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# A binuclear unsymmetrical compartmental Ni$^{II}$ complex: [$\mu$-11,24-dimethyl-16,19-dioxa-3,7,15,20-tetraazatricyclo-[20.3.1.1$^{9,13}$]heptacosa-1(25),2,7,9,11,-13(27),14,20,22(26),23-decaene-26,27-diolato]bis[diaquanickel(II)] bis(perchlorate) tetrahydrate

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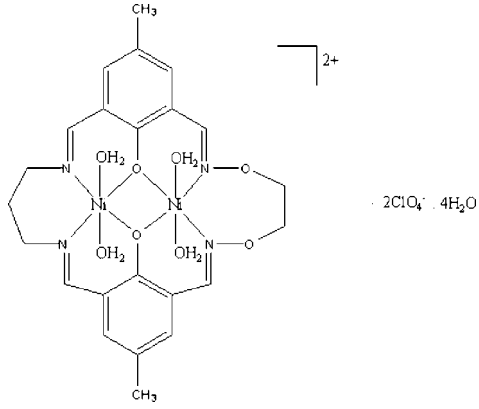
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.002 Å; disorder in main residue; $R$ factor = 0.034; $wR$ factor = 0.113; data-to-parameter ratio = 24.3.

In the title compound, $[Ni_2(C_{23}H_{24}N_4O_4)(H_2O)_4](ClO_4)_2\cdot 4H_2O$, each Ni$^{II}$ atom is coordinated by two bridging phenoxide O atoms, two azomethine N atoms and two water molecules in a slightly distorted octahedral geometry. The crystal packing is stabilized by intermolecular O—H···O hydrogen bonds mediated through the water molecules and perchlorate anions. The bis(aminooxy)ethane and diaminopropane groups are disordered across the centre of the molecule, and as a result the complex molecule and the crystal structure is centrosymmetric.

## Related literature

For synthesis, see: Dixon & Weiss (1984); Verani *et al.* (2000). For general background on dinuclear metal complexes, see: Hong *et al.* (2005); Krishnapriya & Kandaswamy (2005); Lacroix (2001); Mckenzie & Robson (1988); Tsou *et al.* (1982). For a related structure, see: Black *et al.* (1998).




## Experimental

### Crystal data

$[Ni_2(C_{23}H_{24}N_4O_4)(H_2O)_4](ClO_4)_2\cdot 4H_2O$
$M_r$ = 880.91
Triclinic, $P\overline{1}$
$a$ = 7.5227 (3) Å
$b$ = 10.3081 (3) Å
$c$ = 12.2764 (5) Å
$\alpha$ = 107.167 (2)°
$\beta$ = 94.932 (2)°
$\gamma$ = 103.092 (2)°
$V$ = 873.89 (6) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 1.32 mm$^{-1}$
$T$ = 293 (2) K
0.30 × 0.20 × 0.20 mm

### Data collection

Bruker Kappa-APEXII area-detector diffractometer
Absorption correction: multi-scan (Blessing, 1995)
$T_{min}$ = 0.732, $T_{max}$ = 0.825
(expected range = 0.681–0.768)
24651 measured reflections
7176 independent reflections
5831 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.113
$S$ = 1.04
7176 reflections
295 parameters
25 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.59 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.36 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1$A$···O3$^{i}$ | 0.858 (9) | 2.06 (1) | 2.8475 (15) | 152 (1) |
| O1—H1$B$···O11$^{ii}$ | 0.838 (8) | 2.06 (1) | 2.8455 (19) | 155 (2) |
| O3—H3$B$···O4 | 0.831 (9) | 1.96 (1) | 2.766 (2) | 165 (2) |
| O3—H3$A$···O11 | 0.846 (9) | 1.95 (1) | 2.775 (2) | 164 (1) |
| O11—H11$A$···O8$^{iii}$ | 0.846 (10) | 1.97 (1) | 2.806 (3) | 170 (3) |
| O11—H11$B$···O9$^{iv}$ | 0.856 (10) | 2.40 (2) | 3.127 (5) | 143 (3) |
| O11—H11$B$···O10$^{iv}$ | 0.856 (10) | 2.46 (2) | 3.229 (4) | 150 (3) |
| O4—H4$A$···O7$^{v}$ | 0.839 (10) | 2.43 (3) | 3.137 (5) | 142 (4) |
| O4—H4$B$···O7$^{iii}$ | 0.831 (10) | 2.43 (2) | 3.120 (4) | 140 (3) |

Symmetry codes: (i) $-x, -y, -z$; (ii) $x+1, y, z$; (iii) $-x, -y, -z-1$; (iv) $x-1, y, z$; (v) $x-1, y-1, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT-Plus* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2420).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m2330-m2331 [ **doi:10.1107/S1600536807039001** ]

# A binuclear unsymmetrical compartmental $Ni^{II}$ complex: [$\mu$-11,24-dimethyl-16,19-dioxa-3,7,15,20-tetraazatricyclo[20.3.1.1$^{9,13}$]heptacosa-1(25),2,7,9,11,13(27),14,20,22(26),23-decaene-26,27-diolato]bis[diaquanickel(II)] bis(perchlorate) tetrahydrate

