

Synthesis and Crystal Structure of a New 2D Honeycomb-like Cadmium(II) Complex with Tripodal Ligand

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A new cadmium(II) coordination polymer, $[\text{Cd}(\text{TITMB})_2] \cdot (\text{SO}_4) \cdot 21\text{H}_2\text{O}$, where TITMB = 1, 3, 5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene, was obtained by self-assembly of tripodal ligand TITMB with $\text{CdSO}_4 \cdot 2.7\text{H}_2\text{O}$ in acetonitrile, and characterized by X-ray crystallography. The crystal data belongs to monoclinic space group C_c with cell parameters $a = 1.16891(4)$ nm, $b = 2.06671(6)$ nm, $c = 2.48185(7)$ nm, $\beta = 97.8560(10)^\circ$, $R = 0.0487$, $wR = 0.1211$. The results of structure analysis indicate that each TITMB ligand coordinates three metal atoms and in turn each Cd(II) atom with octahedral coordination geometry connects six nitrogen atoms of imidazole group from six different TITMB ligands to produce a 2D honeycomb network structure. There are a lot of water molecules linked by hydrogen bonds and occupied the channels formed intra- and inter-sheets.

Keywords honeycomb network, crystal structure, cadmium(II) complex, tripodal ligand

Introduction

In the past several years, considerable progress has been achieved in controlling the assembly of individual building blocks into structures with specific topologies and interesting properties such as molecular recognition, ion exchange and selective guest inclusion.¹⁻³ It is possible for rational design and synthesis of supramolecular architectures with one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) networks including

cage, brick-wall, ladder, honeycomb, etc.⁴⁻⁸

Previous studies have demonstrated that tripodal ligands with aromatic core are one of the most important ligands in design and construction of novel supramolecular architectures.⁹⁻¹¹ For example, a nanometer-sized hexahedral coordination capsule was obtained by the reaction of 1, 3, 5-tris(3, 5-pyrimidyl) benzene with $\text{Pd}(\text{en})(\text{NO}_3)_2$.¹⁰ 1, 3, 5-Tricyanobenzene and 1, 3, 5-tris(4-ethylbenzonitrile) benzene react with silver(I) trifluoromethanesulfonate to give honeycomb-like and hinge-like coordination networks, respectively.¹¹ However, most of these reported complexes were obtained by assembly of the rigid tripodal ligands with metal ions. The reported flexible tripodal ligands with aromatic core in this field are relatively rare.¹²⁻¹⁴ The possible coordination modes of flexible ligands are more abundant than those of the rigid one due to the flexibility and low symmetry of the ligands since the flexible ligands can adopt different conformations according to the geometric needs of different metal ions. While in the case of rigid tripodal ligands, there is only one kind of conformation whenever it reacts with metal ions. Previous studies have shown that flexible tripodal ligand 1, 3, 5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB) (Scheme 1) can adopt *cis*, *cis*, *cis* and *cis*, *trans*, *trans* conformations when it reacts with different metal ions.¹⁵⁻¹⁷ Now we extended our study to construct coordination polymer using the TITMB ligand.

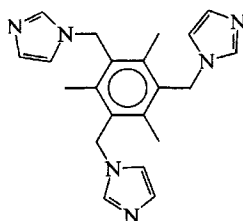
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Here the preparation and crystal structure, a new cadmium(II) complex with 2D honeycomb-like structure, $[\text{Cd}(\text{TITMB})_2](\text{SO}_4) \cdot 21\text{H}_2\text{O}$, were reported.

