

Chang-Qing Li, Li-Na Zhu,
Xiao-Zeng Li* and Rong LiDepartment of Chemistry, Tianjin University,
Tianjin 300072, People's Republic of ChinaCorrespondence e-mail:
lixiaozeng321@tju.edu.cn

Key indicators

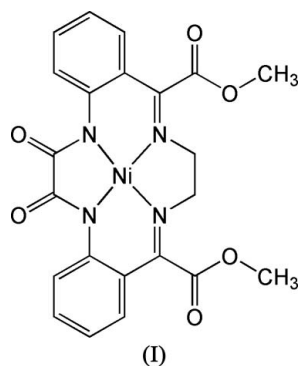
Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.030
 wR factor = 0.079
Data-to-parameter ratio = 12.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A new polymorph of (dimethyl 5,6,7,8,15,16-
hexahydro-6,7-dioxo-5,8,14,17-tetraazadibenzo[*a,g*]-
cyclotetradecine-13,18-dicarboxylato- $\kappa^4\text{N}$)nickel(II)

A new polymorph of the title complex, $[\text{Ni}(\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_6)]$, has been synthesized and structurally characterized. Ni(II) is coordinated by the four nitrogen donors of the macrocyclic ligand with a distorted square-planar geometry. C—H \cdots O hydrogen bonds and $\pi\cdots\pi$ stacking interactions link the complex molecules, forming an infinite three-dimensional supramolecular network.

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Comment

Macrocyclic complexes have been a significant research area for decades because of their relationship to biomimetic and catalytic systems and their applications in biology, medicine and chemical techniques (Li *et al.*, 2005). Some mononuclear complexes of macrocyclic oxamido Schiff bases have been used as 'complex ligands' to design polynuclear complexes (Christodoulou *et al.*, 1990; Gao *et al.*, 1999; Gao *et al.*, 2001; Li, Liao *et al.*, 2002; Li, Yu *et al.*, 2002). The title complex was first prepared by Black & Moss (1987) and an X-ray crystal structure in space group $P\bar{1}$ was reported by Li *et al.* (2003). Here we report the synthesis and structure of a new polymorph of the complex, in space group $C2/c$.



The structure of the title complex is shown in Fig. 1, and there is no significant difference compared with that in the formerly reported polymorph. The macrocyclic ligand coordinates to Ni(II) through its two deprotonated oxamido N and two imine N atoms in a distorted square-planar geometry. The deviations of the four donor atoms (N1, N2, N3 and N4) from their mean plane are +0.104 (3) Å, -0.095 (3) Å, +0.105 (3) Å and -0.094 (3) Å, respectively, and Ni1 is -0.020 (3) Å out of the plane. The two benzene rings tilt towards the same side of this plane. The dihedral angles between the plane (N1, N2, N3 and N4) and the C3-C8 and C17-C22 benzene ring planes are 25.7 (7) and 11.3 (5)°, respectively. Previous studies (Taylor & Kennard, 1984) have suggested that C—H \cdots O hydrogen bonds occur when the C \cdots O separations are in the range

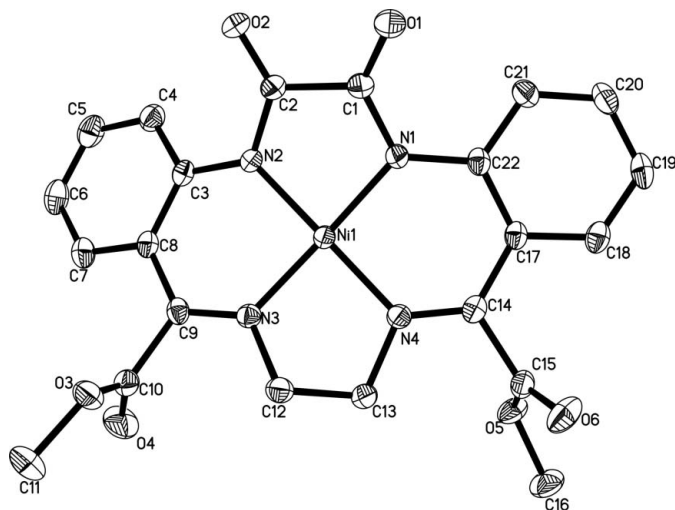


Figure 1
View of the molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and, for the sake of clarity, H atoms are not shown.

