

catena-Poly[[dichlorocadmium(II)]bis[μ -1,3-bis(imidazol-1-ylmethyl)benzene- $\kappa^2N^3:\kappa^2N^{3'}$]]Tao Li^{a,b} and Shao-Wu Du^{a*}^aState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China, and ^bCollege of Life Science, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, People's Republic of China

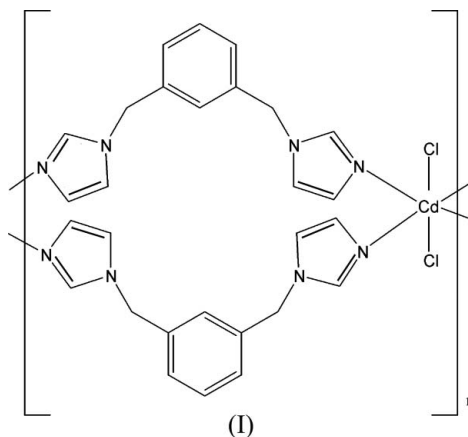
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Key indicatorsSingle-crystal X-ray study
 $T = 173$ K
Mean $\sigma(C-C) = 0.003$ Å
 R factor = 0.024
 wR factor = 0.048
Data-to-parameter ratio = 17.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

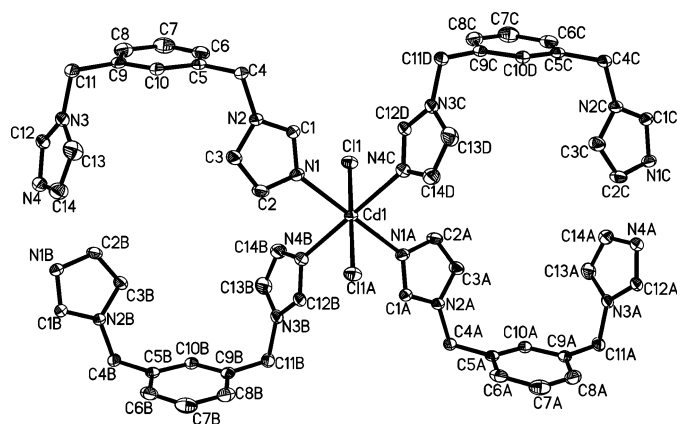
The title compound, $[CdCl_2(C_{14}H_{14}N_4)_2]_n$, has been synthesized by the hydrothermal method. The Cd^{II} atom is six-coordinate with an octahedral geometry and the Cl^- ions are in *trans* positions. The structure contains double-stranded chains with nanometre-sized cavities linked *via* π - π interactions to form two-dimensional layers. Solid-state fluorescent analyses show that the compound displays a strong violet emission band.

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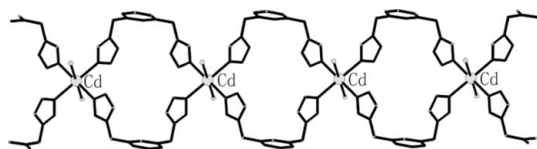
Recently, considerable efforts have been focused on the design, synthesis and characterization of novel single- and double-stranded chains because of their fascinating potential applications in molecular wires (Bruce *et al.*, 2000), electrical conductors (Bunn *et al.*, 1992), molecular magnets (Caneschi *et al.*, 2001), host-guest chemistry (Tanatani *et al.*, 2001) and catalysis (Fujita *et al.*, 1994). It is well known that the diversity in structure and topology of new metal-organic coordination polymers was attributed to the selection of metal centers and organic building blocks. In this paper, we adopted the ligand 1,3-bis(imidazol-1-ylmethyl)benzene (L1) and dichlorocadmium(II), which has an ability of forming metallomacrocycles. We report here the synthesis, structure and properties of the complex $[Cd(L1)_2Cl_2]_n$, (I).



X-ray crystallographic analysis provides direct evidence for the M_2L_2 metallocyclic ring-like structure of the title complex, (I). In the molecule of (I) (Fig. 1), the bond lengths and angles (Table 1) are within normal ranges (Allen *et al.*, 1987). The coordination around the Cd^{II} ion has a square-planar arrangement (Table 1). The terminal chloride ligands are coordinated in axial positions, thus affording an octahedral geometry around the metal ion. The 28-membered M_2L_2


Figure 1

A drawing of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity [symmetry codes: (A) $2 - x, -y, 1 - z$; (B) $2 - x, -y, -z$; (C) $x, y, z - 1$].


Figure 2

The metalocyclic ring double chain with a Cd...Cd distance of 11.0814 (12) Å.

metalocyclic ring of the complex contains two cadmium(II) chloride units (Fig. 2).

