

Tetraaquabis(2-methoxybenzaldehyde isonicotinoylhydrazone)cadmium(II) dinitrate

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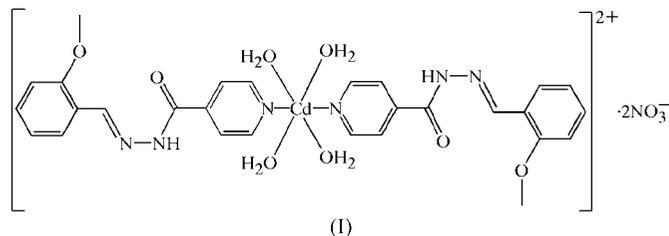
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The Cd^{II} centre in the title complex, [Cd(C₁₄H₁₃N₃O₂)₂·(H₂O)₄](NO₃)₂, occupies a crystallographic inversion centre and is coordinated by two donor N atoms [N1 and N1ⁱ; symmetry code: (i) $-x + 1, -y, -z + 1$] of two *L* ligands and four coordinated water O atoms (O6, O7, O6ⁱ and O7ⁱ), conferring a slightly distorted octahedral coordination. The equatorial plane is formed by atoms O6, O7, O6ⁱ and O7ⁱ, while the axial positions are occupied by atoms N1 and N1ⁱ. The two hydrazone ligands are in a *trans* configuration.

Comment

Supramolecular assembly through hydrogen bonds has been extensively exploited to generate extended one-, two- and three-dimensional structures (Beatty, 2003; Li *et al.*, 2006; Russell & Ward, 1996). It is interesting that polytopic ligands based on isonicotinoylhydrazone have led to a number of

complexes with multidimensional structures or extended multidimensional structures (Bu *et al.*, 2000; Ge *et al.*, 2006). We present here the synthesis and structural characterization of the title cadmium complex, [CdL₂(H₂O)₄](NO₃)₂, (I), where *L* is neutral 2-methoxybenzaldehyde isonicotinoylhydrazone.



As shown in Fig. 1, the title complex consists of one complex cation, [CdL₂(H₂O)₄]²⁺, on an inversion centre and two nitrate anions. The cadmium centre is six-coordinated by two pyridine N atoms [N1 and N1ⁱ; symmetry code: (i) $-x + 1, -y, -z + 1$] of two *L* ligands and four coordinated water O atoms (O6, O7, O6ⁱ and O7ⁱ), conferring a slightly distorted octahedral coordination. The equatorial plane is formed by atoms O6, O7, O6ⁱ and O7ⁱ, while the axial positions are occupied by atoms N1 and N1ⁱ. The two hydrazone ligands are in a *trans* configuration.

As listed in Table 2, the Cd—O(water) bond lengths in known cadmium complexes range from 2.273 (2) to 2.350 (2) Å (Chen *et al.*, 2007; Liu *et al.*, 2007; Ochoa & Alexandre, 2005; Wei *et al.*, 2006). The Cd—O(water) bond lengths in (I) (Cd1—O6 and Cd1—O7) are 2.267 (2) and 2.311 (2) Å, respectively, the former being the shortest Cd—O(water) value among known cadmium complexes. It is interesting to note that the difference between Cd—O(water) bond lengths in same complex ranges from 0.014 (3) to 0.073 (2) Å. The Cd1—N1 bond distance of 2.326 (2) Å is in agreement with the values reported by Mautner *et al.* (2004) and Vreshch *et al.* (2005).

The structural parameters of *L* in the title complex are within normal ranges (Qiu *et al.*, 2006; Yang *et al.*, 2006). The