Scheme 1



Tripodal ligand (TITMB)

Experimental

Materials

All commercially available chemicals are of reagent grade and used as received without further purification. Acetonitrile was dried and purified by distillation before use. The TITMB ligand was prepared by methods reported previously.^{16,17} Thermogravimetric and differential analyses were taken on a simultaneous SDT 2960 thermal analyzer under N_2 with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

Synthesis of $[\text{Cd}(\text{TITMB})_2](\text{SO}_4) \cdot 21\text{H}_2\text{O}$

The title complex was synthesized by layering method. A solution of TITMB (18.0 mg, 0.05 mmol) in acetonitrile (5 mL) was carefully layered over a solution of $\text{CdSO}_4 \cdot 2.7\text{H}_2\text{O}$ (19.2 mg, 0.075 mmol) in water (10 mL). Colorless crystals were isolated by filtration after several weeks, 23 mg, yield 50%. Anal. calcd for $\text{C}_{42}\text{H}_{84}\text{CdN}_{12}\text{O}_{25}\text{S}$: C 38.53, H 6.82, N 12.85; found C 38.76, H 6.51, N 12.91.

X-Ray crystal structure determination

The intensity data for the title complex were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated $\text{Mo } K_\alpha$ radiation ($\lambda = 0.071069\text{ nm}$). The structure was solved by direct methods with SIR92,¹⁸ and expanded using Fourier techniques.¹⁹ All data were refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. The hydrogen atoms were generated geometrically except

for the lattice water. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation.²⁰ Details of the crystal parameters, data collection and refinement are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are given in Table 2.

Table 1 Crystallographic data for $[\text{Cd}(\text{TITMB})_2](\text{SO}_4) \cdot 21\text{H}_2\text{O}$

Formula	$\text{C}_{42}\text{H}_{84}\text{CdN}_{12}\text{O}_{25}\text{S}$
Formula weight	1301.67
Crystal system	Monoclinic
Space group	C_c
a (nm)	1.16891(4)
b (nm)	2.06671(6)
c (nm)	2.48185(7)
β (deg)	97.8560(10)
V (nm) ³	5.9394(3)
Z	4
Absorption correction	Ψ scan
$T_{\text{min,max}}$	0.791, 0.976
D_c (g/cm ³)	1.456
Flack parameter	0.48(4)
$F(000)$	2736
Crystal size (mm)	$0.25 \times 0.25 \times 0.05$
Index ranges	$-15 \leq h \leq 15$; $-26 \leq k \leq 26$; $-32 \leq l \leq 32$
μ (cm ⁻¹)	4.91
Reflections collected	13230
Unique reflections	13220
R_{int}	0.0073
$R [I > 2\sigma(I)]$	$R = 0.0487$, $wR = 0.1211^a$
R (all data)	$R = 0.0658$, $wR = 0.1281$
Goodness of fit	1.129

$$^a w = 1/[\sigma^2(F_0)^2 + (0.0515P)^2 + 20.1379P], \text{ where } P = (F_0^2 + 2F_c^2)/3.$$

Results and discussion

Description of the crystal structure

The title compound crystallizes in space group C_c and the repeat unit contains one molecule of $[\text{Cd}(\text{TITMB})_2](\text{SO}_4) \cdot 21\text{H}_2\text{O}$, namely one cadmium sulfate, two TITMC ligands and 21 crystal water molecules. A perspective view of the Cd(II) center of the title compound is shown in Fig. 1 with atom numbering scheme. Each cadmium(II) atom is coordinated by six N atoms of

imidazole groups derived from six different TITMB ligands. The coordination geometry of the Cd(II) center is slightly distorted octahedral with coordination angles (N—Cd—N) ranging between $86.4(3)^\circ$ to $178.2(4)^\circ$ and the Cd—N bond lengths ranging from 0.2289(8) to 0.2425(7) nm [Cd—N_{av} = 0.2359(7) nm] as listed in Table 2. Similar Cd—N bond lengths have been reported in other cadmium(II) complexes.^{21,22} For example, the average Cd—N bond lengths in [Cd(Py₂CH₂)₂(NO₃)₂] and [Cd(bppz)₂(NO₃)₂] [bppz = 2,5-bis(2-pyridyl)pyrazine] are 0.2350(1) nm and 0.2403(6) nm, re-

spectively.^{21,22} Each TITMB ligand connects three Cd(II) atoms, which form an equilateral triangle with an edge length (Cd···Cd separation) of 1.18 nm. Such coordination mode makes the compound a 2D network on the *ab* plane with honeycomb structure in which the Cd(II) atoms serve as nodes (Fig. 2). It is clear that all the TITMB ligands in the network have *cis*, *cis*, *cis* conformation with up- and down-orientations alternatively. The distance between the two benzene ring planes of up- and down-orientations is 0.88 nm and the dihedral angle between these two benzene ring planes is 3.2° .