**S. Anbu, M. Kandaswamy and B. Varghese**

## Comment

Dinuclear metal complexes of diphenolic Schiff base macrocyclic ligands have attracted much attention as they have contributed significantly to the understanding of the relationship between chemical behaviour and structural properties (Hong *et al.*, 2005). Complexes of ligands which contain two or more metal ions in close proximity are important as potential catalysts (Mckenzie & Robson, 1988), models of reaction centers for metalloenzymes (Tsou *et al.*, 1982) and non-linear optical materials (Lacroix *et al.*, 2001). Stability of the complexes depend upon the cavity size of the ligand and the radius of the metal ion. In continuation of our earlier studies (Krishnapriya & Kandaswamy, 2005) we report here the crystal structure of a dinuclear $Ni^{II}$ complex with a ligand containing two compartments with different compartmental sizes, in which one of the compartments has 1,3-diamino propane and the another compartment has 1,2-bis(aminooxy)ethane.

The coordination geometry at each $Ni^{II}$ ion is distorted octahedral (Fig. 1), in which the equatorial plane is formed by two bridging phenoxide O atoms and two azomethine N atoms while the axial coordination sites are occupied by two water molecules. The *trans* angles at the $Ni^{II}$ centres are close to 180°, ranging from 170.78 (5) to 173.88 (4)°. All other angles subtended at the $Ni^{II}$ centres are close to 90°, ranging from 81.64 (4) to 99.47 (5), which indicates a slightly distorted octahedral geometry of $Ni^{II}$ atoms. The Ni—N and Ni—O bond lengths lie in the range 1.9984 (13)–2.0263 (13) Å and 2.0122 (10)–2.1604 (11) Å, respectively, and the bond lengths are comparable to those observed in a related structure (Black *et al.*, 1998). The two benzene rings in the molecule are parallel to each other, within the limits of standard deviations.

The crystal packing is stabilized by intermolecular O—H···O hydrogen bonding involving the water molecules and perchlorate anions. The inversion disorder of bis-aminooxy ethane and diamino propane groups shows an apparent centrosymmetry in the crystal structure.

## Experimental

To a vigorously stirred suspension of *N*,*N*'-propylene-bis(3-formyl-5-methyl-salicylaldimino)nickel(II) (Verani *et al.*, 2000) (1.0 g, 2.36 mmol) in methanol (25 ml), a methanolic solution (10 ml) of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.86 g, 2.36 mmol) was added slowly and the mixture was stirred for 15 min to obtain a clear solution. Then a methanolic solution (5 ml) of 1,2-bis(aminooxy)ethane (Dixon & Weiss, 1984) (0.10 g, 2.36 mmol) was added dropwise to the above solution. The resulting solution was refluxed for 3 h. A pale green coloured solid was separated on evaporating the solution at 398 K and the compound was washed with ether and dried. Green crystals suitable for X-ray analysis were obtained after several days by slow evaporation of a acetonitrile solution (yield 69%).

### Refinement

Eventhough there is only one molecule in the unit cell and molecule does not possess center of symmetry, a near perfect inversion disorder makes it possible for structure to be solved in the centrosymmetric space group $P\bar{1}$. Physically, it may be interpreted as, 50% of the unit cells are inversion of the other 50%. Hence, strictly speaking, the space group of the unit cell is P1. The structure could be solved and refined to the same *R*-factor in P1 space group with appropriate disorder on either side of the molecule. However, The shift/e.s.d. parameters were oscillating rather than converging. Therefore, it was decided to adopt the $P\bar{1}$ space group for solving and refining the structure, with the bis-aminooxy ethane and diamino propane groups disordered across the inversion center. As electron densities of these groups may overlap at many places, the unrestrained refinement will lead to abnormal geometries. Therefore the following restraints on distances were applied to atoms of the disordered groups: N—O = 1.450 (1) Å, N—C = 1.470 (1) Å, C—C = 1.530 (1) Å and O—C = 1.470 (1) Å. Water H atoms were located in a difference map and refined isotropically, with O—H and H···H distance restraints of 0.85 (1) and 1.38 (1) Å, respectively. Further Ni···H distances were fixed at 2.6Å for H atoms of coordinated water molecules. All the hydrogen atoms except the ones at disordered sites were located in difference maps. They were relocated in idealized positions (C—H = 0.93–0.97 Å) and refined as riding with $U_{iso}$(H) = 1.2–1.5 $U_{eq}$(C).

