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A seven-coordinate pyridine-2,6-dicarboxylate-bridged cadmium(II) complex, at 110 K

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The reaction of cadmium(II) chloride monohydrate with a self-assembling pyridine-containing ligand, LH_2 {LH_2 is $[H_2pyda]^{2+}[pydc]^{2-}$, where pyda = 2,6-diaminopyridine and H_2pydc = pyridine-2,6-dicarboxylic acid}, in water leads to the formation of a centrosymmetric dinuclear Cd^{II} complex, di-μ-pyridine-2,6-dicarboxylato-bis[triaquacadmium(II)], $[Cd(pydc)(H_2O)_3]_2\cdot 2H_2pydc$ or $[Cd_2(C_7H_3NO_4)_2(H_2O)_6]\cdot 2C_7H_5NO_4$. Each Cd atom is seven-coordinate and has a distorted pentagonal-bipyramidal geometry. The two metal fragments are linked *via* the central four-membered Cd_2O_2 ring and there is no $[Hpyda]^+$ moiety in the structure of the complex. The structure self-assembles into layers *via* hydrogen bonds.

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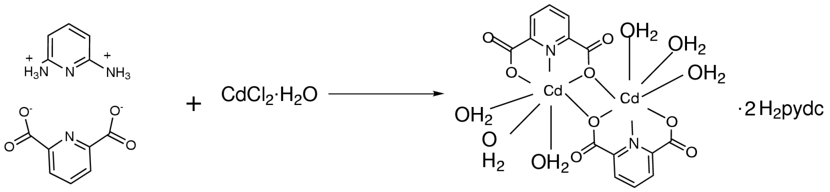
Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.004 Å
R factor = 0.039
wR factor = 0.091
Data-to-parameter ratio = 17.9

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

Comment

Recently, we reported the synthesis of a novel self-assembling pyridine-containing ligand LH_2 (Moghimi *et al.*, 2002), which we have used successfully in making different mononuclear, dinuclear and polymeric complexes. Some of these contain the $[Hpyda]^+$ unit (pyda = 2,6-diaminopyridine) as a counter-ion, *e.g.* with Cr^{III}, $[Hpyda][Cr(pydc)_2]\cdot H_2pydc\cdot 0.5H_2O$ (H_2pydc = pyridine-2,6-dicarboxylic acid; Ranjbar *et al.*, 2001*b*), with Cu^{II}, $[Hpyda]_2[Cu(pydc)_2]\cdot H_2O$ (Ranjbar, Taghavipur *et al.*, 2002), and with Zn^{II}, $[Hpyda][Zn(Hpydc)(pydc)]\cdot 3H_2O$ (Ranjbar, Aghabozorg *et al.*, 2002). The Bi^{III} complex $[Bi_2(pydc)_2Cl(H_2O)]_n$ (Ranjbar *et al.*, 2001*a*) is polymeric and does not contain the $[Hpyda]^+$ counter-ion.



(I)

Our goal was the generation of a self-assembling coordination compound using a self-assembling ligand. The presence of $[H_2pyda]^{2+}$ in the starting material, LH_2, causes the $[pydc]^{2-}$ ligand to form a crystalline complex which is different from those reported earlier, such as $Rb[Cr(pydc)_2]$ (Furst *et al.*, 1979), $[Cu(Hpydc)_2]\cdot H_2O$ and $[Zn(Hpydc)_2]\cdot 3H_2O$ (Okabe & Oya, 2000), and $[Bi(Hpydc)(pydc)(DMSO)\cdot H_2O]_2$ (Zevaco *et al.*, 1992). Here we report the results of the complexation reaction between the self-assembling ligand LH_2 and cadmium(II) chloride monohydrate.

The structure of the Cd^{II} complex $[Cd(pydc)(H_2O)_3]_2\cdot 2H_2pydc$, (I), was reported recently (Odoko *et al.*,

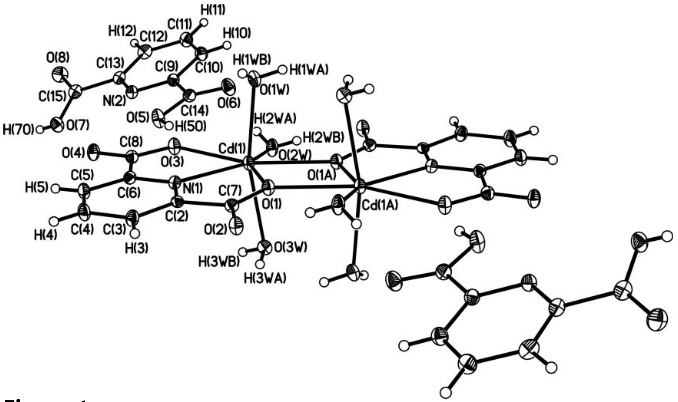


Figure 1

The structure of the title complex, showing the atom-numbering scheme. Displacement displacement parameters are drawn at the 50% probability level; H atoms are drawn as spheres of arbitrary radii.