Table 2 Selected bond distances ($\times 10^{-1}$ nm) and angles (deg) for [Cd(TITMB)₂](SO₄)·21H₂O

Cd(1)—N(52)	2.289(8)	Cd(1)—N(32)	2.379(7)
Cd(1)—N(12)	2.425(7)	Cd(1)—N(102)	2.321(7)
Cd(1)—N(302)	2.345(7)	Cd(1)—N(502)	2.396(6)
N(52)-Cd(1)-N(102)	86.4(3)	N(52)-Cd(1)-N(302)	88.3(3)
N(102)-Cd(1)-N(302)	91.9(3)	N(32)-Cd(1)-N(52)	91.0(3)
N(102)-Cd(1)-N(32)	176.6(3)	N(302)-Cd(1)-N(32)	90.2(3)
N(52)-Cd(1)-N(502)	178.1(3)	N(102)-Cd(1)-N(502)	91.9(2)
N(302)-Cd(1)-N(502)	91.0(3)	N(32)-Cd(1)-N(502)	90.7(2)
N(52)-Cd(1)-N(12)	89.9(3)	N(12)-Cd(1)-N(102)	87.6(2)
N(302)-Cd(1)-N(12)	178.2(4)	N(32)-Cd(1)-N(12)	90.1(3)
N(12)-Cd(1)-N(502)	90.7(2)		

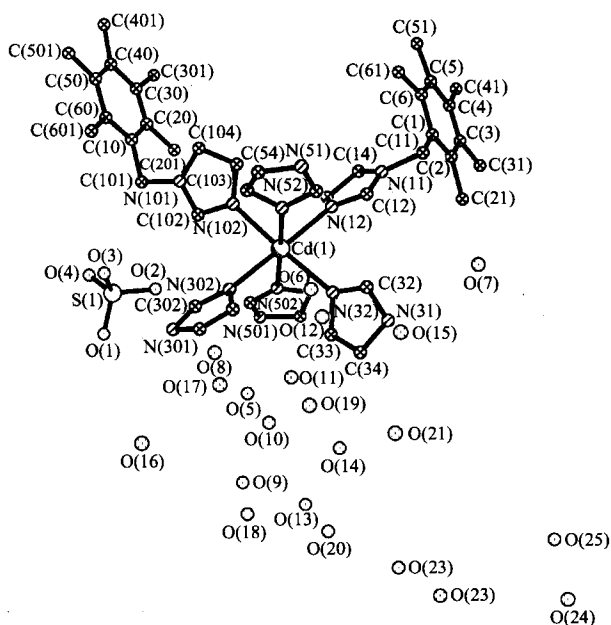


Fig. 1 Coordination environment of Cd(II) in the title complex with atom numbering scheme and hydrogen atoms were omitted for clarity.

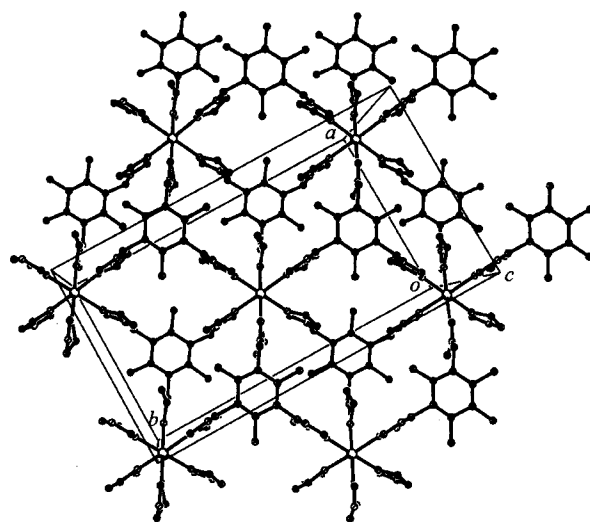


Fig. 2 View of the 2D cationic layer with the honeycomb network.