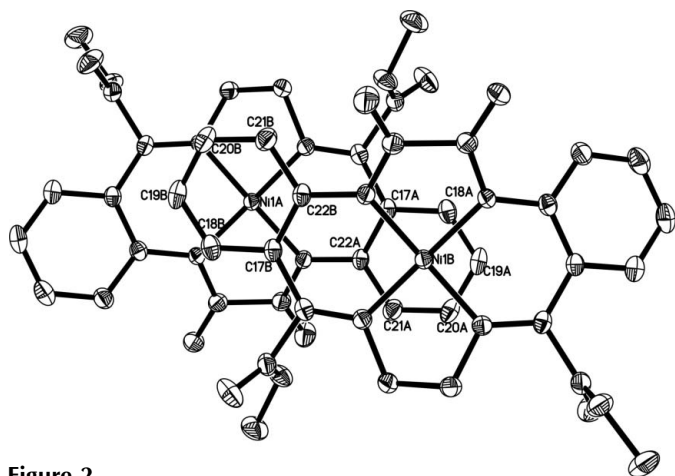


Figure 2
Plot showing the offset $\pi \cdots \pi$ stacking interactions. Symmetry code relating molecules *A* and *B*: $1 - x, -y, 1 - z$.

3.0–4.0 Å and with C–H \cdots O angles above 110°. In (I), each complex molecule provides O2, O4 and O6 as acceptors and the H atoms bound to C7, C11, C12 and C13, respectively, as donors, forming a network of C–H \cdots O hydrogen bonds (Table 2).

In the crystal structure of the new polymorph, each [NiL] molecule overlaps significantly with a neighboring [NiL] molecule, forming inversion-related dimers. Some atom-to-atom distances between these overlapping molecules (Fig. 2) are Ni1A \cdots C17B 3.722 (3), Ni1A \cdots C18B 3.379 (3), Ni1A \cdots C19B 3.508 (3), C8A \cdots C19B 3.415 (3), C19A \cdots C3B 3.471 (3), C18A \cdots C3B 3.516 (3) and C18A \cdots N2B 3.397 (3) Å. (symmetry code relating molecules *A* and *B*: $1 - x, -y, 1 - z$). This is consistent with offset $\pi \cdots \pi$ stacking interactions between the overlapping molecules (Janiak 2000; Li *et al.*, 2004). Thus C–H \cdots O hydrogen bonds and $\pi \cdots \pi$ stacking interactions link the complex molecules, forming an infinite three-dimensional supramolecular network. The intermolecular interactions in the crystal structures of the two

polymorphs are quite different. In the crystal structure of the earlier polymorph, C–H \cdots O hydrogen bonds form between C–H donors provided by the ethylene group in the macrocycle of a molecule and O acceptors of the oxamido group of a neighboring molecule. These hydrogen bonds link the complex molecules in a head-to-tail motif, forming infinite one-dimensional chains. A benzene ring of a complex molecule in one chain is involved in a $\pi \cdots \pi$ interaction with a benzene ring of a molecule in an adjacent chain, linking the chains into pairs.

Experimental

The title complex was prepared by a literature method (Black & Moss, 1987). The new polymorph was obtained by the following process: 12.4 mg (0.025 mmol) [NiL], 11.2 mg (0.030 mmol) Ni(ClO₄)₂·6H₂O, 4.4 mg (0.032 mmol) sodium succinate, 2.0 ml H₂O and 16 ml CH₃OH were mixed. The mixture was stirred and refluxed for 30 minutes. The resulting solution was cooled to room temperature and filtered. The filtrate was slowly evaporated at room temperature, and red crystals suitable for X-ray single-crystal investigations were obtained. The solid product was washed with CH₃OH and dried in vacuum; yield 37%.