### Figures

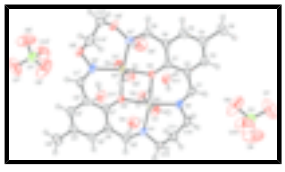

Fig. 1. The unit-cell contents of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Only one disorder component is shown. Symmetry code (i): −*x*, −*y*, −*z*

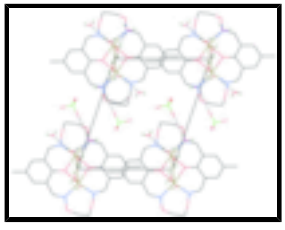

Fig. 2. The crystal packing of the title compound, viewed down the *a* axis. C-bound H atoms have been omitted for clarity. Both disorder components are shown.

### [μ-11,24-dimethyl-16,19-dioxa-3,7,15,20- tetraazatricyclo[20.3.1.1$^{9,13}$]heptacosa-1(25),2,7,9,11,13 (27),14,20,22 (26),23-decaene-26,27- diolato]bis[diaquanickel(II)] bis(perchlorate) tetrahydrate

*Crystal data*

| | |
|---|---|
| $[Ni_2(C_{23}H_{24}N_4O_4)(H_2O)_4](ClO_4)_2{\cdot}4H_2O$ | $Z = 1$ |
| $M_r = 880.91$ | $F_{000} = 456$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.674$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation<br>λ = 0.71073 Å |
| $a = 7.5227$ (3) Å | Cell parameters from 7997 reflections |
| $b = 10.3081$ (3) Å | θ = 2.2–33.5º |
| $c = 12.2764$ (5) Å | μ = 1.32 mm$^{-1}$ |

| | |
|---|---|
| $\alpha = 107.167\ (2)^{\circ}$ | $T = 293\ (2)$ K |
| $\beta = 94.932\ (2)^{\circ}$ | Block, green |
| $\gamma = 103.092\ (2)^{\circ}$ | 0.30 × 0.20 × 0.20 mm |
| $V = 873.89\ (6)$ Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker Kappa-APEXII area-detector diffractometer | 7176 independent reflections |
| Radiation source: fine-focus sealed tube | 5831 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.020$ |
| $T = 293(2)$ K | $\theta_{max} = 37.3^{\circ}$ |
| ω and φ scans | $\theta_{min} = 1.8^{\circ}$ |
| Absorption correction: multi-scan (Blessing, 1995) | $h = -9 \rightarrow 12$ |
| $T_{min} = 0.732$, $T_{max} = 0.825$ | $k = -15 \rightarrow 15$ |
| 24651 measured reflections | $l = -18 \rightarrow 17$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.034$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.113$ | $w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 0.1283P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.04$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 7176 reflections | $\Delta\rho_{max} = 0.59$ e Å$^{-3}$ |
| 295 parameters | $\Delta\rho_{min} = -0.36$ e Å$^{-3}$ |
| 25 restraints | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| C1 | 0.0971 (2) | 0.15878 (19) | −0.23328 (13) | 0.0444 (3) | |
| H1 | 0.1215 | 0.1875 | −0.2968 | 0.053* | |
| C2 | 0.13711 (19) | 0.27002 (16) | −0.12198 (13) | 0.0371 (3) | |
| C3 | 0.2263 (2) | 0.40586 (18) | −0.12170 (15) | 0.0428 (3) | |
| H3 | 0.2584 | 0.4173 | −0.1904 | 0.051* | |
| C4 | 0.26796 (19) | 0.52242 (17) | −0.02416 (16) | 0.0433 (3) | |
| C5 | 0.2108 (2) | 0.50310 (16) | 0.07479 (15) | 0.0414 (3) | |
| H5 | 0.2314 | 0.5814 | 0.1406 | 0.050* | |
| C6 | 0.12309 (18) | 0.37082 (15) | 0.08068 (12) | 0.0353 (3) | |
| C7 | 0.08787 (16) | 0.24933 (14) | −0.01828 (12) | 0.0322 (2) | |
| C8 | 0.0622 (2) | 0.37031 (16) | 0.18958 (13) | 0.0412 (3) | |
| H8 | 0.0627 | 0.4570 | 0.2414 | 0.049* | |
| C9 | 0.3681 (3) | 0.66680 (19) | −0.0250 (2) | 0.0554 (4) | |
| H9C | 0.3963 | 0.6606 | −0.1009 | 0.083* | |
| H9B | 0.4809 | 0.7017 | 0.0297 | 0.083* | |
| H9A | 0.2908 | 0.7297 | −0.0044 | 0.083* | |
| N1 | −0.00792 (18) | −0.26233 (14) | −0.22116 (10) | 0.0388 (2) | |
| N2 | 0.03246 (19) | 0.02623 (15) | −0.25431 (10) | 0.0415 (3) | |
| O5 | 0.0838 (8) | −0.2869 (9) | −0.3212 (5) | 0.0556 (13) | 0.50 |
| O6 | 0.0362 (10) | −0.0402 (6) | −0.3736 (5) | 0.0577 (14) | 0.50 |
| C13 | −0.0346 (6) | −0.2933 (5) | −0.4219 (3) | 0.0556 (9) | 0.50 |
| H13A | −0.1384 | −0.3761 | −0.4412 | 0.067* | 0.50 |
| H13B | 0.0337 | −0.3050 | −0.4861 | 0.067* | 0.50 |
| C14 | −0.1078 (7) | −0.1681 (5) | −0.4099 (4) | 0.0531 (10) | 0.50 |
| H14B | −0.1774 | −0.1781 | −0.4835 | 0.064* | 0.50 |
| H14A | −0.1918 | −0.1638 | −0.3540 | 0.064* | 0.50 |
| C10 | −0.0080 (15) | −0.0655 (8) | −0.3768 (6) | 0.0563 (18) | 0.50 |
| H10B | 0.1043 | −0.0476 | −0.4095 | 0.068* | 0.50 |
| H10A | −0.0988 | −0.0351 | −0.4173 | 0.068* | 0.50 |
| C11 | −0.0782 (7) | −0.2234 (5) | −0.4048 (4) | 0.0521 (10) | 0.50 |
| H11C | −0.0815 | −0.2676 | −0.4868 | 0.063* | 0.50 |
| H11D | −0.2044 | −0.2444 | −0.3901 | 0.063* | 0.50 |
| C12 | 0.0324 (12) | −0.2907 (11) | −0.3390 (6) | 0.0520 (16) | 0.50 |
| H12B | 0.0008 | −0.3916 | −0.3779 | 0.062* | 0.50 |
| H12A | 0.1635 | −0.2531 | −0.3369 | 0.062* | 0.50 |
| O1 | 0.29581 (15) | −0.01748 (13) | −0.08643 (10) | 0.0431 (2) | |
| O2 | 0.00840 (13) | 0.12288 (10) | −0.01495 (8) | 0.03364 (18) | |
| O3 | −0.29405 (15) | −0.11087 (13) | −0.15299 (10) | 0.0420 (2) | |
| O4 | −0.5126 (3) | −0.3673 (2) | −0.30007 (17) | 0.0826 (5) | |
| O7 | 0.6566 (5) | 0.3989 (3) | −0.4449 (3) | 0.1479 (12) | |
| O8 | 0.5456 (5) | 0.1699 (4) | −0.5264 (3) | 0.1534 (14) | |
| O9 | 0.4749 (5) | 0.2772 (5) | −0.3522 (3) | 0.1690 (15) | |
| O10 | 0.7589 (4) | 0.2542 (3) | −0.3600 (2) | 0.1299 (10) | |
| O11 | −0.4866 (3) | 0.03465 (19) | −0.25509 (14) | 0.0650 (4) | |
| Cl1 | 0.60736 (8) | 0.27329 (6) | −0.42118 (4) | 0.06240 (13) | |