The packing diagram of the title complex is illustrated in Fig. 3. The overall crystal packing displays an $\cdots ABAB \cdots$ arrangement, where A is a cationic layer and B is an anionic layer. The sulfate anions are located in the channels formed between two adjacent cationic layers, held there by seven C—H \cdots O (sulfate) hydrogen bonds. In addition, there are seven C—H \cdots O (water) hydrogen bonds as tabulated in Table 3. The framework creates open channels in each honeycomb sheet as shown in Fig. 3, which are filled with the lattice water molecules. The water molecules and sulfate anions in the channels formed intra- and inter-sheets are connected by O—H \cdots O hydrogen bonds crossed the channels (Fig. 3 and Table 3). Furthermore, benzene rings in one layer are stacking face-to-face with those neighboring in the adjacent layer with a centroid-centroid distance of 0.038 nm.

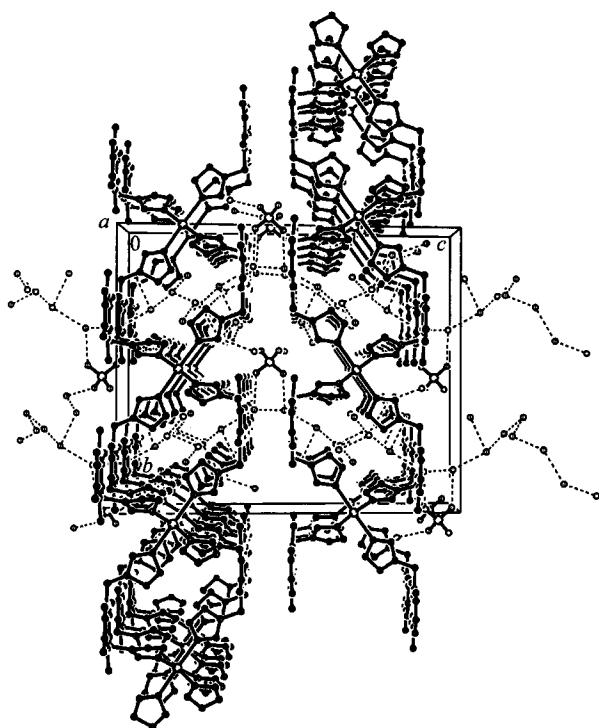


Fig. 3 Crystal packing diagram for 2 on *bc* plane with channels formed between two adjacent layers.

The existence of the water molecule in the title complex was confirmed by thermogravimetric analysis. The TGA data of the complex exhibited an initial weight loss of 29.2% (calcd 28.9%) between 30 °C and 100 °C, representing the loss of 21 uncoordinated water molecules and the residue is stable at least up to 225 °C.

In conclusion, the present study provides an exam-

ple of construction of new coordination polymer with honeycomb-like structure by using flexible tripodal ligand and transitional metal ions. The combination of the *cis*, *cis*, *cis* conformation and potential of forming π - π interactions between the benzene rings of TITMB ligands result in the formation of layered structure.

