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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
 Disorder in main residue
 R factor = 0.037
 wR factor = 0.106
 Data-to-parameter ratio = 11.0

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

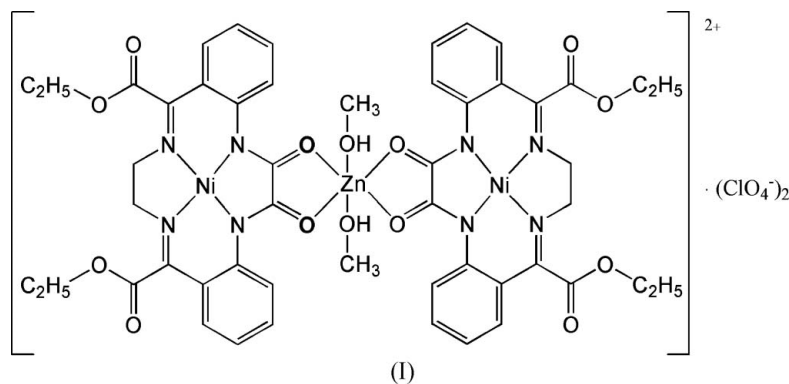
A new heterotrinnuclear macrocyclic complex: bis(μ -diethyl 5,6,7,8,15,16-hexahydro-6,7-dioxo-5,8,14,17-tetraazadibenzo[*a,g*]cyclotetradecine-13,18-dicarboxylato)- $1\kappa^4\text{N}:2\kappa^2\text{O}^6,\text{O}^7;2\kappa\text{O}^6,\text{O}^7:3\kappa^4\text{N}$ -dimethanoldinickel(II)zinc(II) bis(perchlorate)

The title compound, $[\text{Ni}_2\text{Zn}(\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_6)_2(\text{CH}_3\text{O})_2](\text{ClO}_4)_2$, was synthesized using a mononuclear complex ligand NiL (*L* is diethyl 5,6,7,8,15,16-hexahydro-6,7-dioxo-5,8,14,17-tetraazadibenzo[*a,g*]cyclotetradecine-13,18-dicarboxylate), $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and CH_3OH . X-ray single-crystal analysis reveals that the Zn^{2+} ion is in a slightly distorted octahedral O_6 environment. The trinuclear complex cation is centrosymmetric. The Zn^{2+} and both Ni^{2+} ions are bridged by the oxamide group from the macrocyclic ligand *L*. Intermolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds exist between the perchlorate anion and the complex cation, and $\pi-\pi$ interactions organize the trinuclear cations to form supramolecular one-dimensional chains in the crystal structure.

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Comment

Polynuclear complexes are currently of considerable interest and have been researched widely. Black & Moss (1987) first synthesized a series of *ML*-like complexes (*L* is diethyl 5,6,7,8,15,16-hexahydro-6,7-dioxo-5,8,14,17-tetraazadibenzo[*a,g*]cyclotetradecine-13,18-dicarboxylate), and many polynuclear complexes with interesting structures and properties have been synthesized using these mononuclear complexes as ligands (Gao *et al.*, 2001; Zhang *et al.*, 2003; Wang, Yang, Liao & Li, 2004; Sun *et al.*, 2004; Wang, Yang, Li *et al.*, 2004). We have synthesized a number of heterotrinnuclear complexes with NiL-like ligands (Li, Liao *et al.*, 2002; Li, Yu *et al.*, 2002; Li, Liao *et al.*, 2003). In this report, we present the structure of the title heterotrinnuclear complex of Zn with NiL, (I).



