoms being 0.172 (3) Å (for atom O5). The three pyridine rings of the tpda$H_2$ ligand are not coplanar. The dihedral angles between the planes of the central pyridine ring and two peripheral rings are 26.71 (11) and 22.51 (11)°. The planes of the nitrate groups form a dihedral angle of 11.22 (11)° with each other.

There are four ‘active’ H atoms in the structure. Atoms H2*A* and H4*A* of the tpda$H_2$ ligand are involved in hydrogen bonds with water atom O7 as an acceptor. The water H atoms, H7*B* and H7*C*, form hydrogen bonds with atoms O5 and O6 of one of the chelate nitrate groups (Table 2). These hydrogen bonds link the molecules of the complex as well as the solvent water molecules into an infinite three-dimensional network (Fig. 2).

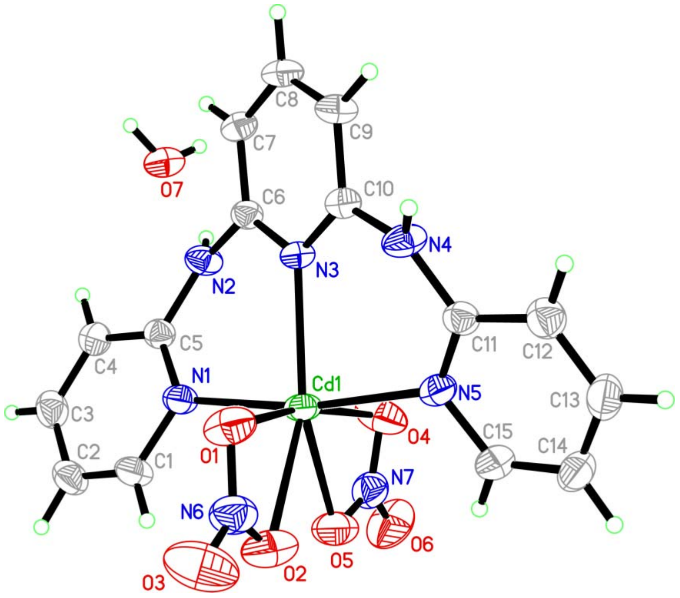

**Figure 1**
Molecular structure of the title complex. Displacement ellipsoids are drawn at the 30% probability level.

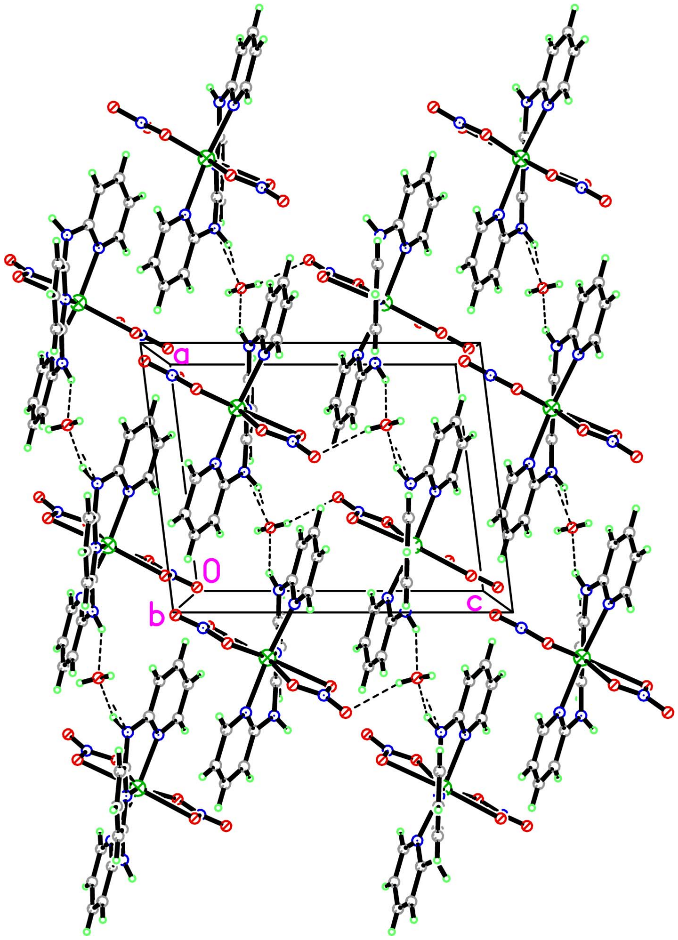

**Figure 2**
Packing diagram of the title compound, viewed along the *b* axis; hydrogen bonds are shown as dashed lines.

**m1124** Fang *et al.* • [Cd(NO$_3$)$_2$(C$_{15}$H$_{13}$N$_5$)]·H$_2$O *Acta Cryst.* (2005). E**61**, m1123–m1125

## Experimental

Tripyridyldiamine (0.157 g) and $Cd(NO_3)_2{\cdot}4H_2O$ (0.12 g) were mixed in methanol (20 ml) and heated for several hours under reflux. The solvent was then removed, and the residue was recrystallized from a 1:1 mixture of diethyl ether and dichloromethane; single crystals suitable for X-ray diffraction analysis precipitated after 2 d.

### *Crystal data*

$[Cd(NO_3)_2(C_{15}H_{13}N_5)]{\cdot}H_2O$
$M_r = 517.74$
Monoclinic, $P2_1/c$
$a = 9.3371$ (3) Å
$b = 17.5155$ (5) Å
$c = 11.6735$ (3) Å
$\beta = 96.964$ (1)°
$V = 1895.05$ (9) Å$^3$
$Z = 4$

$D_x = 1.815$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 6355 reflections
$\theta = 2.1$–27.5°
$\mu = 1.21$ mm$^{-1}$
$T = 295$ (2) K
Irregular fragment, yellow
0.25 × 0.25 × 0.20 mm

### *Data collection*

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998; Blessing, 1995)
