

The chain structure of *catena*-poly- [[*(2,2'*-bipyridine)cadmium(II)]- di- μ -chloro]

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$

R factor = 0.025

wR factor = 0.065

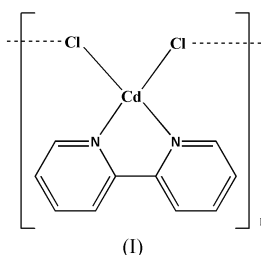
Data-to-parameter ratio = 13.6

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

In the title compound, $[\text{CdCl}_2(\text{C}_{10}\text{H}_8\text{N}_2)]_n$, the Cd^{II} ion is six-coordinate and has a distorted octahedral geometry. The basal plane is formed by the two N atoms of the 2,2'-bipyridine ligand [$\text{Cd}-\text{N}$ 2.352 (3) \AA] and two Cl atoms [$\text{Cd}-\text{Cl}$ 2.5519 (8) \AA]. The apical sites are occupied by Cl atoms from neighbouring monomeric units [$\text{Cd}-\text{Cl}$ 2.7517 (9) \AA]. All the Cl atoms act as bridging ligands. The adjacent Cd coordination polyhedra share Cl-Cl edges, thus giving rise to a polymeric chain along the c axis. The Cd^{II} ion is positioned on a twofold axis.

Comment

Polynuclear d^{10} metal complexes have been found to exhibit intriguing structural and photoluminescent properties. Chloride-bridged cadmium(II) polymeric complexes are of considerable interest, because they may act as photoactive materials. Structural studies of chloride-bridged Cd^{II} polymeric complexes are common (Bell *et al.*, 1982; Griffith *et al.*, 1982; Bigoli *et al.*, 1983; Huang *et al.*, 1998). However, Cd^{II} polymeric complexes with a CdCl_2N_2 coordination polyhedron have rarely been reported (Bonomo *et al.*, 1989). We have introduced 2,2'-bipyridine as a terminal ligand which favours crystal growth of the product. Through a hydrothermal reaction, we have successfully synthesized the title crystalline chloride-bridged Cd complex $[\text{CdCl}_2(\text{bpy})]_n$ (bpy is 2,2'-bipyridine), (I).



The structure of the title compound, (I) (Fig. 1), forms one-dimensional chains extending in the c direction (Fig. 2). It is isostructural with an analogous bromide-bridged Cu^{II} complex (Garland *et al.*, 1988). The Cd^{II} ion is positioned on a twofold axis, so the primarily monomeric unit is generated by symmetry (Fig. 1, Table 1).

The Cd^{II} ion in (I) is coordinated by two N atoms from one chelating bpy ligand and four Cl atoms, to furnish a distorted coordination octahedron, as depicted in Fig. 2. The basal plane is formed by the two *cis* N atoms from the bpy ligand [$\text{Cd}-\text{N}_{\text{cis}}\text{Cl}$ atoms [$\text{Cd}-\text{Cl}$ 2.5519 (8) \AA]. The axial positions of the octahedron are occupied by Cl atoms from neighbouring

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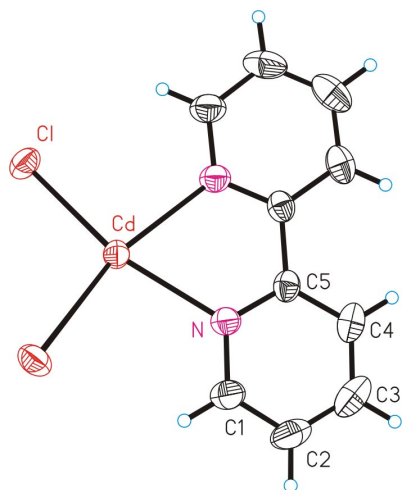


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

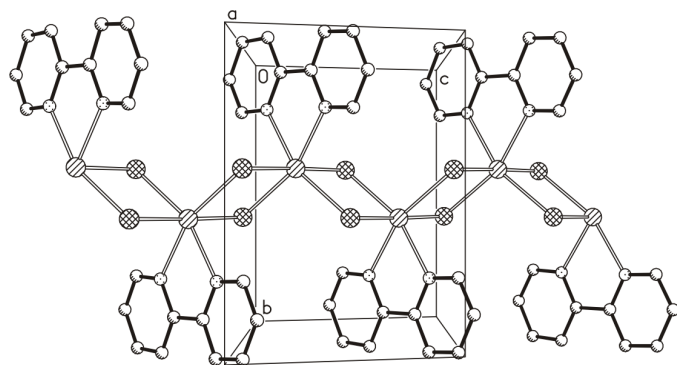


Figure 2
A view of the one-dimensional chain of chloride-bridged Cd^{II} ions in (I), along the *a* axis.

monomeric units [Cd—Clⁱ 2.7517 (9) Å] (symmetry code in Table 1). Adjacent Cd coordination octahedra share Cl—Cl edges, thus forming a one-dimensional chain along the *c* axis. All bpy ligands are coordinated in a chelating mode and they lie on alternate sides of the chain. The Cd···Cd distance between neighbouring Cd^{II} ions in the chain is 3.931 (9) Å, which is shorter than that of the Cu^{II} isomorph [3.974 (1) Å]. The closest distance between the pyridyl rings of two bpy ligands in neighbouring chains is 3.342 (3) Å, indicating the existence of π – π interactions between the adjacent chains. Thus the chains are connected to each other via π – π interactions to form two-dimensional layers parallel to the *bc* plane.

