Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Diaquadiperchlorato[μ-11,23-dimethyl-3,7,15,19-tetraazatricyclo[19.3.1.$1^{9,13}$]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[μ-11,23-dimethyl-3,7,15,19-tetraazatricyclo[19.3.1.$1^{9,13}$]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

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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_2O_3 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

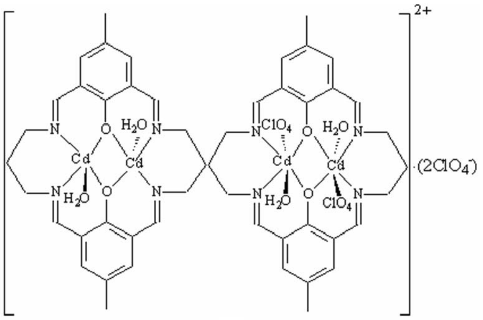
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(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.

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 2,6-diformyl-4-*R*-phenol and alkylenediamine have been obtained by a stepwise template reaction (*R* is CH_3, *n*-butyl or Cl; Shangguan *et al.*, 2000; Zhou *et al.*, 2005; Wang *et al.*, 1997).



(I)

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 cyclocondensation 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^{II} coordination spheres are listed in Table 1.

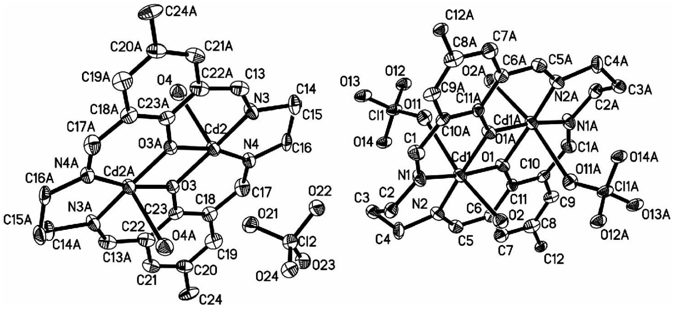


Figure 1

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^{II} 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^{II} 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_2O_4 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_2O_3 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 $Cd(OAc)_2(H_2O)_2$ (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$_2$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 solution over one month. Analysis calculated for $C_{24}H_{30}N_4O_{12}Cl_2Cd_2$: C 33.43, H 3.50, N 6.49%; found: C 33.56, H 3.57, N 6.40. IR (KBr, ν, cm^{-1}): 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) Å
$b = 12.3987$ (11) Å
$c = 14.7440$ (13) Å
$\beta = 105.512$ (1)°
$V = 2914.9$ (5) Å^3

$Z = 2$
$D_x = 1.965$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5603 reflections
$\theta = 2.2$–22.9°
$\mu = 1.71$ mm^{-1}
$T = 293$ (2) K
Block, red-brown
0.34 × 0.24 × 0.22 mm

Data collection

Bruker SMART Apex CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.62$, $T_{max} = 0.69$
16225 measured reflections

5731 independent reflections
4747 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 26.0°$
$h = -20 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.119$
$S = 1.08$
5731 reflections
399 parameters
H-atom parameters constrained

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

Table 1
Selected bond length (Å).

Cd1—N1	1.962 (5)	Cd2—O3	1.949 (4)
Cd1—O1	1.964 (4)	Cd2—N4	1.961 (5)
Cd1—O1^{i}	1.971 (4)	Cd2—O3^{ii}	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)		

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 $U_{iso}(H) = 1.2$–$1.5U_{eq}(C,O)$.

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*.

The authors thank the National Science Foundation of China (grant No.20271039).

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