Table 3 Hydrogen bonds data for the title complex

C—H \cdots O hydrogen bond	Distance of C \cdots O (10^{-1} nm)
C(11)—H(1) \cdots O(1) # 1	3.324(11)
C(12)—H(3) \cdots O(4) # 1	3.418(12)
C(32)—H(11) \cdots O(4) # 1	3.190(13)
C(52)—H(19) \cdots O(4) # 1	3.257(11)
C(102)—H(27) \cdots O(2)	3.122(10)
C(302)—H(35) \cdots O(2)	3.486(11)
C(502)—H(43) \cdots O(2)	3.279(12)
C(14)—H(5) \cdots O(14) # 2	3.345(10)
C(31)—H(10) \cdots O(25) # 2	3.364(11)
C(34)—H(13) \cdots O(14)	3.247(9)
C(54)—H(21) \cdots O(14) # 3	3.163(11)
C(104)—H(29) \cdots O(8) # 2	3.236(12)
C(304)—H(37) \cdots O(8)	3.295(13)
C(504)—H(45) \cdots O(8) # 4	3.231(15)
O—H \cdots O hydrogen bond	Distance of O \cdots O (10^{-1} nm)
O(19)—H \cdots O(21)	2.92(1)
O(22)—H \cdots O(20)	2.78(1)
O(23)—H \cdots O(1) # 5	2.83(1)
O(7)—H \cdots O(2) # 6	2.76(1)
O(25)—H \cdots O(4) # 7	2.76(1)
O(6)—H \cdots O(25) # 3	2.84(1)
O(7)—H \cdots O(18) # 8	2.76(1)
O(7)—H \cdots O(25) # 3	2.80(1)
O(8)—H \cdots O(22) # 3	2.65(1)
O(12)—H \cdots O(23) # 3	2.79(1)

Equivalent atoms generated by (# 1) $x, -y, z+0.5$; (# 2) $x+0.5, y-0.5, z$; (# 3) $x+1, y, z$; (# 4) $x-0.5, y-0.5, z$; (# 5) $x+0.5, -y+0.5, z-0.5$; (# 6) $x, -y, z-0.5$; (# 7) $x+1, -y, z-0.5$; (# 8) $x+0.5, -y+0.5, z+0.5$.

References

- 1 Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975.
- 2 Munakata, M.; Wu, L. P.; Kuroda-sowa, T. *Adv. Inorg. Chem.* **1998**, *46*, 173.
- 3 Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1460.
- 4 Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.;

- Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287.
- 5 Biradha, K.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 6431.
- 6 Choi, H. J.; Suh, M. P. *J. Am. Chem. Soc.* **1998**, *120*, 10622.
- 7 Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327.
- 8 Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148.
- 9 Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649.
- 10 Takeda, N.; Umemoto, K.; Yamaguchi, K.; Fujita, M. *Nature* **1999**, *398*, 794.
- 11 Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792.
- 12 Hong, M.; Zhao, Y.; Su, W.; Cao, R.; Fujita, M.; Zhou, Z.; Chan, A. S. C. *Angew. Chem., Int. Ed.* **2000**, *39*, 2468.
- 13 Hartshorn, C. M.; Steel, P. J. *Chem. Commun.* **1997**, 541.
- 14 Liu, H. K.; Sun, W. Y.; Ma, D. J.; Yu, K. B.; Tang, W. X. *Chem. Commun.* **2000**, 591.
- 15 Sun, W. Y.; Fan, J.; Okamura, T.; Xie, J.; Yu, K. B.; Ueyama, N. *Chem. Eur. J.* **2001**, *7*, 2557.
- 16 Liu, H. K.; Sun, W. Y.; Tang, W. X.; Yamamoto, T.; Ueyama, N. *Inorg. Chem.* **1999**, *38*, 6313.
- 17 Liu, H. K.; Sun, W. Y.; Zhu, H. L.; Yu, K. B.; Tang, W. X. *Inorg. Chem. Acta* **1999**, *295*, 129.
- 18 SIR92: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.* **1994**, *27*, 435.
- 19 Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *DIRDIF94*, The DIRFID-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1994**.
- 20 *TeXsan*, Crystal Structure Analysis Package, Molecular Structure Corporation, **1999**.
- 21 Plater, M. J.; Foreman, M. R. St. J.; Gelbrich, T.; Coles, S. J.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2000**, 3065.
- 22 Neels, A.; Stoeckli-Evans, H. *Inorg. Chem.* **1999**, *38*, 6164.

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