The packing of (I) (Fig. 3) is determined by van der Waals interactions and possible hydrogen bonds involving the C atoms of the bpy ligand and Cl atoms of the same [C4—H4A···Cl^{iv} 3.534 (5) Å] or adjacent [C2—H2A···Cl^v 3.751 (5) Å] chains [symmetry codes: (iv) $1 - x, 1 + y, \frac{3}{2} - z$; (v) $x - \frac{1}{2}, \frac{1}{2} + y, z - 1$].

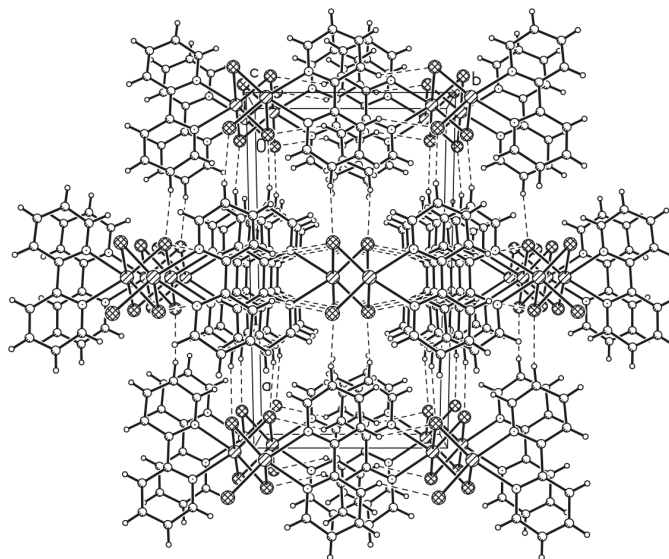


Figure 3
A packing diagram for (I), viewed down the *c* axis. Dashed lines indicate hydrogen bonds.

Experimental

The hydrothermal reaction of cadmium chloride (0.06 g, 0.26 mmol), 2,2'-bipyridine (0.04 g, 0.25 mmol) and water (15.0 ml) was carried out at 433 K for 4 d. After cooling to room temperature at 5 K h⁻¹, the crystalline complex, (I), was isolated in 63% yield (based on Cd). IR (KBr, ν , cm⁻¹): 3417, 1604, 1558, 1439, 1375, 1171, 1016, 771, 735. Elemental analysis, calculated for C₁₀H₈N₂CdCl₂: C 35.38, H 2.38, N 8.25%; found: C 35.16, H 2.17, N 8.23%.

Crystal data

[CdCl₂(C₁₀H₈N₂)]
 $M_r = 339.49$
 Monoclinic, *C*2/*c*
 $a = 17.5517$ (6) Å
 $b = 9.3166$ (6) Å
 $c = 7.1710$ (4) Å
 $\beta = 110.860$ (2)°
 $V = 1095.8$ (1) Å³
 $Z = 4$

$D_x = 2.058$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 35 reflections
 $\theta = 2.5$ – 25.0°
 $\mu = 2.44$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.56 \times 0.22 \times 0.20$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.494$, $T_{\max} = 0.613$
 1693 measured reflections

954 independent reflections
 885 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\max} = 25^\circ$
 $h = -20 \rightarrow 10$
 $k = -11 \rightarrow 6$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.065$
 $S = 1.12$
 954 reflections
 70 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.4415P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.43$ e Å⁻³
 $\Delta\rho_{\min} = -0.53$ e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.0037 (4)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|--------------------------------------|------------|---------------------------------------|------------|
| Cd—N | 2.352 (3) | C2—C3 | 1.368 (7) |
| Cd—Cl | 2.5519 (8) | C3—C4 | 1.373 (6) |
| Cd—Cl ⁱ | 2.7517 (9) | C4—C5 | 1.390 (5) |
| Cl—N | 1.342 (4) | C5—N | 1.338 (4) |
| Cl—C2 | 1.381 (6) | C5—C5 ⁱⁱ | 1.502 (7) |
| N ⁱⁱ —Cd—N | 69.93 (14) | Cl—Cd—Cl ⁱ | 84.40 (3) |
| N ⁱⁱ —Cd—Cl ⁱⁱ | 160.22 (7) | Cl ⁱ —Cd—Cl ⁱⁱⁱ | 178.73 (4) |
| N—Cd—Cl ⁱⁱ | 94.29 (7) | Cd—Cl—Cd ⁱ | 95.60 (3) |
| N—Cd—Cl | 160.22 (7) | N—C1—C2 | 122.6 (4) |
| Cl ⁱⁱ —Cd—Cl | 103.40 (4) | C3—C2—C1 | 118.6 (4) |
| N ⁱⁱ —Cd—Cl ⁱ | 95.66 (7) | C2—C3—C4 | 119.7 (4) |
| N—Cd—Cl ⁱ | 85.39 (7) | C3—C4—C5 | 118.9 (4) |
| Cl ⁱ —Cd—Cl ⁱⁱ | 94.81 (3) | N—C5—C4 | 121.7 (4) |

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

All H atoms were located in a difference Fourier map but were introduced in idealized positions (C—H = 0.93 Å) and treated as riding, with displacement parameters fixed at 120% of those of their parent atoms. The maximum residual electron-density peak is 0.84 Å from the Cd atom.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XPREP* (Bruker,

1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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