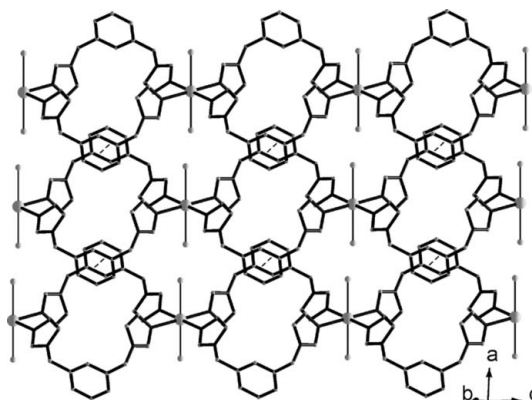
Rings *A* (N1/N2/C1–C3), *B* (C5–C10) and *C* (N3/N4/C12–C14) are, of course, planar and the dihedral angles between them are $A/B = 84.4 (2)^\circ$, $A/C = 72.7 (3)^\circ$ and $B/C = 72.3 (2)^\circ$. Ligand L1 adopts a *cis* conformation. The two opposite benzene rings in the macrocycle are strictly parallel to each other at a distance of 9.945 Å. The separation between the two Cd^{II} atoms (*i.e.* Cd1...Cd1A) is 11.0814 (12) Å. Two benzene rings in one M_2L_2 metalocycle are in a *gauche* conformation, which was also observed in the previously reported complexes [Zn(bib)₂(H₂O)₂](NO₃)₂·2H₂O (Fan *et al.*, 2004).

Nevertheless, ligand L1 in a *cis* conformation has a preference not only for forming an M_2L_2 metalocycle but also for forming an extended chain by using a ditopic acceptor with the bonding angle about 83.3° (Fig. 2). Moreover, adjacent chains interact *via* π – π interactions between two adjacent aromatic rings (centroid–centroid distance = 4.026 Å, offset 3.524 Å) to form two-dimensional layers (Janiak, 2000), as shown in Fig. 3.

When excited at 260 nm, (I) displays a strong violet emission band at $\lambda_{\max} = 294$ nm. The higher-energy band of 294 nm for (I) can be attributed to either metal-to-ligand charge transfer or ligand-to-metal charge transfer in nature (Tao *et al.*, 2001).

Experimental

Ligand L1 was prepared as described in the literature (Hoskins *et al.*, 1997). Compound (I) was hydrothermally synthesized under autogenous pressure. A mixture of CdCl₂ (0.0916 g, 0.5 mmol), L1 dihy-


Figure 3

Two-dimensional supramolecular layer in (I) constructed by π – π interactions (shown as dashed lines).

drate (0.138 g, 0.5 mmol) and H₂O (8 ml) was sealed in a 20 ml Teflon-lined autoclave and heated to 398 K for two days. After slow cooling to room temperature, colorless block-shaped crystals were obtained by filtration. The crystals were washed with distilled water several times and finally dried in air.

Crystal data

[CdCl₂(C₁₄H₁₄N₄)₂]
 $M_r = 659.88$
 Triclinic, $P\bar{1}$
 $a = 7.8698 (11) \text{ \AA}$
 $b = 8.8455 (14) \text{ \AA}$
 $c = 11.0814 (12) \text{ \AA}$
 $\alpha = 106.727 (4)^\circ$
 $\beta = 91.021 (4)^\circ$
 $\gamma = 107.385 (5)^\circ$

$V = 700.45 (17) \text{ \AA}^3$
 $Z = 1$
 $D_x = 1.564 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.00 \text{ mm}^{-1}$
 $T = 173 (2) \text{ K}$
 Block, colorless
 $0.25 \times 0.15 \times 0.15 \text{ mm}$

Data collection

Rigaku Mercury70 diffractometer
 ω scans
 Absorption correction: multi-scan
 (CrystalClear; Rigaku, 2000)
 $T_{\min} = 0.751, T_{\max} = 0.860$

5408 measured reflections
 3166 independent reflections
 3065 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.048$
 $S = 1.01$
 3166 reflections
 178 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0112P)^2 + 0.4778P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cd1–N1	2.3445 (14)	Cd1–Cl1	2.6473 (6)
Cd1–N4 ⁱ	2.3686 (15)		
N1–Cd1–N4 ⁱ	91.72 (5)	N1 ⁱⁱ –Cd1–Cl1	92.07 (4)
N1 ⁱⁱ –Cd1–N4 ⁱ	88.28 (5)	N4 ⁱ –Cd1–Cl1	93.20 (4)

Symmetry codes: (i) $-x + 2, -y, -z + 1$; (ii) $-x + 2, -y, -z$.

H atoms were positioned geometrically, with C–H = 0.95 and 0.99 Å for aromatic and methylene H atoms, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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