

Bis[aquachlorobis(1,10-phenanthroline)cadmium(II)]  
benzene-1,4-dioxydiacetate sesquihydrateYong-Cai Qiu,<sup>a</sup> Chen-Long  
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## Key indicators

Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
Disorder in solvent or counterion  
 $R$  factor = 0.025  
 $wR$  factor = 0.066  
Data-to-parameter ratio = 17.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

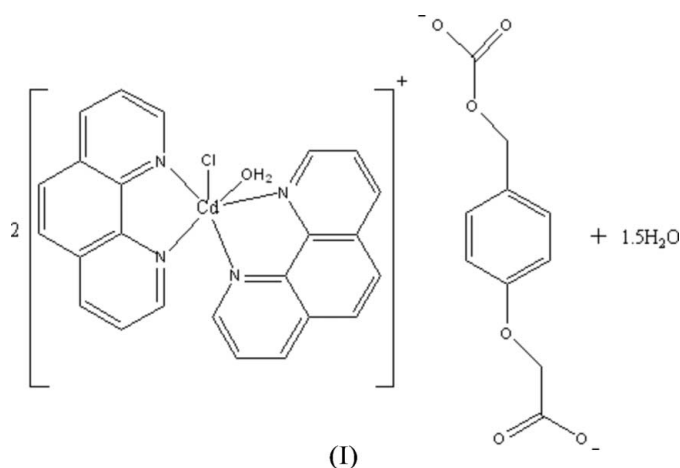
In the title compound,  $[\text{CdCl}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})]_2(\text{C}_{10}\text{H}_8\text{O}_6) \cdot 1.5\text{H}_2\text{O}$ , the  $\text{Cd}^{\text{II}}$  atom is coordinated by four N atoms from two phenanthroline ligands, one Cl ligand and one water molecule, and displays a distorted octahedral geometry. The anion is centrosymmetric. The packing is governed by intermolecular hydrogen bonds and a  $\pi-\pi$  stacking interaction.

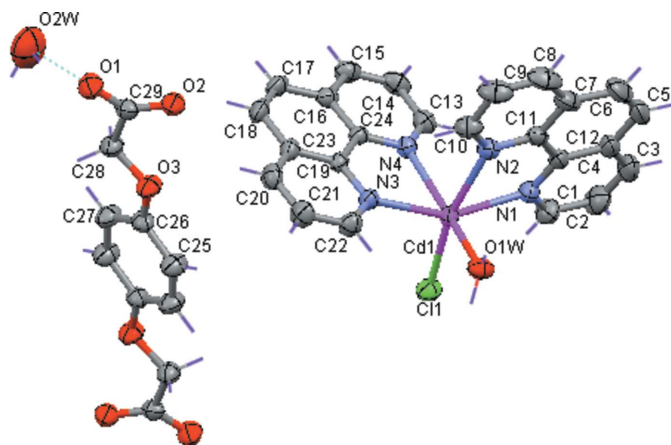
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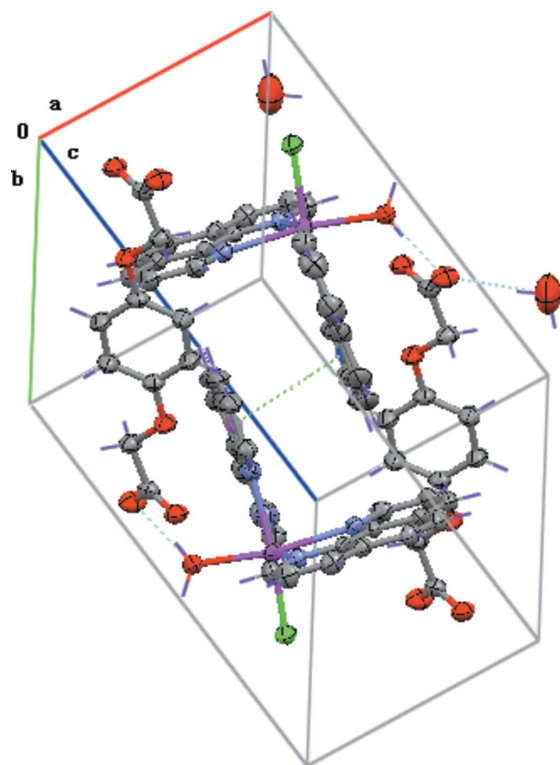
## Comment

In recent years, much attention has been paid to the design and construction of metal-organic frameworks because of their interesting structural motifs (Dakanali *et al.*, 2003), fluorescent properties (Shi *et al.*, 2004) and other potential applications (Seo *et al.*, 2000; Kitaura *et al.*, 2002; Rowsell *et al.*, 2004) in molecular-based materials. Phenylenedioxydiacetic acids, which are biologically active compounds and widely used in agriculture, are a family of flexible ligands of versatile binding modes. To the best of our knowledge, investigations of the phenylenedioxydiacetic acid complexes have mainly focused on the zinc, manganese, nickel, copper and cobalt salts of benzene-1,2-dioxyacetic acid (Kennard *et al.*, 1986; Smith *et al.*, 1991; Mccann *et al.*, 1994, 1995). The flexible benzene-1,4-dioxyacetic acid was successfully used as a ligand to design and synthesize a wide variety of metal complexes (Gao *et al.*, 2004, 2005), but its isolated anion is scarcely reported. We have selected cadmium(II), 1,10-phenanthroline (phen) and benzene-1,4-dioxyacetate as a central ion, a ligand and a counter-ion, respectively, to synthesize an anion-cation complex, (I), which exhibits strong fluorescence at 366 and 382 nm.