| | | | | |
|---|---|---|---|---|
| Ni1 | 0.00424 (2) | −0.064272 (18) | −0.128772 (13) | 0.03218 (6) |
| H1A | 0.3359 (15) | 0.028 (2) | −0.0145 (8) | 0.073 (8)* |
| H1B | 0.3590 (14) | 0.023 (2) | −0.1257 (13) | 0.054 (6)* |
| H3B | −0.3473 (15) | −0.1940 (11) | −0.191 (2) | 0.077 (8)* |
| H3A | −0.3323 (15) | −0.0541 (17) | −0.180 (2) | 0.076 (8)* |
| H11A | −0.518 (5) | −0.030 (2) | −0.3197 (15) | 0.110 (13)* |
| H11B | −0.443 (4) | 0.1130 (16) | −0.266 (2) | 0.099 (11)* |
| H4A | −0.498 (6) | −0.449 (2) | −0.318 (3) | 0.150 (18)* |
| H4B | −0.589 (4) | −0.357 (3) | −0.348 (2) | 0.101 (11)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0518 (8) | 0.0572 (9) | 0.0346 (7) | 0.0199 (7) | 0.0128 (6) | 0.0246 (7) |
| C2 | 0.0355 (6) | 0.0454 (7) | 0.0374 (7) | 0.0126 (5) | 0.0087 (5) | 0.0214 (6) |
| C3 | 0.0399 (6) | 0.0514 (8) | 0.0477 (8) | 0.0141 (6) | 0.0125 (6) | 0.0289 (7) |
| C4 | 0.0343 (6) | 0.0448 (7) | 0.0575 (9) | 0.0094 (5) | 0.0066 (6) | 0.0273 (7) |
| C5 | 0.0395 (6) | 0.0382 (7) | 0.0465 (8) | 0.0091 (5) | 0.0033 (6) | 0.0156 (6) |
| C6 | 0.0337 (5) | 0.0369 (6) | 0.0374 (7) | 0.0100 (5) | 0.0048 (5) | 0.0148 (5) |
| C7 | 0.0280 (5) | 0.0388 (6) | 0.0345 (6) | 0.0112 (4) | 0.0062 (4) | 0.0166 (5) |
| C8 | 0.0490 (7) | 0.0376 (7) | 0.0364 (7) | 0.0133 (6) | 0.0086 (6) | 0.0092 (5) |
| C9 | 0.0479 (8) | 0.0468 (9) | 0.0750 (13) | 0.0043 (7) | 0.0080 (8) | 0.0318 (9) |
| N1 | 0.0432 (6) | 0.0421 (6) | 0.0316 (5) | 0.0131 (5) | 0.0116 (4) | 0.0099 (5) |
| N2 | 0.0469 (6) | 0.0548 (7) | 0.0274 (5) | 0.0161 (5) | 0.0096 (4) | 0.0175 (5) |
| O5 | 0.066 (3) | 0.066 (2) | 0.040 (2) | 0.022 (2) | 0.0271 (19) | 0.0164 (18) |
| O6 | 0.081 (4) | 0.055 (2) | 0.0329 (16) | 0.005 (2) | 0.0250 (17) | 0.0149 (14) |
| C13 | 0.069 (2) | 0.054 (2) | 0.0342 (18) | 0.0033 (18) | 0.0128 (15) | 0.0085 (16) |
| C14 | 0.054 (2) | 0.069 (3) | 0.0304 (16) | 0.009 (2) | 0.0015 (13) | 0.014 (2) |
| C10 | 0.074 (5) | 0.067 (4) | 0.030 (2) | 0.009 (3) | 0.013 (2) | 0.027 (2) |
| C11 | 0.070 (3) | 0.054 (3) | 0.0280 (16) | 0.014 (2) | 0.0050 (15) | 0.0098 (19) |
| C12 | 0.073 (5) | 0.047 (2) | 0.037 (3) | 0.017 (3) | 0.027 (3) | 0.0095 (19) |
| O1 | 0.0356 (4) | 0.0546 (6) | 0.0416 (6) | 0.0117 (4) | 0.0110 (4) | 0.0180 (5) |
| O2 | 0.0370 (4) | 0.0354 (4) | 0.0302 (4) | 0.0085 (3) | 0.0089 (3) | 0.0130 (4) |
| O3 | 0.0366 (5) | 0.0490 (6) | 0.0403 (6) | 0.0107 (4) | 0.0044 (4) | 0.0152 (5) |
| O4 | 0.0912 (13) | 0.0749 (12) | 0.0683 (11) | 0.0135 (10) | −0.0104 (9) | 0.0165 (9) |
| O7 | 0.179 (3) | 0.0998 (18) | 0.171 (3) | 0.0049 (18) | −0.002 (2) | 0.084 (2) |
| O8 | 0.171 (3) | 0.138 (2) | 0.0934 (18) | 0.050 (2) | −0.0225 (18) | −0.0410 (17) |
| O9 | 0.139 (3) | 0.268 (5) | 0.126 (2) | 0.066 (3) | 0.080 (2) | 0.076 (3) |
| O10 | 0.138 (2) | 0.145 (2) | 0.1073 (18) | 0.0674 (19) | −0.0220 (16) | 0.0308 (17) |
| O11 | 0.0833 (10) | 0.0713 (10) | 0.0509 (8) | 0.0242 (8) | 0.0179 (7) | 0.0304 (8) |
| Cl1 | 0.0776 (3) | 0.0597 (3) | 0.0468 (2) | 0.0139 (2) | 0.0083 (2) | 0.0164 (2) |
| Ni1 | 0.03454 (9) | 0.03765 (10) | 0.02645 (9) | 0.00998 (6) | 0.00817 (6) | 0.01227 (7) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—N2 | 1.280 (2) | C13—H13A | 0.97 |
| C1—C2 | 1.456 (2) | C13—H13B | 0.97 |
| C1—H1 | 0.93 | C14—H14B | 0.97 |
| C2—C3 | 1.408 (2) | C14—H14A | 0.97 |