The molecular structure of (I) is illustrated in Fig. 1. The trinuclear complex cation is centrosymmetric. There is an oxamide bridge between atom Zn1 and each of the two Ni

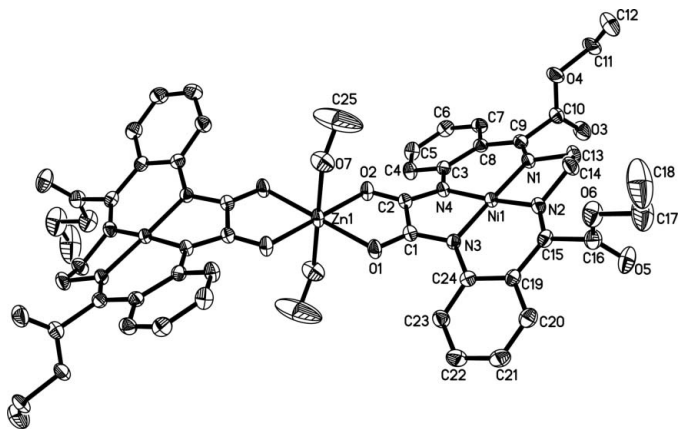


Figure 1

A view of the trinuclear cation of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and, for the sake of clarity, H atoms have been omitted. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x, 1 - y, -z)$.

atoms. The coordination environment (Table 1) of the Ni atom is slightly distorted square-planar, with two deprotonated oxamido N atoms and two imino N atoms as donors. The deviations of the four donor atoms (N1, N2, N3 and N4) from their mean plane are -0.0562 (5), 0.0732 (5), -0.0571 (5) and 0.0725 (5) Å, respectively, and Ni1 is -0.0324 (5) Å out of the plane. Atom Zn1 resides in the centre of a slightly distorted octahedral environment, with four completely coplanar O atoms of two oxamide groups in the equatorial positions and two atoms of two CH₃OH ligands in the axial positions. The dihedral angle between the Zn equatorial plane and the coordination plane of the Ni atom is 27.8 (9)°. The three metal atoms in the trinuclear cation are arranged in a straight line, and the distance between atom Zn1 and each Ni atom is 5.180 (4) Å. The trinuclear cation provides atoms O7 and H7A to form intermolecular O—H...O hydrogen bonds with atoms O8 and O9' of the disordered perchlorate anion, respectively (Table 2).

Each of the two NiL fragments of a trinuclear cation overlaps with an NiL fragment of another trinuclear cation (Fig. 2). Some atom-to-atom distances between overlapping NiL fragments are in the range of strong π – π interactions (Janiak, 2000). For example, the distances between atom Ni1 of one fragment of a trinuclear cation and atoms C7 and C8 of a fragment of another trinuclear cation are 3.591 (5) and 3.634 (5) Å, respectively, and the distance between atoms C15 of the former and C6 of the latter is 3.266 (5) Å. The π – π interactions among these overlapping fragments are evident. These π – π interactions also result in one-dimensional chains of overlapping trinuclear cations in the crystal structure. Although the anion–cation interplay certainly contributes much to the stabilization of the crystal structure, it is the O—H...O hydrogen bonds and π – π interactions which provide directionality, selectivity and reproducibility to organize the ions in space (Braga & Grepioni, 1999).

Experimental

NiL (Black & Moss, 1987; Li, Yang *et al.*, 2003) (0.044 mmol), Zn(ClO₄)₂·6H₂O (0.088 mmol) and CH₃OH (40 ml) were mixed. The mixture was stirred and heated under reflux. After a few minutes, the mixture became a clear orange solution. This solution was stored for 12 weeks at room temperature, and red crystals of (I) suitable for X-ray single-crystal investigation were obtained. The solid product was washed with CH₃OH and dried in a vacuum to yield 39%. Spectroscopic analysis: IR (KBr, ν , cm⁻¹): 3450, 1730, 1615, 1605, 1590, 1100. (IR spectra were recorded on a BIO-RAD FTS 3000 infrared spectrophotometer). The complex decomposes at 561–563 K. Analysis, required for [Zn^{II}(Ni^{II}L)₂(CH₃OH)₂](ClO₄)₂: C 43.81, H 3.82, N 8.18%; found: C 43.94, H 3.70, N 8.39%.