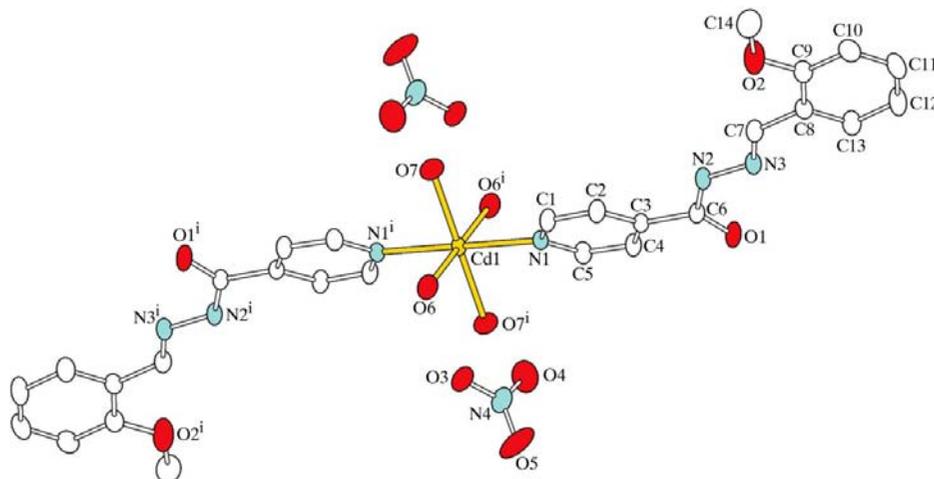


Figure 1

A view of the title complex, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, -y, -z + 1$.]

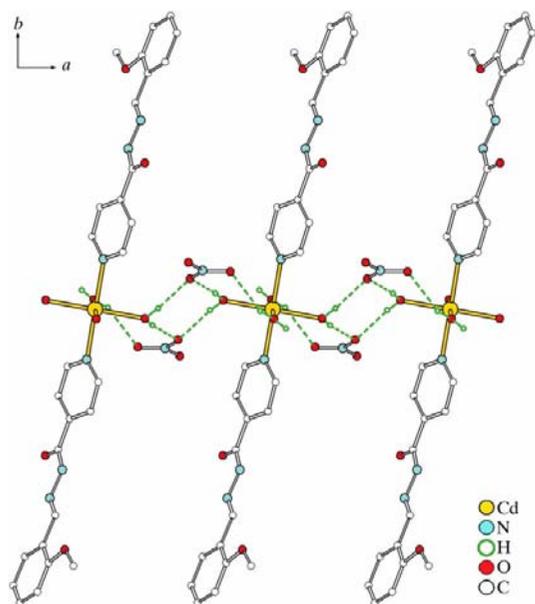


Figure 2
A view of the one-dimensional chain of (I) along the *a* axis. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

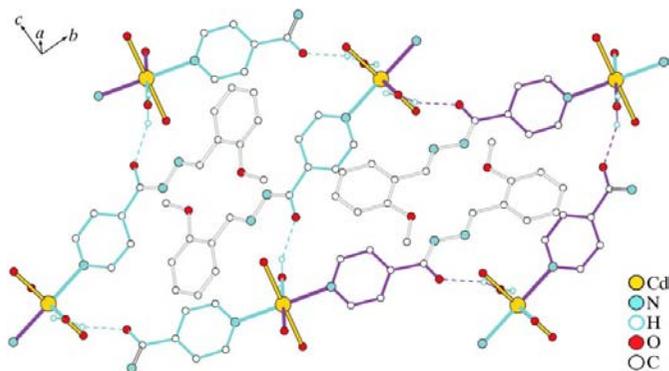


Figure 3
A view of the two-dimensional structure of (I) in the *bc* plane. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

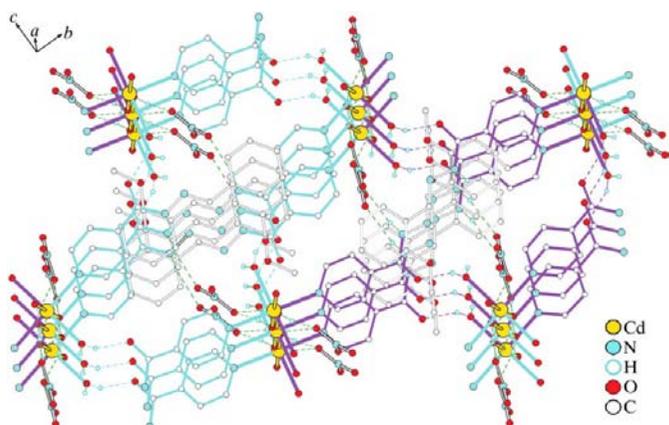


Figure 4
The three-dimensional structure of (I). Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

C7=N3 bond distance of 1.268 (3) Å in (I) confirms the presence of a double bond; the corresponding bonds in the uncoordinated ligand *L* are 1.277 (2) and 1.269 (7) Å (Qiu *et al.*, 2006; Yang *et al.*, 2006). The C6–N2 bond distance of 1.338 (3) Å in (I) is similar to the corresponding distances [1.340 (8) and 1.350 (2) Å] reported by Qiu *et al.* (2006) and Yang *et al.* (2006). The dihedral angle between the benzene (C8–C13) and pyridine (N1/C1–C5) rings is 18.8 (2)°; these rings are slightly more inclined than normal (Fun *et al.*, 1997) and we attribute this to the steric effect of the C9 methoxy substituent.