| | | | |
|---|---|---|---|
| C2—C7 | 1.4174 (18) | C10—C11 | 1.515 (7) |
| C3—C4 | 1.375 (3) | C10—H10B | 0.97 |
| C3—H3 | 0.93 | C10—H10A | 0.97 |
| C4—C5 | 1.376 (2) | C11—C12 | 1.518 (8) |
| C4—C9 | 1.512 (2) | C11—H11C | 0.97 |
| C5—C6 | 1.400 (2) | C11—H11D | 0.97 |
| C5—H5 | 0.93 | C12—H12B | 0.97 |
| C6—C7 | 1.418 (2) | C12—H12A | 0.97 |
| C6—C8 | 1.451 (2) | O1—Ni1 | 2.1191 (11) |
| C7—O2 | 1.3193 (16) | O1—H1A | 0.858 (9) |
| C8—N1$^{i}$ | 1.277 (2) | O1—H1B | 0.838 (8) |
| C8—H8 | 0.93 | O2—Ni1 | 2.0122 (10) |
| C9—H9C | 0.96 | O2—Ni1$^{i}$ | 2.0297 (10) |
| C9—H9B | 0.96 | O3—Ni1 | 2.1604 (11) |
| C9—H9A | 0.96 | O3—H3B | 0.831 (9) |
| N1—C8$^{i}$ | 1.277 (2) | O3—H3A | 0.846 (9) |
| N1—O5 | 1.445 (5) | O4—H4A | 0.839 (10) |
| N1—C12 | 1.461 (7) | O4—H4B | 0.831 (10) |
| N1—Ni1 | 1.9984 (13) | O7—Cl1 | 1.386 (2) |
| N2—O6 | 1.427 (5) | O8—Cl1 | 1.371 (2) |
| N2—C10 | 1.483 (7) | O9—Cl1 | 1.362 (3) |
| N2—Ni1 | 2.0263 (13) | O10—Cl1 | 1.394 (3) |
| O5—C13 | 1.437 (6) | O11—H11A | 0.846 (10) |
| O6—C14 | 1.426 (6) | O11—H11B | 0.856 (10) |
| C13—C14 | 1.488 (6) | Ni1—O2$^{i}$ | 2.0297 (10) |
| N2—C1—C2 | 127.86 (13) | O6—C14—H14A | 109.2 |
| N2—C1—H1 | 116.1 | C13—C14—H14A | 109.2 |
| C2—C1—H1 | 116.1 | H14B—C14—H14A | 107.9 |
| C3—C2—C7 | 119.81 (14) | N2—C10—C11 | 119.2 (5) |
| C3—C2—C1 | 115.97 (13) | N2—C10—H10B | 107.5 |
| C7—C2—C1 | 124.19 (13) | C11—C10—H10B | 107.5 |
| C4—C3—C2 | 122.83 (14) | N2—C10—H10A | 107.5 |
| C4—C3—H3 | 118.6 | C11—C10—H10A | 107.5 |
| C2—C3—H3 | 118.6 | H10B—C10—H10A | 107.0 |
| C3—C4—C5 | 117.12 (14) | C10—C11—C12 | 116.2 (7) |
| C3—C4—C9 | 121.99 (16) | C10—C11—H11C | 108.2 |
| C5—C4—C9 | 120.87 (16) | C12—C11—H11C | 108.2 |
| C4—C5—C6 | 122.87 (15) | C10—C11—H11D | 108.2 |
| C4—C5—H5 | 118.6 | C12—C11—H11D | 108.2 |
| C6—C5—H5 | 118.6 | H11C—C11—H11D | 107.4 |
| C5—C6—C7 | 120.13 (13) | N1—C12—C11 | 109.9 (5) |
| C5—C6—C8 | 115.70 (14) | N1—C12—H12B | 109.7 |
| C7—C6—C8 | 124.03 (13) | C11—C12—H12B | 109.7 |
| O2—C7—C2 | 121.32 (12) | N1—C12—H12A | 109.7 |
| O2—C7—C6 | 121.57 (12) | C11—C12—H12A | 109.7 |
| C2—C7—C6 | 117.08 (12) | H12B—C12—H12A | 108.2 |
| N1$^{i}$—C8—C6 | 126.29 (14) | Ni1—O1—H1A | 112.7 (9) |