Crystal data

[Ni₂Zn(C₂₄H₂₂N₄O₆)₂(CH₃O)₂](ClO₄)₂
 $M_r = 1370.69$
 Monoclinic, $P2_1/c$
 $a = 10.4582$ (16) Å
 $b = 12.8031$ (19) Å
 $c = 21.161$ (3) Å
 $\beta = 99.308$ (2)°
 $V = 2796.1$ (7) Å³
 $Z = 2$

$D_x = 1.628$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4578 reflections
 $\theta = 2.5$ – 26.4 °
 $\mu = 1.28$ mm⁻¹
 $T = 293$ (2) K
 Block, red
 $0.32 \times 0.22 \times 0.14$ mm

Data collection

Bruker APEX-II CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.674$, $T_{\max} = 0.836$
 14921 measured reflections

4941 independent reflections
 4033 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$
 $\theta_{\max} = 25.0$ °
 $h = -12 \rightarrow 12$
 $k = -15 \rightarrow 13$
 $l = -25 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.106$
 $S = 1.07$
 4941 reflections
 450 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 2.4619P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.57$ e Å⁻³
 $\Delta\rho_{\min} = -0.46$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—O2	2.041 (2)	Ni1—N4	1.872 (2)
Zn1—O1	2.107 (2)	N1—C9	1.285 (4)
Zn1—O7	2.123 (3)	N2—C15	1.291 (4)
Ni1—N2	1.859 (3)	N3—C24	1.411 (4)
Ni1—N1	1.862 (3)	N4—C3	1.407 (4)
Ni1—N3	1.866 (2)		
O2 ⁱ —Zn1—O2	180	O2—Zn1—O7 ⁱ	90.00 (10)
O2—Zn1—O1 ⁱ	99.64 (8)	O1—Zn1—O7 ⁱ	90.20 (11)
O2 ⁱ —Zn1—O1	99.64 (8)	O7—Zn1—O7 ⁱ	180
O2—Zn1—O1	80.36 (8)	N2—Ni1—N1	87.28 (12)
O1 ⁱ —Zn1—O1	180	N2—Ni1—N3	92.54 (11)
O2 ⁱ —Zn1—O7	90.00 (10)	N1—Ni1—N3	178.49 (11)
O2—Zn1—O7	90.00 (10)	N2—Ni1—N4	173.47 (11)
O1 ⁱ —Zn1—O7	90.20 (11)	N1—Ni1—N4	93.63 (11)
O1—Zn1—O7	89.80 (11)	N3—Ni1—N4	86.72 (10)

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

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O7—H7A...O8	0.93	2.28	2.9264	126
O7—H7A...O9'	0.93	2.05	2.7681	133

The anion is disordered over two different orientations with the same fixed occupancies of 0.50 and 0.50. The two CH₃OH molecules coordinated to Zn²⁺ are disordered over two different positions with fixed occupancies of 0.55 and 0.45. The two ethoxy groups (involving atoms C17 and C18) of the complex ligand are disordered over two different positions with the same fixed occupancies of 0.50 and 0.50. The values of the occupancies were initially refined and then fixed. The *R* factors and the *U*_{eq} values based on the refined values of the occupancies are not so good as those based on the fixed values of the occupancies. The disordered anion was refined with geometrical restraints. All H atoms were located in a difference Fourier map and were refined as riding, with O—H = 0.93 Å and C—H = 0.93–0.97 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,O) or 1.5*U*_{eq}(methyl C).

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

X-ray data were collected at Tianjin Normal University.

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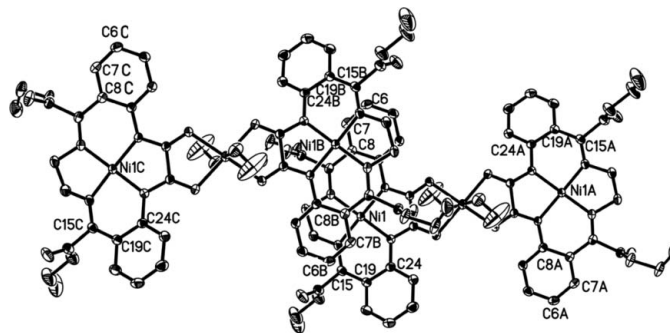


Figure 2
A portion of the one-dimensional chains of the trinuclear cations linked by π – π interactions. H atoms have been omitted. [Symmetry codes: (A) $-x, 1 - y, -z$; (B) $-x, 2 - y, -z$; (C) $x, 1 + y, z$.]

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