As can be seen from Table 1, there are many hydrogen bonds in the title complex. Each $[\text{CdL}_2(\text{H}_2\text{O})_4]^{2+}$ cation is connected to four nitrate anions *via* O–H(H₂O)···O(NO₃[−])-type hydrogen bonds (O6–H6A···O3, O6–H6B···O3ⁱⁱⁱ and O7–H7A···O4ⁱ; symmetry codes as in Table 1), forming an extended chain along the *a* axis (Fig. 2).

At the same time, every *L* ligand is coordinated to one Cd atom through its pyridine N atom (N1) and linked to another cadmium complex cation by an O7–H7B···O1^{iv} hydrogen bond. This means that the hydrazone ligand acts as a bridging ligand. Therefore, four $[\text{CdL}_2(\text{H}_2\text{O})_4]^{2+}$ units are combined by four hydrogen bonds, forming a 36-membered ring. Two such rings are presented in Fig. 3; one ring is composed of the four ligands with lightly shaded bonds (coloured cyan in the electronic version of the paper) and the other ring is composed of the three more darkly shaded (purple) and one lightly shaded (cyan) ligands. These rings are then connected together to form an extended layer along the *bc* plane.

These layers and chains are linked together to form an extended three-dimensional network (see Fig. 4). O–H(water)···O(NO₃[−]) and O–H(water)···O(carbonyl) hydrogen bonds play an important role in the formation of this network.

Experimental

Ligand *L* was prepared by condensation (Qiu *et al.*, 2006; Yang *et al.*, 2006). To a solution of *L* (51 mg, 0.2 mmol) in methanol (10 ml), cadmium nitrate tetrahydrate (60 mg, 0.2 mmol) was added slowly. After stirring for 1.5 h, the solution was filtered. Slow evaporation from the solution afforded yellow crystals suitable for X-ray diffraction analysis.

Crystal data

$[\text{Cd}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2)_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$	$V = 1697.9 (15) \text{ \AA}^3$
$M_r = 819.03$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.062 (5) \text{ \AA}$	$\mu = 0.72 \text{ mm}^{-1}$
$b = 17.955 (8) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 11.853 (6) \text{ \AA}$	$0.28 \times 0.21 \times 0.15 \text{ mm}$
$\beta = 98.26 (2)^\circ$	

Data collection

Rigaku Weissenberg IP diffractometer	16376 measured reflections
Absorption correction: empirical (using intensity measurements) (TEXRAY; Molecular Structure Corporation, 1999)	3892 independent reflections
$T_{\min} = 0.824$, $T_{\max} = 0.907$	3210 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	232 parameters
$wR(F^2) = 0.073$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\max} = 0.54 \text{ e } \text{\AA}^{-3}$
3892 reflections	$\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$

Table 1Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O6-H6A\cdots O3$	0.89	1.84	2.705 (3)	164
$N2-H2N\cdots O5^{ii}$	0.86	2.18	3.011 (3)	164
$O6-H6B\cdots O3^{iii}$	0.84	1.99	2.811 (3)	164
$O7-H7A\cdots O4^i$	0.87	2.24	3.006 (4)	146
$O7-H7B\cdots O1^{iv}$	0.82	2.00	2.771 (2)	156

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

Table 2Comparative geometrical parameters (\AA) for Cd—O(water) bonds in cadmium complexes.

Δ is the difference between Cd—O(water) bond distances in the same complex.