**Figure 1**  
The asymmetric unit of (I), together with the other half of the centrosymmetric anion. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are related to labelled atoms by  $(-x - 1, -y + 2, -z)$ .



**Figure 2**  
A packing view of (I), showing the intermolecular hydrogen bonds and the  $\pi$ - $\pi$  interaction as broken lines.

The asymmetric unit of (I) consists of a mononuclear  $[\text{CdCl}(\text{phen})_2(\text{H}_2\text{O})]^+$  cation, half of a benzene-1,4-dioxyacetate dianion, and 0.75 of an uncoordinated water molecule (Fig. 1). The anion is centrosymmetric. In the  $\text{Cd}^{\text{II}}$  complex, the  $\text{Cd}^{\text{II}}$  atom displays a distorted octahedral geometry, with four N donors from two bidentate chelating phen ligands, a water molecule and a Cl atom. The coordination bond lengths

and the angles at the  $\text{Cd}^{\text{II}}$  atom are given in Table 1. In the crystal structure, intermolecular hydrogen bonds (Table 2) and a  $\pi$ - $\pi$  stacking interaction link the components (Fig. 2). The centroid-centroid and interplanar distances of the  $\pi$ - $\pi$  stacking interaction between the phen planes are 3.760 (4) and 3.534 (3) Å, respectively.

## Experimental

The title compound was prepared by the addition of  $\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$  (0.114 g, 0.5 mmol) and 1,10-phenanthroline (0.099 g, 0.5 mmol) to a hot ethanol solution (50%) of benzene-1,4-dioxyacetic acid (0.113 g, 5 mmol), adjusted with an aqueous solution of sodium hydroxide ( $0.1 \text{ mol l}^{-1}$ ) to pH = 7.0. The mixture was stirred for 30 min and filtered. Colorless prismatic single crystals were obtained from the filtrate at room temperature after 3 d. Thermogravimetric analysis showed the loss of 3.5 water molecules between 353 and 529 K (calculated: 4.82; found: 4.87%).

### Crystal data

$[\text{CdCl}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})]_2 \cdot (\text{C}_{10}\text{H}_8\text{O}_6) \cdot 1.5\text{H}_2\text{O}$	$\gamma = 72.597 (1)^\circ$
$M_r = 1303.76$	$V = 1333.41 (5) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 10.1053 (2) \text{ \AA}$	$D_x = 1.624 \text{ Mg m}^{-3}$
$b = 12.1099 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 12.9095 (3) \text{ \AA}$	$\mu = 0.97 \text{ mm}^{-1}$
$\alpha = 62.297 (1)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 84.131 (1)^\circ$	Block, colorless
	$0.50 \times 0.40 \times 0.35 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer	18805 measured reflections
$\varphi$ and $\omega$ scans	6461 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	5895 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.630$ , $T_{\max} = 0.713$	$R_{\text{int}} = 0.020$
	$\theta_{\text{max}} = 28.2^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 0.4242P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.066$	$(\Delta\sigma)_{\text{max}} = 0.004$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$
6461 reflections	$\Delta\rho_{\text{min}} = -0.57 \text{ e \AA}^{-3}$
363 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cd1—N1	2.3495 (15)	Cd1—N4	2.4269 (16)
Cd1—N2	2.4101 (16)	Cd1—O1W	2.3226 (14)
Cd1—N3	2.3249 (15)	Cd1—Cl1	2.4831 (5)
O1W—Cd1—N1	98.20 (6)	N1—Cd1—Cl1	98.41 (4)
O1W—Cd1—N2	82.45 (5)	N2—Cd1—N3	91.04 (6)
O1W—Cd1—N3	96.96 (5)	N2—Cd1—N4	86.96 (5)
O1W—Cd1—N4	163.49 (5)	N2—Cd1—Cl1	167.25 (4)
O1W—Cd1—Cl1	93.81 (4)	N3—Cd1—N4	70.52 (5)
N1—Cd1—N2	70.24 (6)	N3—Cd1—Cl1	101.54 (4)
N1—Cd1—N3	153.99 (6)	N4—Cd1—Cl1	99.14 (4)
N1—Cd1—N4	90.03 (5)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1WB\cdots O1^i$	0.94	1.85	2.773 (2)	168
$O1W-H1WA\cdots O2^{ii}$	0.93	1.81	2.741 (2)	177
$O2W-H2WB\cdots O1$	0.95	2.07	2.967 (4)	158

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

H atoms of water molecules were located in a difference Fourier map and then refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$  ( $\text{O}-\text{H} = 0.94\text{--}0.98$  Å). Other H atoms were placed in calculated positions ( $\text{C}-\text{H} = 0.93\text{--}0.97$  Å) and were refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . For the final cycles, the O2W occupancy was fixed at 0.75, near the value obtained from free refinement of the O2W occupancy.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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