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Diaqua-1κO,2κO-[μ-11,23-dichloro-3,7,15,19-tetraazatricyclo[19.3.1.1^{19,13}]hexacosa-1(25),2,7,9,11,13(26),14,19,21,23-decaene-25,26-diolato-1$\kappa^4 N^3$,N^7,O^{25},O^{26}:2$\kappa^4 N^{15}$,N^{19},O^{25},O^{26}]dizinc(II) dinitrate

Zhao-Lian Chu and Wei Huang*

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail: whuang@nju.edu.cn

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The title compound, $[Zn_2(C_{22}H_{20}Cl_2N_4O_2)(H_2O)_2](NO_3)_2$, was obtained by the ion-exchange reaction of a dinuclear zinc(II)–diperchlorate complex of the macrocycle with $Zn(NO_3)_2 \cdot 6H_2O$. The complex lies about a centre of symmetry and the coordination about the Zn atom is distorted square pyramidal. Intermolecular hydrogen bonds and π–π stacking interactions form a three-dimensional supramolecular network.

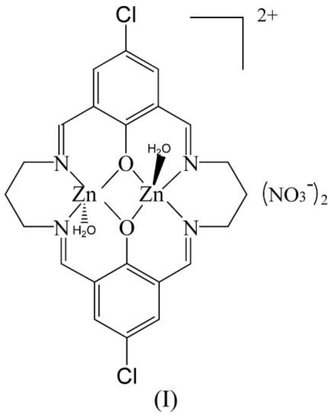
Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.102
Data-to-parameter ratio = 13.0

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

Comment

Since the first homodinuclear Schiff base macrocyclic complexes were synthesized by Pilkington & Robson (1970), a large body of work has been reported on this and related macrocyclic systems. In our recent work in this area, special emphasis has been placed on the self-assembly of macrocyclic dinuclear zinc(II) complexes with diverse architectures and functions (Fang *et al.*, 2000; Huang, Gou, Hu, Chantrapromma *et al.*, 2001; Huang *et al.*, 2006).



(I)

We have previously reported the crystal structure of a dinuclear zinc(II) diperchlorate complex of a Robson macrocycle (Huang, Gou, Hu, Xu *et al.*, 2001). We were interested in substituting the potentially explosive perchlorate anions, and replacement with NO_3^- anions gave the title complex, (I) (Fig. 1)

The asymmetric unit of (I) comprises a nitrate anion and one half of the complex cation, which lies about a centre of symmetry located at the centroid of the four-membered ring formed by the two Zn atoms and bridging O atoms of the phenolate groups. Each zinc(II) center is five-coordinate with a square-pyramidal configuration. The basal plane of the square pyramid consists of the N1, N2, O1 and O1($2 - x$, $-y$, $-z$) atoms of the macrocyclic ligand with the O atom of a coordinated water molecule in the apical position (Fig. 1). The

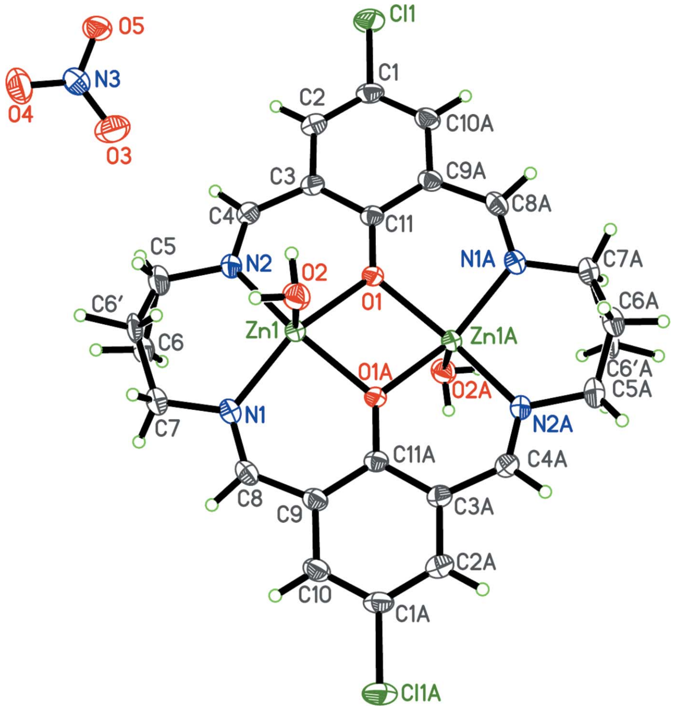


Figure 1
The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. Both disorder components are shown. Atoms labelled A are related to other atoms by the symmetry operation $2 - x, -y, -z$.

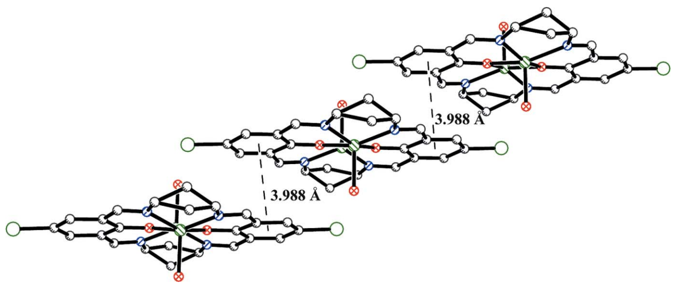


Figure 2
A perspective view of the π–π stacking in the title compound.

two coordinated water molecules in the dinuclear complex are mutually *trans*. The subtle change of counter-ions leads to a modification of the crystal system and space group from orthorhombic *Pbcn* for the perchlorate salt to monoclinic $P2_1/n$ in (I). The two Zn centers are separated by 3.221 (4) Å, slightly longer than in the dinuclear zinc(II) diperchlorate complex [3.192 (4) Å]. Each Zn atom lies out of the square plane by 0.416 (1) Å.