$T_{\min} = 0.687$, $T_{\max} = 0.773$
16 790 measured reflections

4346 independent reflections
3059 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -22 \rightarrow 22$
$l = -15 \rightarrow 13$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.060$
$S = 1.01$
4346 reflections
278 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.37$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.50$ e Å$^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00097 (18)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cd1—N1 | 2.2345 (19) | Cd1—O2 | 2.431 (2) |
| Cd1—N3 | 2.3148 (17) | Cd1—O4 | 2.603 (2) |
| Cd1—N5 | 2.2351 (19) | Cd1—O5 | 2.441 (2) |
| Cd1—O1 | 2.4644 (19) | | |
| N1—Cd1—N3 | 85.62 (6) | N5—Cd1—O2 | 92.73 (7) |
| N1—Cd1—N5 | 169.39 (6) | N5—Cd1—O4 | 87.53 (7) |
| N1—Cd1—O1 | 96.37 (7) | N5—Cd1—O5 | 99.33 (7) |
| N1—Cd1—O2 | 97.71 (7) | N5—Cd1—N3 | 84.70 (6) |
| N1—Cd1—O4 | 88.99 (7) | O1—Cd1—O4 | 169.50 (7) |
| N1—Cd1—O5 | 85.90 (7) | O2—Cd1—O1 | 51.22 (6) |
| N3—Cd1—O1 | 94.57 (6) | O2—Cd1—O4 | 119.20 (7) |
| N3—Cd1—O2 | 145.78 (7) | O2—Cd1—O5 | 70.97 (7) |
| N3—Cd1—O4 | 94.83 (6) | O5—Cd1—O1 | 121.99 (6) |
| N3—Cd1—O5 | 143.15 (6) | O5—Cd1—O4 | 49.23 (6) |
| N5—Cd1—O1 | 88.70 (7) | | |

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N2—H2$A\cdots$O7$^{\rm i}$ | 0.86 | 2.14 | 2.938 (3) | 153 |
| N4—H4$A\cdots$O7 | 0.86 | 2.22 | 3.009 (3) | 153 |
| O7—H7$B\cdots$O5$^{\rm ii}$ | 0.86 (3) | 2.03 (3) | 2.843 (2) | 158 |
| O7—H7$C\cdots$O6$^{\rm iii}$ | 0.78 (3) | 2.31 (3) | 3.063 (2) | 163 |

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

All H atoms bonded to C and N atoms were placed geometrically and refined in a riding model (C—H = 0.93 Å and N—H = 0.86 Å). $U_{\rm iso}$(H) values were constrained to be $1.2U_{\rm eq}$ of the carrier atom. Water H atoms were refined isotropically with $U_{\rm iso}$(H) constrained to $1.5U_{\rm eq}$(O).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL-Plus*.

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