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Bis[μ-1-(1,10-phenanthrolin-2-yl)-2-pyridone]bis{aqua[1-(1,10-phenanthrolin-2-yl)-2-pyridone]cadmium(II)} tetrakis(perchlorate)

Qi Sheng Liu, Lian Dong Liu and Jing Min Shi*

Department of Chemistry, Shandong Normal University, Jinan 250014, People's Republic of China
Correspondence e-mail: shijingmin@beelink.com

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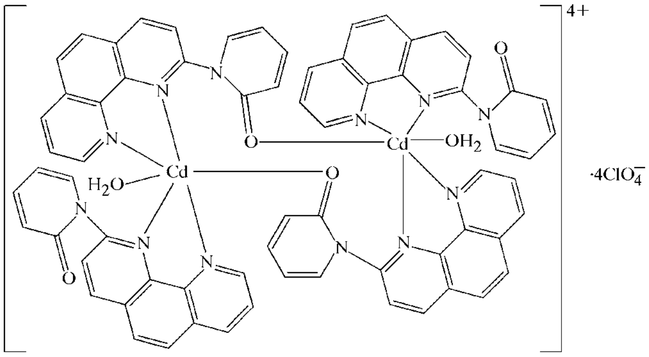
In the title centrosymmetric binuclear complex, $[Cd_2(C_{17}H_{11}N_3O)_4(H_2O)_2](ClO_4)_4$, the Cd^{II} ion assumes a distorted octahedral geometry. There are π–π stacking interactions between the pyridine and 1,10-phenanthroline ring systems of adjacent ligands at the same Cd^{II} centre. Intermolecular hydrogen bonds between the coordinated aqua ligand and the O atom of a keto group connect adjacent complex cations into extended chains. Hydrogen bonds also exist between the complex cations and the perchlorate anions. Compared with the fluorescence spectrum of the organic ligand, the complex displays strong fluorescent emission and an ipsochromic shift of the emission peaks, which may be attributed to the structural character.

Comment

Derivatives of 1,10-phenanthroline play a pivotal role in modern coordination chemistry and a number of complexes with these ligands have been synthesized. Some of them exhibit interesting properties as molecular electrical conductors (Zheng *et al.* 2003), as photoluminescent materials (Zhang *et al.*, 2006) and for cancer therapy (Liu *et al.*, 2004). Complexes with 1-(1,10-phenanthrolin-2-yl)-2-pyridone (PP) as a ligand have not, to our knowledge, been reported to date. Our interest in synthesizing new complexes with derivatives of 1,10-phenanthroline as ligands resulted in the title binuclear complex, (I). We report here the structure and fluorescence properties of (I).

Fig. 1 shows the dinuclear cation, which sits about a crystallographic centre of inversion. The Cd^{II} ion assumes a distorted octahedral CdN_4O_2 coordination geometry (Table 1). Each Cd^{II} ion is coordinated in a bidentate fashion by the N atoms of two PP ligands. One of the PP ligands also bridges *via* keto atom O3 to the other Cd^{II} ion in the cation. The two Cd^{II} ions are separated by 5.8159 (11) Å. The other PP ligand only functions as a terminal bidentate ligand, but its keto atom O2 is a hydrogen-bond acceptor (Table 2). This interaction is with a water ligand of an adjacent cation and leads to the formation of a supramolecular one-dimensional chain, which runs parallel to the [100] direction (Fig. 2). Table 2 and Fig. 2 also depict the hydrogen bonds and weaker C—H···O interactions between the complex cations and surrounding perchlorate anions.