| | | | |
|---|---|---|---|
| N1$^{i}$—C8—H8 | 116.9 | Ni1—O1—H1B | 117.1 (9) |
| C6—C8—H8 | 116.9 | H1A—O1—H1B | 108.8 (12) |
| C4—C9—H9C | 109.5 | C7—O2—Ni1 | 127.60 (8) |
| C4—C9—H9B | 109.5 | C7—O2—Ni1$^{i}$ | 126.25 (9) |
| H9C—C9—H9B | 109.5 | Ni1—O2—Ni1$^{i}$ | 98.36 (4) |
| C4—C9—H9A | 109.5 | Ni1—O3—H3B | 113.9 (9) |
| H9C—C9—H9A | 109.5 | Ni1—O3—H3A | 111.3 (9) |
| H9B—C9—H9A | 109.5 | H3B—O3—H3A | 111.6 (13) |
| C8$^{i}$—N1—O5 | 114.5 (3) | H4A—O4—H4B | 113.0 (17) |
| C8$^{i}$—N1—C12 | 115.8 (4) | H11A—O11—H11B | 108.9 (16) |
| O5—N1—C12 | 16.4 (5) | O9—Cl1—O8 | 112.2 (3) |
| C8$^{i}$—N1—Ni1 | 125.50 (10) | O9—Cl1—O7 | 110.1 (3) |
| O5—N1—Ni1 | 118.8 (3) | O8—Cl1—O7 | 105.8 (2) |
| C12—N1—Ni1 | 118.5 (4) | O9—Cl1—O10 | 106.5 (2) |
| C1—N2—O6 | 106.9 (3) | O8—Cl1—O10 | 112.06 (19) |
| C1—N2—C10 | 117.7 (3) | O7—Cl1—O10 | 110.2 (2) |
| O6—N2—C10 | 14.2 (5) | N1—Ni1—O2 | 170.85 (4) |
| C1—N2—Ni1 | 123.23 (11) | N1—Ni1—N2 | 99.47 (5) |
| O6—N2—Ni1 | 127.8 (3) | O2—Ni1—N2 | 89.65 (5) |
| C10—N2—Ni1 | 118.9 (3) | N1—Ni1—O2$^{i}$ | 89.29 (5) |
| C13—O5—N1 | 111.0 (4) | O2—Ni1—O2$^{i}$ | 81.64 (4) |
| C14—O6—N2 | 106.3 (4) | N2—Ni1—O2$^{i}$ | 170.78 (5) |
| O5—C13—C14 | 114.9 (4) | N1—Ni1—O1 | 90.78 (5) |
| O5—C13—H13A | 108.5 | O2—Ni1—O1 | 89.95 (4) |
| C14—C13—H13A | 108.5 | N2—Ni1—O1 | 90.20 (5) |
| O5—C13—H13B | 108.5 | O2$^{i}$—Ni1—O1 | 86.79 (4) |
| C14—C13—H13B | 108.5 | N1—Ni1—O3 | 91.14 (5) |
| H13A—C13—H13B | 107.5 | O2—Ni1—O3 | 87.24 (4) |
| O6—C14—C13 | 112.1 (5) | N2—Ni1—O3 | 95.21 (5) |
| O6—C14—H14B | 109.2 | O2$^{i}$—Ni1—O3 | 87.43 (4) |
| C13—C14—H14B | 109.2 | O1—Ni1—O3 | 173.88 (4) |
| N2—C1—C2—C3 | 173.41 (16) | Ni1—N1—C12—C11 | −49.5 (8) |
| N2—C1—C2—C7 | −8.3 (3) | C10—C11—C12—N1 | 76.3 (8) |
| C7—C2—C3—C4 | −0.5 (2) | C2—C7—O2—Ni1 | 18.74 (17) |
| C1—C2—C3—C4 | 177.90 (14) | C6—C7—O2—Ni1 | −163.04 (9) |
| C2—C3—C4—C5 | −3.0 (2) | C2—C7—O2—Ni1$^{i}$ | 161.14 (9) |
| C2—C3—C4—C9 | 178.42 (15) | C6—C7—O2—Ni1$^{i}$ | −20.64 (17) |
| C3—C4—C5—C6 | 3.5 (2) | C8$^{i}$—N1—Ni1—N2 | −165.19 (14) |
| C9—C4—C5—C6 | −177.85 (15) | O5—N1—Ni1—N2 | 27.8 (3) |
| C4—C5—C6—C7 | −0.6 (2) | C12—N1—Ni1—N2 | 9.1 (4) |
| C4—C5—C6—C8 | −176.51 (14) | C8$^{i}$—N1—Ni1—O2$^{i}$ | 17.70 (14) |
| C3—C2—C7—O2 | −178.27 (13) | O5—N1—Ni1—O2$^{i}$ | −149.3 (3) |
| C1—C2—C7—O2 | 3.5 (2) | C12—N1—Ni1—O2$^{i}$ | −168.0 (4) |
| C3—C2—C7—C6 | 3.43 (19) | C8$^{i}$—N1—Ni1—O1 | 104.47 (14) |
| C1—C2—C7—C6 | −174.83 (13) | O5—N1—Ni1—O1 | −62.5 (3) |

