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# Di-$\mu$-bromo-bis[bromo(di-2-pyridylmethanediol-*N*,*O*,*N*′)cadmium(II)] trihydrate

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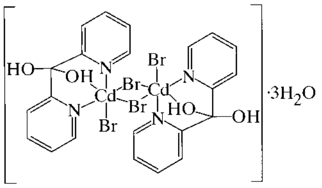
Di-2-pyridyl ketone reacts with $\mathrm{CdBr_2}$ in water to form the title centrosymmetric dinuclear complex, $[\mathrm{Cd_2Br_4(C_{11}H_{10}N_2O_2)_2}]\cdot 3\mathrm{H_2O}$, in which each metal atom is coordinated by an *N*,*O*,*N*′-chelated di-2-pyridylmethanediol ligand, two bridging bromo ligands and one terminal bromo ligand in a distorted octahedral geometry.

## Comment

Reactions of di-2-pyridyl ketone (DPK), a versatile polydentate ligand, with metal ions have attracted considerable attention for many years. A number of nucleophiles, including water and alcohols, have been shown to add to the carbonyl group upon coordination of the pyridyl groups to metal ions such as $\mathrm{Ag^{I}}$, $\mathrm{Cu^{II}}$, $\mathrm{Sb^{III}}$, $\mathrm{Co^{III}}$, $\mathrm{Ni^{II}}$, $\mathrm{Bi^{III}}$, $\mathrm{Cr^{III}}$, $\mathrm{Pd^{II}}$, $\mathrm{Pt^{II}}$ and $\mathrm{Au^{III}}$ (Tong *et al.*, 1998, 1999; Yang *et al.*, 1998, 2000), although exceptions have also been observed. In $\mathrm{Ag^{I}}$–DPK complexes, for instance, the ligand exists in its ketone form without hydration, even though these complexes were obtained from aqueous solution (Sommerer *et al.*, 1994; Yang *et al.*, 2000). The coordination of DPK to cadmium(II) has been reported only once (Tong *et al.*, 1999) and, in this case, the complex is mononuclear. We present here the crystal structure of the title dinuclear $\mathrm{Cd^{II}}$–DPK complex, (I).



(I)

The structure of (I) consists of discrete neutral $[\mathrm{Cd_2(di\text{-}2\text{-}pyridylmethanediol)_2(\mu_2\text{-}Br)_2Br_2}]$ molecules and interstitial water molecules. A view of the dinuclear molecule is shown in Fig. 1. Each molecule contains di-$\mu_2$-bromo bridging between the two metal atoms, and each metal atom is also bonded to a non-bridging bromo ligand and is capped by the organic ligand which functions in an *N*,*O*,*N*′-tridentate mode, resulting in a distorted octahedral coordination environment. The most distorted angle in the octahedron [N2—Cd1—O1 64.54 (15)°] is due to the chelating coordination of the organic ligand. The two terminal bromo ligands are *trans* oriented with respect to the bridge plane.

The Cd—O bond distance [2.601 (4) Å] is slightly longer than the Cd—N distances [2.355 (5) and 2.396 (5) Å]. These Cd—N bond lengths fall in the range expected for $\mathrm{Cd—N_{amine}}$ bonds (Benecini *et al.*, 1989; Cannas *et al.*, 1980; Tan *et al.*, 1993).

The $\mathrm{Cd—Br_{bridge}}$ bond distances [2.7072 (9) and 2.8556 (9) Å] are longer than the $\mathrm{Cd—Br_{terminal}}$ distance [2.5889 (10) Å]. The asymmetric bridging mode of atom Br1 may be attributed to the *trans* effect, since Br1 is *trans* to the stronger donor, the N atom, while $\mathrm{Br1^{i}}$ is *trans* to a weaker donor, the O atom [symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$].

It is also noteworthy that the coordination of atom O1 results in a longer C6—O1 bond [1.432 (6) Å] compared with that of C6—O2 [1.395 (7) Å]. Similar structures have been observed in $[\mathrm{Cd_2([9]aneN_3)_2(\mu_2\text{-}Cl)_2Cl_2}]$ and $[\mathrm{Cd_2([11]aneN_3)_2(\mu_2\text{-}Cl)_2Br_2}]$ ($\mathrm{[9]aneN_3}$ and $\mathrm{[11]aneN_3}$ are 1,4,7-triazacyclononane and 1,4,7-triazaundecane, respectively; Zompa *et al.*, 1995), where the capping organic ligands are cyclotriamines. The distance between the two metal atoms in the title complex is 3.9345 (11) Å, indicating no significant metal–metal interaction.