(I)

The dihedral angles between the pyridine and 1,10-phenanthroline ring system planes are 64.44 (18)° for PP as a terminal ligand and 80.15 (15)° for PP as a bridging ligand. These differences can be expected in terms of steric relief. There are π–π stacking interactions between the pyridine and 1,10-phenanthroline ring systems of adjacent ligands at the same Cd^{II} centre [$Cg1\cdots Cg2$ = 3.439 (2) Å, $Cg1\cdots Cg2_{perp}$ = 3.333 Å and α = 8.05°, and $Cg3\cdots Cg4$ = 3.426 (3) Å, $Cg3\cdots Cg4_{perp}$ = 3.238° and α = 9.23°; $Cg1$, $Cg2$, $Cg3$ and $Cg4$ are the centroids of the Cd1/N1/C10/C11/N2, N5/C30–C34, Cd1/N3/C26/C22/N4 and N6/C1–C5 rings, respectively;

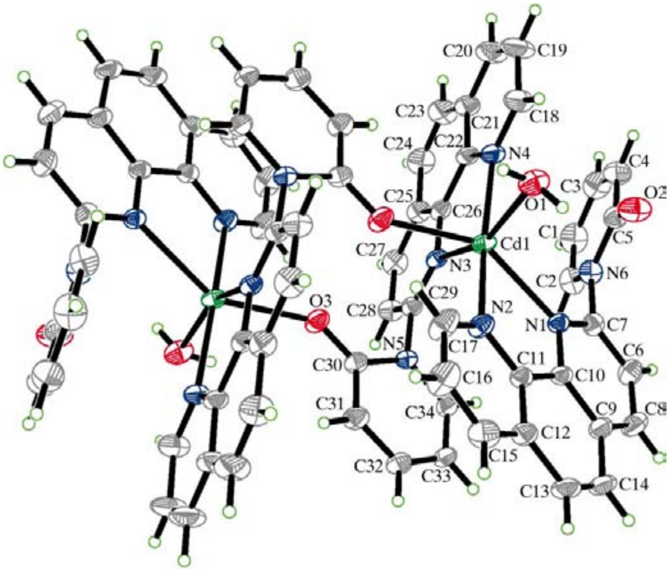


Figure 1
The binuclear complex cation of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme for the asymmetric unit; perchlorate anions have been omitted for clarity.

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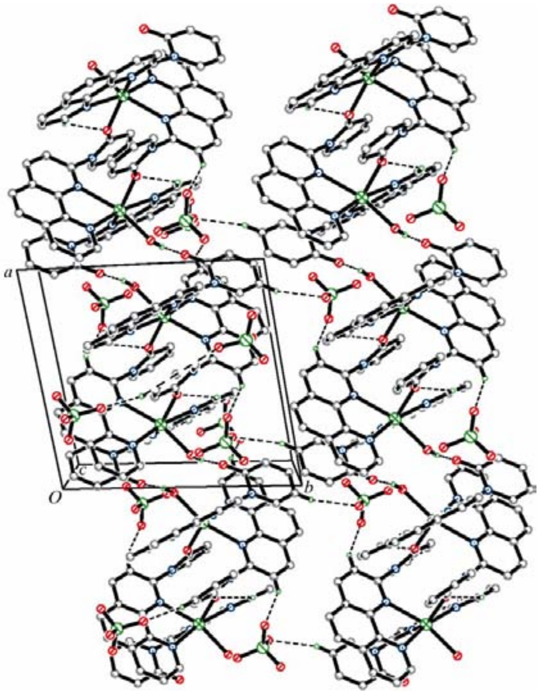

Figure 2
The packing and intermolecular interactions (dashed lines) of (I), viewed along the *c* axis.

CgI···*J*$_{perp}$ is the perpendicular distance from *CgI* to the plane containing ring *J*; α is the dihedral angle between planes *I* and *J*].