2002), but the goal and method of synthesis were completely different from ours. Those authors sought to clarify the coordination mode of [H_2pydc] with the Cd^{II} ion, whereas we aimed to show the influence of the [H_2pyda]$^{2+}$ cation on the complexation process. The starting materials in our study were a self-assembling ligand, LH_2, and $CdCl_2\cdot H_2O$ in a 1:2 molar ratio in aqueous solution; Odoko and co-workers reported the synthesis of this complex using [H_2pydc] and $CdCl_2$ in a 1:4 molar ratio, in a 70% methanol–water solution. The data collection temperature in our work was 110 K, whereas the Japanese investigation was conducted at room temperature. In the present study, the ratio of collected to unique reflections was 18834:4676, while in the earlier work it was 4175:3788.

The molecular structure of (I) consists of two metal fragments linked *via* a central four-membered Cd_2O_2 ring. This ring lies on a crystallographic inversion center, resulting in a centrosymmetric Cd^{II} complex. The asymmetric unit also contains the neutral H_2pydc as a molecule of solvation. It is in a general position and thus there are two solvate molecules for each molecule of the complex. The average values for the Cd—O (2.369 Å) and Cd—N (2.321 Å) bond distances are in agreement with the values previously reported for seven- and eight-coordinate cadmium complexes (Odoko *et al.*, 2002; Cameron *et al.*, 1973; Wang *et al.*, 1997).

The coordination of the Cd atoms is distorted pentagonal bipyramidal (Fig. 1). The axial sites are occupied by the O atoms of two water molecules (O1*W* and O3*W*), while the equatorial plane contains N, two O atoms of the first [pydc]$^{2-}$ group, one O atom of the second [pydc]$^{2-}$ group and one water O atom (O2*W*). One of the two carboxylate O atoms in each of the two [pydc]$^{2-}$ ligands acts as a bridge between the two Cd atoms. In the equatorial plane, the largest and smallest deviations from the ideal value of 72° occur for the angles O2*W*—Cd1—O1*A* [81.47 (7)°] and O3—Cd1—N1 [67.00 (7)], respectively. With respect to the axial angle O1*W*—Cd—O3*W*, involving the O atoms of two water ligands, a significant deviation (14.41°) from linearity was observed.

The range of D—H···A angles and the variation of H···A and D···A distances indicate the presence of both strong and weak hydrogen bonds. In the previous report (Odoko *et al.*, 2002), free ligand molecules, [H_2pydc], are connected weakly by hydrogen bonds, *e.g.* the O10—H12···O4 and O11—H13···O4 angles are 133 and 127°, respectively; also the H12···O4 and H13···O4 distances are 2.42 and 2.57 Å, respectively. In our work (Table 1), the [H_2pydc] molecules are strongly connected, *e.g.* the O1*W*—H1*WB*···O8^{ii} and O2*W*—H2*WA*···O6 angles are 170 and 165°, respectively; also the H1*WB*···O8^{ii} and H2*WA*···O6 distances are 1.88 and 1.96 Å, respectively [symmetry code: (ii) $-1+x$, $-y+3/2$, $z+1/2$]. Moreover in our work, there is an O3*W*—H3*WB*···N2^{iv} hydrogen bond [symmetry code: (iv) x, $-y+3/2$, $z+1/2$], while no such bond is reported in the Japanese paper (Odoko *et al.*, 2002).

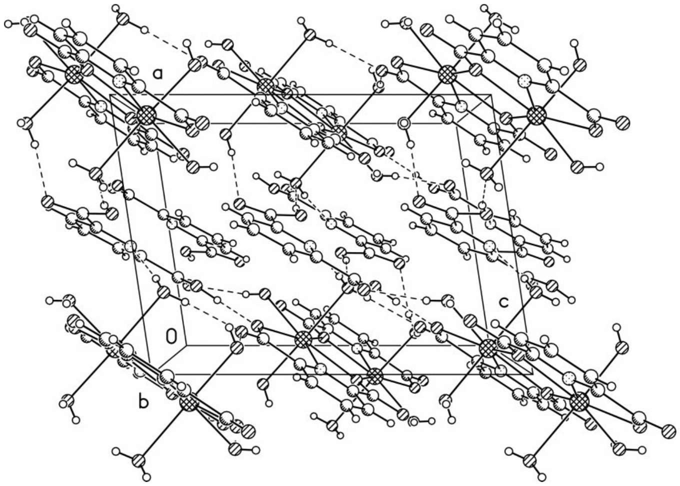


Figure 2

The unit-cell packing diagram. Hydrogen bonds are indicated by dashed lines.