Complex	Cd1—O1	Cd2—O2	Δd
(I) ^a	2.267 (2)	2.311 (2)	0.044
$[\text{Cd}(\text{pmtca})_2(\text{H}_2\text{O})_2]_n^b$	2.277 (2)	2.350 (2)	0.073
$[\text{Cd}(\text{ptca})_2(\text{H}_2\text{O})_4]_n^b$	2.298 (2)	2.347 (2)	0.049
$\text{C}_{54}\text{H}_{70}\text{CdN}_{12}\text{O}_{16}^c$	2.299 (3)	2.321 (2)	0.022
$[\text{Cd}(\text{trtr})_2(\text{H}_2\text{O})_4](\text{SiF}_6)^d$	2.273 (2)	2.289 (2)	0.016
$[\text{Cd}(\text{9-EtGH})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2^e$	2.309 (3)	2.324 (3)	0.015
$[\text{Cd}(\text{9-MeGH})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2^e$	2.317 (3)	2.331 (2)	0.014

Notes: (a) this work; (b) Chen *et al.* (2007) [Hpmtca is 2-(3-pyridyl)-4-methylthiazole-5-carboxylic acid and Hptca is 2-(4-pyridyl)thiazole-4-carboxylic acid]; (c) Wei *et al.* (2006); (d) Liu *et al.* (2007) [trtr is 3-(1,2,4-triazol-4-yl)-1,2,4-triazole]; (e) Ochoa & Alexandre (2005) (9-EtGH is 9-ethylguanidine and 9-MeGH is 9-methylguanidine).

Water H atoms were located in difference Fourier maps and then allowed to ride on the O atoms [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$]. The other H atoms were placed in idealized positions and treated as riding [C—H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms; C—H = 0.96 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms; N—H = 0.86 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ for the amino group].

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3034). Services for accessing these data are described at the back of the journal.

References

- Beatty, A. M. (2003). *Coord. Chem. Rev.* **246**, 131–143.
- Bu, X.-H., Du, M., Zhang, L., Song, X.-B., Zhang, R.-H. & Clifford, T. (2000). *Inorg. Chim. Acta*, **308**, 143–149.
- Chen, X.-D., Wu, H.-F., Zhao, X.-H., Zhao, X.-J. & Du, M. (2007). *Cryst. Growth Des.* **7**, 124–131.
- Fun, H.-K., Lu, Z.-L., Duan, C.-Y., Tian, Y.-P., You, X.-Z., Guo, Y.-M. & Gong, X.-Y. (1997). *Acta Cryst.* **C53**, 1452–1454.
- Ge, C.-H., Cui, A.-L., Ni, Z.-H., Jiang, Y.-B., Zhang, L.-F., Ribas, J. & Kou, H.-Z. (2006). *Inorg. Chem.* **45**, 4883–4885.
- Li, F., Li, T.-H., Su, W., Gao, S.-Y. & Cao, R. (2006). *Eur. J. Inorg. Chem.* pp. 1582–1587.
- Liu, B., Zhang, X.-C. & Wang, Y.-F. (2007). *Inorg. Chem. Commun.* **10**, 199–203.
- McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
- Mautner, F. A., Gspan, C., Gatterer, K., Goher, M. A. S., Abu-Youssef, M. A. M., Bucher, E. & Sitte, W. (2004). *Polyhedron*, **23**, 1217–1224.
- Molecular Structure Corporation (1999). *TEXRAY* and *TEXSAN*. Versions 1.10. MSC, The Woodlands, Texas, USA.
- Ochoa, P. A. & Alexandre, S. S. (2005). *J. Inorg. Biochem.* **99**, 1540–1547.
- Qiu, X.-Y., Xu, H.-J., Liu, W.-S. & Zhu, H.-L. (2006). *Acta Cryst.* **E62**, o2304–o2305.
- Russell, V. A. & Ward, M. D. (1996). *Chem. Mater.* **8**, 1654–1666.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Vreshch, V. D., Lysenko, A. B., Chernega, A. N., Sieler, J. & Domasevitch, K. V. (2005). *Polyhedron*, **24**, 917–926.
- Wei, Y.-H., Tan, A.-Z., Chen, Z.-L., Liang, F.-P. & Hu, R.-X. (2006). *Chin. J. Inorg. Chem.* **22**, 273–280.
- Yang, S., Zhang, S.-P., Wu, Y.-Y. & Shao, S.-C. (2006). *Acta Cryst.* **E62**, o28–o30.