Crystal data

[Ni(C₂₂H₁₈N₄O₆)]
M_r = 493.11
 Monoclinic, *C2/c*
a = 25.944 (9) Å
b = 8.450 (3) Å
c = 22.105 (12) Å
 β = 122.747 (3)°
V = 4076 (3) Å³
Z = 8

D_x = 1.607 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2483 reflections
 θ = 2.2–25.6°
 μ = 1.00 mm⁻¹
T = 273 (2) K
 Block, red
 0.20 × 0.12 × 0.10 mm

Data collection

Bruker APEX II CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 SADABS (Sheldrick, 1996)
T_{min} = 0.737, *T_{max}* = 0.905
 10646 measured reflections

3602 independent reflections
 2870 reflections with *I* > 2σ(*I*)
R_{int} = 0.027
 θ_{\max} = 25.0°
h = -30 → 24
k = -9 → 10
l = -25 → 26

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.030
wR(*F*²) = 0.080
S = 1.07
 3602 reflections
 300 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0456P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1–N1	1.8544 (19)	N1–C22	1.394 (3)
Ni1–N2	1.8553 (18)	N2–C3	1.401 (3)
Ni1–N4	1.8605 (19)	N3–C9	1.292 (3)
Ni1–N3	1.861 (2)	N4–C14	1.295 (3)
N1–Ni1–N2	86.72 (8)	N1–Ni1–N3	172.24 (8)
N1–Ni1–N4	94.17 (8)	N2–Ni1–N3	92.86 (8)
N2–Ni1–N4	175.35 (8)	N4–Ni1–N3	86.88 (8)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C12—H12B \cdots O6 ⁱ	0.97	2.71	3.398 (9)	128
C12—H12A \cdots O4 ⁱⁱ	0.97	2.58	3.225 (9)	124
C13—H13B \cdots O4 ⁱⁱ	0.97	2.39	3.068 (9)	126
C11—H11A \cdots O2 ⁱⁱⁱ	0.96	2.75	3.434 (9)	129
C7—H7 \cdots O2 ⁱⁱⁱ	0.93	2.64	3.148 (4)	115

Symmetry codes: (i) $-x, -y + 2, -z + 2$; (ii) $-x, y, -z + \frac{3}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 2$.

All H atoms were located in a difference Fourier map and were refined as riding, with C—H = 0.93–0.97 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$, and $U_{iso} = 1.5U_{eq}(C)$ for CH₃ atoms

Data collection: *APEXII* (Bruker 2003); cell refinement: *SAINT* (Bruker 2003); 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, 2003); software used to prepare material for publication: *SHELXTL*.

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References

- Black, D., St C. & Moss, G. I. (1987). *Aust. J. Chem.* **40**, 129–142.
- Bruker (2003). *APEXII* (Version 1.022), *SAINT* (Version 7.12A) and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Christodoulou, D., Kanatzidis, M. G. & Coucouvanis, D. (1990). *Inorg. Chem.* **29**, 191–201.
- Gao, E.-Q., Tang, J.-K., Liao, D.-Z., Jiang, Z.-H., Yan, S.-P. & Wang, G.-L. (2001). *Helv. Chim. Acta.* **84**, 908–917.
- Gao, E.-Q., Yang, G.-M., Liao, D.-Z., Jiang, Z.-H., Yan, S.-P., Wang, G.-L. & Kou, H.-Z. (1999). *Transition Met. Chem.* **24**, 244–246.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Li, X.-Z., He, J.-H. & Liao, D.-Z. (2005). *Acta Chim. Slov.* **52**, 332–335.
- Li, X.-Z., He, J.-H., Liu, B.-L. & Liao, D.-Z. (2004). *Inorg. Chem. Commun.* **7**, 420–422.
- Li, X.-Z., Liao, D.-Z., Jiang, Z.-H. & Yan, S.-P. (2002). *J. Mol. Struct.* **643**, 135–139.
- Li, X.-Z., Liao, D.-Z., Jiang, Z.-H. & Yan, S.-P. (2003). *Chin. J. Struct. Chem.* **22**, 293–296.
- Li, X.-Z., Yu, L.-H., Liao, D.-Z., Jiang, Z.-H. & Yan, S.-P. (2002). *Inorg. Chem. Commun.* **5**, 478–481.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Taylor, R. & Kennard, O. (1984). *Acc. Chem. Res.* **17**, 320.