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#### **Key indicators**

Single-crystal X-ray study T = 293 K Mean  $\sigma$ (C–C) = 0.009 Å R factor = 0.050 wR factor = 0.119 Data-to-parameter ratio = 14.4

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

© 2005 International Union of Crystallography Printed in Great Britain – all rights reserved Diaquadiperchlorato[ $\mu$ -11,23-dimethyl-3,7,15,19tetraazatricyclo[19.3.1.1<sup>9,13</sup>]hexacosa-1(25),2,7,9,-11,13(26),14,19,21,23-decaene-25,26-diolato- $1\kappa^2N,N';2\kappa^2N'',N''';1:2\kappa^2O:O'$ ]dicadmium(II) diaqua[ $\mu$ -11,23-dimethyl-3,7,15,19-tetraazatricyclo[19.3.1.1<sup>9,13</sup>]hexacosa-1(25),2,7,9,11,13(26),-14,19,21,23-decaene-25,26-diolato- $1\kappa^2N,N'$ ;- $2\kappa^2N'',N''';1:2\kappa^2O:O'$ ]dicadmium(II) diperchlorate

In the title complex,  $[Cd_2(C_{24}H_{26}N_4O_2)(ClO_4)_2(H_2O)_2]$ - $[Cd_2(C_{24}H_{26}N_4O_2)(H_2O)_2](ClO_4)_2$ , the two distinct macrocycles adopt essentially flat structures. They each encapsulate two Cd atoms. One Cd coordination polyhedron, completed by a water O atom and a perchlorate O atom, is distorted octahedral, while the other is best described as a CdN<sub>2</sub>O<sub>3</sub> square-based pyramid, with water in the apical site. Both dinuclear complexes are centrosymmetric. Received 5 May 2005 Accepted 3 June 2005 Online 10 June 2005

## Comment

Since the first dinuclear macrocyclic complexes were synthesized *via* template condensation at the beginning of the 1970 s, these species, especially those containing Schiff base diphenol macrocyclic ligands, have attracted much attention (Pilkington & Robson, 1970; Mohanta *et al.*, 1998; Wang *et al.*, 1997; Brianese *et al.*, 1999; Gao *et al.*, 2001). Macrocyclic complexes synthesized by the cyclocondensation reaction between 2,6diformyl-4-*R*-phenol and alkylenediamine have been obtained by a stepwise template reaction (*R* is CH<sub>3</sub>, *n*-butyl or Cl; Shangguan *et al.*, 2000; Zhou *et al.*, 2005; Wang *et al.*, 1997).



In order to understand better the different metal–cavity and metal–metal interactions in such species, the title complex, (I), (Fig. 1), with the macrocycle derived from the cyclo-condensation reaction between 2,6-diformyl-4-*R*-phenol and polyamine, was synthesized and its structure is presented here. Selected bond distances and angles relevant to the Cd<sup>II</sup> coordination spheres are listed in Table 1.



Figure 1

A view of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity. Atoms with the suffix A in the Cd1 molecule are generated by the symmetry operation (1 - x, 2 - y, 1 - z). Atoms with the suffix A in the Cd2 cation are generated by the symmetry operation (-x, 1 - y, -z).

There are two distinct dinuclear complexes in (I), both generated from the atoms of the asymmetric unit by inversion symmetry. Each contains a pair of Cd<sup>II</sup> atoms bridged by the two endogenous phenolic O atoms of the macrocycle ligand, with  $Cd1 \cdots Cd1^{i}$  and  $Cd2 \cdots Cd2^{ii}$  separations of 3.0882 (8) and 3.0880 (8) Å, respectively [symmetry codes: (i) 1 - x, 2 - y, 1-z; (ii) -x, 1-y, z]. The phenolic bridging angles are 103.41 (17) and 103.79 (18)° for the Cd1 and Cd2 complexes, respectively.

The Cd<sup>II</sup> coordination is subtly different in the two molecules. Atom Cd1 has a bound water molecule at 2.390 (4) Å and a close perchlorate O atom at 2.610 (4) Å. This results in a distorted CdN<sub>2</sub>O<sub>4</sub> octahedron. Atom Cd2 also possesses a bound water molecule [Cd-O = 2.436(5) Å], but the perchlorate groups associated with the Cd2 complex cation are much further away, at 2.947 Å. Thus, the Cd2 coordination can be described as a CdN<sub>2</sub>O<sub>3</sub> square-based pyramid. All the atoms in each of the macrocycles, except the propylene groups, are approximately coplanar.