In the crystal structure of (I), each nitrate anion is involved in two O—H···O hydrogen bonds with the H atoms of coordinated water molecules, and a C—H···O hydrogen bond with the methylene H atom of C6 (Table 1). In addition, weak offset π–π stacking interactions are present between vicinal benzene rings of the macrocycles [related by $(1 - x, -y, z)$], leading to the formation of layers (Fig. 2). The centroid-centroid separation between them is 3.988 (4) Å. These interactions generate a three-dimensional network (Fig. 3).

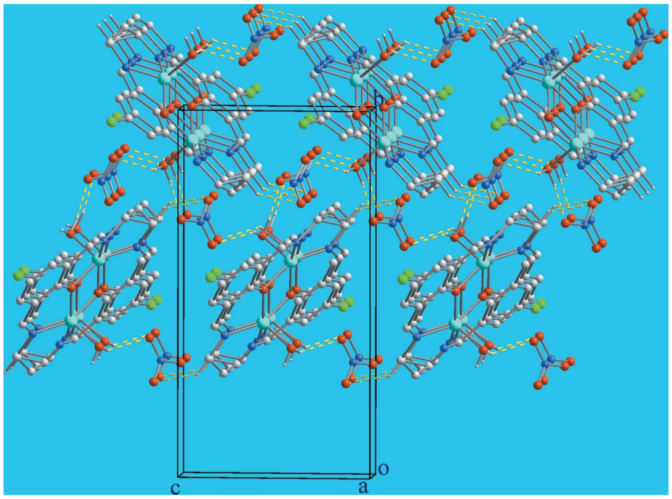


Figure 3
A packing diagram of (I) viewed down the *a* axis. Dashed lines indicate hydrogen bonds.

This is different from the dinuclear zinc(II) diperchlorate complex, in which a two-dimensional hydrogen-bonded network is formed without the additional stabilization of π–π stacking.

Experimental

Compound (I) was prepared *via* an ion-exchange reaction. The dinuclear zinc(II) diperchlorate complex (0.0808 g, 0.1 mmol), prepared *via* a sodium template method as reported previously (Gou & Fenton, 1994), was dissolved in acetonitrile (30 ml) and $Zn(NO_3)_2\cdot 6H_2O$ (0.0595 g, 0.2 mmol) added. The mixture was refluxed for 2 h, and then cooled to room temperature. The yellow precipitate was collected, washed with a small amount of acetonitrile and dried *in vacuo* (yield: 0.0528 g, 72%). Elemental analysis calculated for $C_{22}H_{24}Cl_2N_6O_{10}Zn_2$: C 35.99, H 3.30, N 11.45%; found: C 35.94, H 3.27, N 11.40%. Single crystals suitable for X-ray analysis were grown by slow evaporation of an ethanol and acetonitrile 1:2 (*v*/*v*) solution in air at room temperature. **CAUTION:** Although no problems were encountered in this work, perchlorate compounds are potentially explosive. They should be prepared in small amounts and handled with care.

Crystal data

$[Zn_2(C_{22}H_{20}Cl_2N_4O_2)(H_2O)_2](NO_3)_2$
$M_r = 734.11$
Monoclinic, $P2_1/n$
$a = 8.379$ (3) Å
$b = 17.330$ (6) Å
$c = 9.506$ (3) Å
$\beta = 105.431$ (6)°
$V = 1330.5$ (8) Å^3
$Z = 2$
$D_x = 1.832$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.07$ mm^{-1}
$T = 291$ (2) K
Block, yellow
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.615$, $T_{max} = 0.664$
6999 measured reflections
2605 independent reflections
2196 reflections with $I > 2\sigma(I)$
$R_{int} = 0.071$
$\theta_{max} = 26.0°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.103$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.59$ e Å^{-3}
2605 reflections	$\Delta\rho_{min} = -0.37$ e Å^{-3}
200 parameters	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2B···O5^{i}	0.82	1.89	2.711 (3)	174
O2—H2C···O4^{ii}	0.85	2.20	2.839 (4)	132
C6—H6B···O3^{iii}	0.97	2.48	3.269 (6)	139

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

All H atoms were positioned geometrically (C—H = 0.93–0.97 Å and O—H = 0.82–0.85 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(O). The central carbon of the 1,3-diaminepropane fragment C6 is disordered over two positions with site-occupancy factors of 0.709 (10) and 0.291 (10).

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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References

Bruker (2000). *SMART* (Version 5.622), *SAINT* (Version 6.02a), *SADABS* (Version 2.03) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Fang, J.-L., Huang, W., Chantrapromma, S., Shanmuga Sundara Raj, S., Razak, I. A., Fun, H.-K., Gou, S.-H. & Wang, H.-S. (2000). *Acta Cryst.* C**56**, 1429–1430.

Gou, S.-H. & Fenton, D. E. (1994). *Inorg. Chim. Acta*, **223**, 169–172.

Huang, W., Gou, S.-H., Hu, D.-H., Chantrapromma, S., Fun, H. K. & Meng, Q.-J. (2001). *Inorg. Chem.* **40**, 1712–1715.

Huang, W., Gou, S.-H., Hu, D.-H., Xu, Y., Chantrapromma, S. & Meng, Q.-J. (2001). *J. Mol. Struct.* **561**, 121–129.

Huang, W., Zhu, H.-B. & Gou, S.-H. (2006). *Coord. Chem. Rev.* **250**, 414–423.

Pilkington, N. H. & Robson, R. (1970). *Aust. J. Chem.* **23**, 2226–2236.