Experimental

The $[Cd(pydc)(H_2O)_3]_2\cdot 2H_2pydc$ complex was synthesized by the reaction between ligand LH_2, [H_2pyda]$^{2+}$[pydc]$^{2-}$, (H_2pyda = pyridine-2,6-diammonium and pydc = pyridine-2,6-dicarboxylate) (Moghimi *et al.*, 2002) and cadmium(II) chloride monohydrate in a 1:2 molar ratio aqueous solution. The light-yellow solution was allowed to slowly concentrate at room temperature. After 2 d, colorless crystals were isolated in 78.9% yield.

Crystal data

$[Cd_2(C_7H_3NO_4)_2(H_2O)_6]\cdot 2C_7H_5NO_4$
$M_r = 997.34$
Monoclinic, $P2_1/c$
$a = 9.0531\ (16)$ Å
$b = 14.667\ (3)$ Å
$c = 12.186\ (2)$ Å
$\beta = 98.485\ (4)°$
$V = 1600.4\ (5)$ Å^3
$Z = 2$

$D_x = 2.070$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 967 reflections
$\theta = 3$–$30°$
$\mu = 1.44$ mm^{-1}
$T = 110\ (2)$ K
Plate, colorless
$0.45 \times 0.35 \times 0.10$ mm

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
Data collection
$T_{min} = 0.285$, $T_{max} = 0.862$

18834 measured reflections
4676 independent reflections
3769 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 30.1°$
$h = -12 \rightarrow 12$

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$k = -20 \rightarrow 20$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.091$
$S = 1.21$
4676 reflections
261 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 2.85$ e Å^{-3}
$\Delta\rho_{\min} = -0.96$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O4^{i}	0.83	1.85	2.679 (3)	178
O1*W*—H1*WB*···O8^{ii}	0.87	1.88	2.743 (3)	170
O2*W*—H2*WA*···O6	0.85	1.96	2.787 (3)	165
O2*W*—H2*WB*···O2^{iii}	0.83	1.83	2.628 (3)	162
O3*W*—H3*WA*···O4^{iv}	0.85	2.12	2.940 (3)	162
O3*W*—H3*WB*···N2^{iv}	0.77	2.19	2.927 (3)	160
O5—H5O···O3	0.88	1.64	2.507 (3)	168
O7—H7O···O3*W*^{v}	0.79	1.97	2.761 (3)	173

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $x-1, \frac{3}{2}-y, \frac{1}{2}+z$; (iii) $-x, 2-y, 2-z$; (iv) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (v) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$.

The highest residual difference electron-density peak occurs close to atom O2*W*. The H atoms bonded to oxygen were located in a difference Fourier map; those bonded to carbon were placed geometrically and then included in the refinement in the riding-motion approximation, with displacement parameters $U_{\rm iso}$ set to $1.2U_{\rm eq}$ of the carrier non-H atom.

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

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References

Bruker (1998). *SMART* (Version 5.059) and *SAINT-Plus* (Version 6.01). Bruker AXS Inc., Madison, Wisconsin, USA.

Cameron, A. F., Taylor, D. W. & Nuttall, R. H. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2130–2134.

Furst, W., Gouzerh, P. & Jeannin, Y. (1979). *J. Coord. Chem.* **8**, 237–241.

Moghimi, A., Ranjbar, M., Aghabozorg, H., Jalali, F., Shamispur, M., Yap, G. P. A. & Rahbarnoohi, H. (2002). *J. Mol. Struct.* **605**, 133–149.

Odoko, M., Kusano, A. & Okabe, N. (2002). *Acta Cryst.* E**58**, m25–m27.

Okabe, N. & Oya, N. (2000). *Acta Cryst.* C**56**, 305–307.

Ranjbar, M., Aghabozorg, H. & Moghimi, A. (2002). *Anal. Sci.* Submitted.

Ranjbar, M., Aghabozorg, H., Moghimi, A. & Yanovsky, A. (2001*a*). *Anal. Sci.* **17**, 1469.

Ranjbar, M., Aghabozorg, H., Moghimi, A. & Yanovsky, A. (2001*b*). *Z. Kristallogr. New Cryst. Struct.* **216**, 626–628.

Ranjbar, M., Aghabozorg, H., Moghimi, A. & Yap, G. P. A. (2002). *Anal. Sci.* **18**, 219–220.

Ranjbar, M., Taghavipur, M., Aghabozorg, H., Mogimi, A., Jalali, F. & Shamsipur, M. (2002). *Pol. J. Chem.* In the press.

Sheldrick, G. M. (1998). *SADABS* (Version 2.01) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Wang, J., Xu, X., Chen, J., Luo, Q., Shen, M., Huang, X. & Wu, Q. (1997). *Inorg. Chim. Acta*, **256**, 121–126.

Zevaco, T., Postel, M. & Cherif, N. B. (1992). Main Group *Met. Chem.* **15**, 217–224.

m306 M. Ranjbar *et al.* • $[Cd_2(C_7H_3NO_4)_2(H_2O)_6]\cdot 2C_7H_5NO_4$ *Acta Cryst.* (2002). E**58**, m304–m306