The fluorescence spectra for complex (I) and PP were measured at room temperature in the solid state, and the excitation wavelengths are at 395 nm for the complex and 467 nm for PP. The emission peak positions are at 444 and 473 nm for the complex and at 529 nm for PP. The appearance of the two emission peaks for the complex implies that there may be two different structures for the PP ligand in complex (I), which is consistent with the crystal structure. The peak at 444 nm may be attributed to the PP bridging ligand because of the larger dihedral angle between the pyridine and 1,10-phenanthroline ring system planes and, consequently, the lower degree of conjugation. Compared with the fluorescence spectrum of the complex, the bathochromic shift of the maximum emission peak of uncoordinated PP may imply that there should be a larger degree of conjugation and a smaller dihedral angle between the pyridine and 1,10-phenanthroline ring planes, although the crystal data for the PP ligand are not available as yet. At the same time, the emission intensity of complex (I) is stronger than that of the PP ligand, which may imply the existence of a strong π–π stacking interaction between PP molecules (Mizobe *et al.*, 2006).

Experimental

$Cd(ClO_4)_2 \cdot 6H_2O$ (0.2727 g, 0.65 mmol) was dissolved in 10 ml of methanol and then mixed with 10 ml of a methanol solution of PP (0.1774 g, 0.65 mmol), and the mixed solution was stirred for a few minutes. Yellow single crystals were obtained after allowing the mixed solution to stand at room temperature for two weeks (m.p. 367 K). The IR spectrum displays a strong and sharp peak at 1661 cm^{-1} corresponding to the vibration of the C=O group, and strong peaks at 1145, 1115 and 1085 cm^{-1} which can be attributed to vibrations of the perchlorate ion.

Crystal data

$[Cd_2(C_{17}H_{11}N_3O)_4(H_2O)_2](ClO_4)_4$
M_r = 1751.78
Triclinic, $P\overline{1}$
a = 11.681 (2) Å
b = 12.437 (2) Å
c = 12.709 (2) Å
α = 107.317 (2)°
β = 106.340 (2)°
γ = 91.838 (2)°
V = 1677.9 (5) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.88 mm^{-1}
T = 298 (2) K
0.24 × 0.16 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) T_{min} = 0.816, T_{max} = 0.917
9002 measured reflections
6304 independent reflections
5004 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.103
S = 0.99
6304 reflections
488 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N2	2.296 (3)	Cd1—O3^{i}	2.337 (2)
Cd1—N4	2.303 (3)	Cd1—N1	2.402 (3)
Cd1—O1	2.309 (3)	Cd1—N3	2.412 (3)
N2—Cd1—N4	168.48 (11)	O1—Cd1—N1	105.73 (9)
N2—Cd1—O1	84.05 (11)	O3^{i}—Cd1—N1	147.35 (10)
N4—Cd1—O1	84.52 (10)	N2—Cd1—N3	120.17 (11)
N2—Cd1—O3^{i}	83.31 (10)	N4—Cd1—N3	71.13 (10)
N4—Cd1—O3^{i}	95.45 (10)	O1—Cd1—N3	155.43 (10)
O1—Cd1—O3^{i}	90.95 (10)	O3^{i}—Cd1—N3	88.18 (9)
N2—Cd1—N1	71.08 (10)	N1—Cd1—N3	87.58 (9)
N4—Cd1—N1	113.63 (10)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H9···O2^{ii}	0.90	1.79	2.680 (4)	172
O1—H10···O8	0.90	2.04	2.924 (5)	169
C2—H2···O8^{iii}	0.93	2.56	3.463 (5)	164
C17—H17···O3^{i}	0.93	2.51	3.085 (5)	120
C19—H19···O10^{iv}	0.93	2.50	3.246 (5)	138
C28—H28···O9^{i}	0.93	2.50	3.318 (5)	147
C32—H32···O4^{v}	0.93	2.42	3.342 (5)	172

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

The H atoms of the water ligand were located in a difference map and the other H atoms were placed in calculated positions. All H atoms were refined using a riding model [O—H = 0.897–0.898 Å, C—H = 0.93 Å and $U_{iso}(H) = 1.5U_{eq}(O)$ or $1.2U_{eq}(C)$].

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3071). Services for accessing these data are described at the back of the journal.

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