## **Experimental**

2,6-Diformyl-4-methylphenol was prepared by a modification of the literature method of Taniguchi (1984). N.N'-Bis(3-formyl-5-methylsalicylidene)propylenediimine was prepared by the literature method of Okawa & Kida (1972). A mixture of Cd(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> (0.133 g, 0.5 mmol) and N,N'-bis(3-formyl-5-methylsalicylidene)propylenediimine (0.183 g, 0.5 mmol) in absolute methanol (30 ml) was added dropwise to a methanol solution (10 ml) containing 1,3-diaminopropane (0.037 g, 0.5 mmol). After stirring the mixture for 10 h at room temperature, a green-brown solution formed. A methanol solution (10 ml) containing cadmium perchlorate hexahydrate (0.210 g, 0.5 mmol) was added dropwise. A red-brown solid was obtained after stirring at room temperature for about 3 h. The product was filtered off, recrystallized from MeCN-Et<sub>2</sub>O (4:1), washed with diethyl ether and dried under a vacuum (yield 0.149 g, 35%). Red-brown block-like crystals of (I) suitable for X-ray diffraction were obtained by diffusion of ethyl acetate into an MeCN over one month. Analysis calculated solution for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>12</sub>Cl<sub>2</sub>Cd<sub>2</sub>: C 33.43, H 3.50, N 6.49%; found: C 33.56, H 3.57, N 6.40. IR (KBr, v, cm<sup>-1</sup>): 3482 (O-H), 1638 (C=N), 1096 and 621  $(ClO_4^{-}).$ 

#### Crystal data

 $[Cd_2(C_{24}H_{26}N_4O_2)(ClO_4)_2(H_2O)_2]$ - $[Cd_2(C_{24}H_{26}N_4O_2)( H_2O_2](ClO_4)_2$  $M_r = 1724.44$ Monoclinic,  $P2_1/c$ a = 16.5483 (15) Åb = 12.3987(11) Å c = 14.7440 (13) Å $\beta = 105.512 (1)^{\circ}$ V = 2914.9 (5) Å<sup>3</sup>

#### Data collection

Bruker SMART Apex CCD areadetector diffractometer  $\varphi$  and  $\varphi$  scans Absorption correction: multi-scan (SADABS; Bruker, 2000)  $T_{\min} = 0.62, \ T_{\max} = 0.69$ 16225 measured reflections

## Refinement

$w = 1/[\sigma^2(F_o^2) + (0.054P)^2]$
+ 1.6448P]
where $P = (F_0^2 + 2F_c^2)/2$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta \rho_{\rm max} = 0.74 \text{ e } \text{\AA}^{-3}$
$\Delta \rho_{\rm min} = -0.99 \text{ e } \text{\AA}^{-3}$

# Table 1

Cd1-N1	1.962 (5)	Cd2-O3	1.949 (4)
Cd1-O1	1.964 (4)	Cd2-N4	1.961 (5)
Cd1-O1 <sup>i</sup>	1.971 (4)	Cd2-O3 <sup>ii</sup>	1.976 (4)
Cd1-N2	1.974 (5)	Cd2-N3	1.981 (5)
Cd1-O2	2.390 (4)	Cd2-O4	2.436 (5)
Cd1-O11	2.610 (4)		

Z = 2

 $D_x = 1.965 \text{ Mg m}^{-3}$ 

Cell parameters from 5603

Mo  $K\alpha$  radiation

reflections

 $\theta = 2.2 - 22.9^{\circ}$ 

 $\mu = 1.71 \text{ mm}^{-1}$ 

T = 293 (2) K

 $R_{\rm int} = 0.032$ 

 $\theta_{\rm max} = 26.0^{\circ}$ 

 $h = -20 \rightarrow 10$ 

 $k = -15 \rightarrow 15$ 

 $l = -18 \rightarrow 18$ 

Block, red-brown

 $0.34 \times 0.24 \times 0.22 \text{ mm}$ 

5731 independent reflections

4747 reflections with  $I > 2\sigma(I)$ 

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

All H atoms were placed in calculated positions, with C-H distances in the range 0.93-0.97 Å and O-H equal to 0.85 Å, and included in the refinement in the riding-model approximation, with  $U_{\rm iso}({\rm H}) = 1.2 - 1.5 U_{\rm eq}({\rm C,O}).$ 

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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