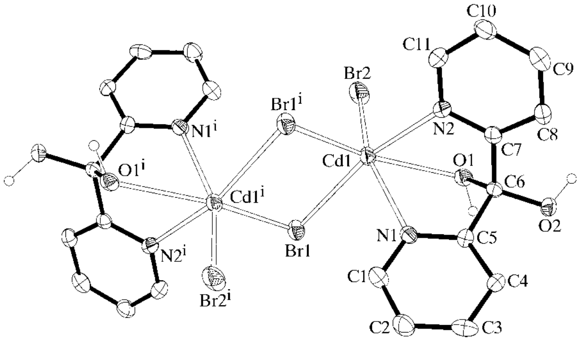


**Figure 1**
A view of the dinuclear complex (I) showing the atom-numbering scheme [symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$]. H atoms are drawn as spheres of arbitrary radii. Ellipsoids are plotted at the 35% probability level.

The structure of (I) is supported by hydrogen bonding involving each hydroxyl group, the lattice water molecules and the terminal Br ligand. The disordered lattice water molecule (O2*W*) forms weak hydrogen bonds with the other water molecule and with the bromo ligand.

## Experimental

$\mathrm{CdBr_2}$ (0.344 g, 1 mmol) was added to an aqueous solution of DPK (0.184 g, 1 mmol). The mixture was stirred until all the solids were totally dissolved and a colourless solution was obtained. The pH of the solution was then adjusted to 4 with $\mathrm{HNO_3}$. After filtration, the filtrate was evaporated slowly in a desiccator to give colourless crystals of (I) over a period of 3 d.

*Crystal data*

$[Cd_2Br_4(C_{11}H_{10}N_2O_2)_2]\cdot 3H_2O$
$M_r$ = 1002.91
Monoclinic, $C2/c$
$a$ = 8.114 (2) Å
$b$ = 22.474 (4) Å
$c$ = 16.642 (3) Å
$\beta$ = 96.08 (2)°
$V$ = 3017.7 (11) Å$^3$
$Z$ = 4

$D_x$ = 2.207 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 7.5–15.0°
$\mu$ = 6.752 mm$^{-1}$
$T$ = 293 (2) K
Block, colourless
0.3 × 0.2 × 0.2 mm

*Data collection*

Siemens $R3m$ diffractometer
$\omega$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{\min}$ = 0.152, $T_{\max}$ = 0.259
4305 measured reflections
2675 independent reflections
1997 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.011
$\theta_{\max}$ = 25.06°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 26$
$l = -19 \rightarrow 19$
2 standard reflections every 150 reflections intensity decay: 1.1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.080
$S$ = 1.066
2675 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 13.965P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 0.77 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.61 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cd1—N1 | 2.355 (5) | Cd1—O1 | 2.601 (4) |
| Cd1—N2 | 2.396 (5) | Cd1—Br1$^{\rm i}$ | 2.7072 (9) |
| Cd1—Br2 | 2.5889 (10) | Cd1—Br1 | 2.8556 (9) |
| | | | |
| N1—Cd1—N2 | 80.74 (17) | N1—Cd1—Br1 | 85.51 (12) |
| N1—Cd1—Br2 | 152.11 (13) | N2—Cd1—Br1 | 166.23 (13) |
| N2—Cd1—Br2 | 98.30 (12) | Br2—Cd1—Br1 | 93.53 (3) |
| N1—Cd1—O1 | 66.54 (15) | O1—Cd1—Br1 | 109.19 (9) |
| N2—Cd1—O1 | 64.54 (15) | O1—Cd1—Cd1$^{\rm i}$ | 150.12 (9) |
| Br2—Cd1—O1 | 87.72 (8) | C6—O1—Cd1 | 100.1 (3) |
| N1—Cd1—Br1$^{\rm i}$ | 102.01 (13) | C5—N1—Cd1 | 118.1 (4) |
| N2—Cd1—Br1$^{\rm i}$ | 93.47 (12) | C1—N1—Cd1 | 122.9 (4) |
| Br2—Cd1—Br1$^{\rm i}$ | 105.86 (3) | C7—N2—Cd1 | 117.3 (4) |
| O1—Cd1—Br1$^{\rm i}$ | 155.99 (9) | C11—N2—Cd1 | 125.2 (4) |

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

The H atoms of the interstitial water molecules were located in difference maps and included with $U_{\rm iso}$ fixed, but were not refined. All other H atoms were generated geometrically. One of the water molecules (O2$W$) is disordered about a twofold axis.

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1—H1$B\cdots$O1$W$ | 0.97 | 1.75 | 2.678 (7) | 159 |
| O2—H2$H\cdots$O1$^{\rm i}$ | 0.97 | 2.07 | 2.973 (6) | 154 |
| O2—H2$H\cdots$Br2$^{\rm i}$ | 0.97 | 3.11 | 3.686 (4) | 119 |
| O1$W$—H1$WA\cdots$O2$W$ | 0.97 | 2.17 | 2.996 (17) | 142 |
| O1$W$—H1$WB\cdots$Br1$^{\rm ii}$ | 0.96 | 2.96 | 3.590 (6) | 124 |
| O2$W$—H2$WA\cdots$Br2 | 0.95 | 2.56 | 3.51 (2) | 179 |

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

Data collection: *R*3*m Software* (Siemens, 1990); cell refinement: *R*3*m Software*; data reduction: *R*3*m Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1134). Services for accessing these data are described at the back of the journal.

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