| | | | |
|---|---|---|---|
| C5—C6—C7—O2 | 178.79 (12) | C12—N1—Ni1—O1 | −81.2 (4) |
| C8—C6—C7—O2 | −5.7 (2) | C8$^{i}$—N1—Ni1—O3 | −69.72 (14) |
| C5—C6—C7—C2 | −2.92 (19) | O5—N1—Ni1—O3 | 123.3 (3) |
| C8—C6—C7—C2 | 172.64 (13) | C12—N1—Ni1—O3 | 104.6 (4) |
| C5—C6—C8—N1$^{i}$ | −167.56 (16) | C7—O2—Ni1—N2 | −26.78 (11) |
| C7—C6—C8—N1$^{i}$ | 16.7 (2) | Ni1$^{i}$—O2—Ni1—N2 | −176.96 (5) |
| C2—C1—N2—O6 | −173.9 (4) | C7—O2—Ni1—O2$^{i}$ | 150.18 (13) |
| C2—C1—N2—C10 | 176.1 (5) | Ni1$^{i}$—O2—Ni1—O2$^{i}$ | 0.0 |
| C2—C1—N2—Ni1 | −9.3 (2) | C7—O2—Ni1—O1 | 63.42 (11) |
| C8$^{i}$—N1—O5—C13 | 105.4 (5) | Ni1$^{i}$—O2—Ni1—O1 | −86.76 (4) |
| C12—N1—O5—C13 | 7(2) | C7—O2—Ni1—O3 | −122.01 (11) |
| Ni1—N1—O5—C13 | −86.3 (6) | Ni1$^{i}$—O2—Ni1—O3 | 87.81 (4) |
| C1—N2—O6—C14 | −152.8 (5) | C1—N2—Ni1—N1 | −159.75 (13) |
| C10—N2—O6—C14 | −12 (3) | O6—N2—Ni1—N1 | 1.5 (4) |
| Ni1—N2—O6—C14 | 43.5 (7) | C10—N2—Ni1—N1 | 14.8 (5) |
| N1—O5—C13—C14 | 55.4 (7) | C1—N2—Ni1—O2 | 21.03 (14) |
| N2—O6—C14—C13 | −104.3 (5) | O6—N2—Ni1—O2 | −177.7 (4) |
| O5—C13—C14—O6 | 54.2 (6) | C10—N2—Ni1—O2 | −164.4 (5) |
| C1—N2—C10—C11 | 177.8 (6) | C1—N2—Ni1—O1 | −68.92 (13) |
| O6—N2—C10—C11 | 135 (4) | O6—N2—Ni1—O1 | 92.3 (4) |
| Ni1—N2—C10—C11 | 3.0 (11) | C10—N2—Ni1—O1 | 105.6 (5) |
| N2—C10—C11—C12 | −50.5 (11) | C1—N2—Ni1—O3 | 108.22 (13) |
| C8$^{i}$—N1—C12—C11 | 125.4 (5) | O6—N2—Ni1—O3 | −90.5 (4) |
| O5—N1—C12—C11 | −145 (3) | C10—N2—Ni1—O3 | −77.2 (5) |

Symmetry codes: (i) −*x*, −*y*, −*z*.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1A···O3$^{i}$ | 0.858 (9) | 2.06 (1) | 2.8475 (15) | 152 (1) |
| O1—H1B···O11$^{ii}$ | 0.838 (8) | 2.06 (1) | 2.8455 (19) | 155 (2) |
| O3—H3B···O4 | 0.831 (9) | 1.96 (1) | 2.766 (2) | 165 (2) |
| O3—H3A···O11 | 0.846 (9) | 1.95 (1) | 2.775 (2) | 164 (1) |
| O11—H11A···O8$^{iii}$ | 0.846 (10) | 1.97 (1) | 2.806 (3) | 170 (3) |
| O11—H11B···O9$^{iv}$ | 0.856 (10) | 2.40 (2) | 3.127 (5) | 143 (3) |
| O11—H11B···O10$^{iv}$ | 0.856 (10) | 2.46 (2) | 3.229 (4) | 150 (3) |
| O4—H4A···O7$^{v}$ | 0.839 (10) | 2.43 (3) | 3.137 (5) | 142 (4) |
| O4—H4B···O7$^{iii}$ | 0.831 (10) | 2.43 (2) | 3.120 (4) | 140 (3) |

Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) *x*+1, *y*, *z*; (iii) −*x*, −*y*, −*z*−1; (iv) *x*−1, *y*, *z*; (v) *x*−1, *y*−1, *z*.

**Fig. 1**

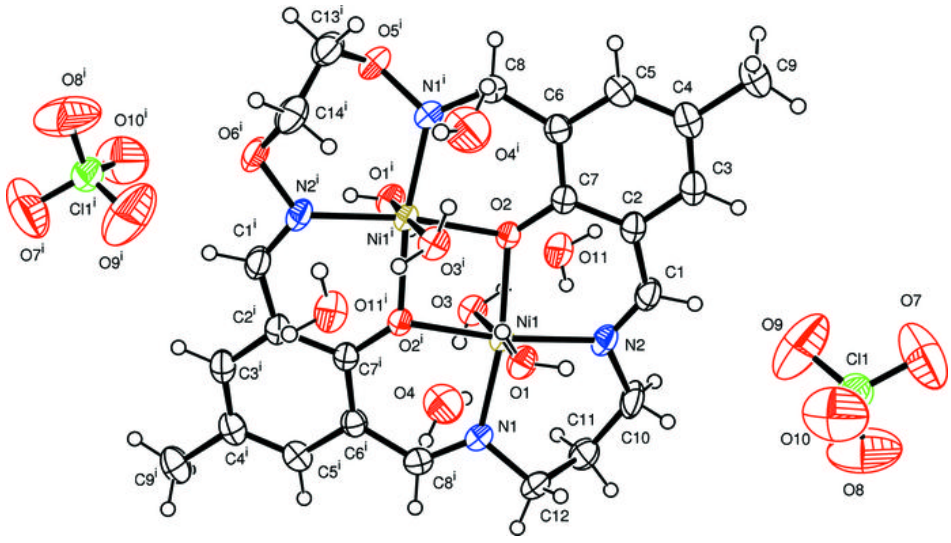
C13i
O5i
N1i
C8
C5
C4
C9
O8i
O10i
C14i
C6
O6i
O4i
C3
N2i
O1i
C7
Cl1i
O2
C2
C1i
Ni1i
O11
O7i
O9i
O3i
C1
O11i
O3
C2i
Ni1
O2i
N2
C7i
C3i
O4
O1
C11
C10
N1
C9i
C4i
C6i
C5i
C8i
C12
O7
O9
Cl1
O10
O8

**Fig. 2**