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Bis[μ_2-2,2′-dimethyl-*N*,*N*′-bis(2-oxidobenzyl)propane-1,3-diamine]-1κ^4O,*N*,*N*′,*O*′:2κ^2O,*O*′;2κ^2O,*O*′:3κ^4O,*N*,*N*′,*O*′-bis(*N*,*N*′-dimethylformamide)-1κO,3κO-di-μ_2-formato-1:2κ^2O:*O*′;2:3κ^2O:*O*′-trinickel(II)

Leyla Tatar Yıldırım,[a] Orhan Atakol[b] and Gülten Kavak[c]*

[a]Department of Physics Engineering, Hacettepe University, 06800 Beytepe, Ankara, Turkey, [b]Department of Chemistry, Ankara University, Ankara, Turkey, and [c]Department of Physics, University of Dicle, 21280 Diyarbakır, Turkey
Correspondence e-mail: tatar@hacettepe.edu.tr

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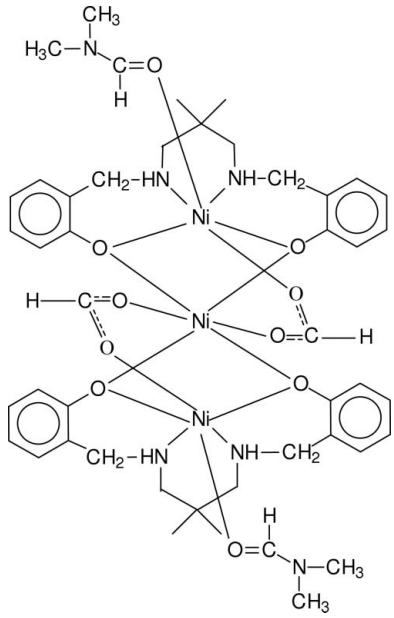
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; R factor = 0.056; wR factor = 0.150; data-to-parameter ratio = 13.8.

The title crystal structure, $[Ni_3(C_{19}H_{24}N_2O_2)_2(CHO_2)_2(C_3H_7NO)_2]$, consists of discrete centrosymmetric homotrinuclear nickel complex molecules. In each molecule, the central Ni^{II} ion is in a distorted octahedral coordination environment, formed by four O atoms from two chelating DML^{2-} ligands [$DMLH_2$ = *N*,*N*′-bis(salicylidene)-2,2′-dimethyl-1,3-propanediamine] in the equatorial plane and two O atoms of two symmetry-related formate ligands in the axial positions. The terminal Ni^{II} ions also have distorted octahedral coordination environments and these are formed by two O and N atoms from chelating DML^{2-} ligands in the equatorial plane; the axial positions are occupied by O atoms from a dimethylformamide ligand and a formate ligand. The overall result is three edge-shared octahedra in which the closest Ni···Ni distance is 3.0857 (14) Å. The crystal structure is stabilized by weak C—H···O hydrogen bonds (agnostic interactions).

Related literature

For general background, see: Martell & Calvin (1958); Drew *et al.* (1985); Fukuhara *et al.* (1990); Barandika *et al.* (1999). For related literature, see: Tatar (2002); Tatar & Atakol (2002); Durmuş *et al.* (2005). For related literature, see: Barkelew & Calvin (1946); Cremer & Pople (1975); Du *et al.* (2005); Reglinski *et al.* (2006); Ribas *et al.* (1999); Spek (2003).



Experimental

Crystal data

$[Ni_3(C_{19}H_{24}N_2O_2)_2(CHO_2)_2(C_3H_7NO)_2]$
M_r = 1037.10
Monoclinic, $P2_1/n$
a = 10.289 (2) Å
b = 14.054 (5) Å
c = 17.005 (4) Å
β = 103.433 (19)°
V = 2391.7 (11) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 1.88 mm^{-1}
T = 293 (2) K
0.2 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.720, T_{max} = 0.828
5007 measured reflections
4740 independent reflections
2200 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.150
S = 1.03
4740 reflections
343 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O4	0.93	2.52	3.242 (7)	135
C8—H8A···O5^{i}	1.01 (5)	2.56 (5)	3.133 (6)	116 (3)
C12—H12A···O5^{i}	1.04 (6)	2.56 (5)	3.156 (8)	116 (4)
C18—H18···O4	0.93	2.52	3.228 (6)	133
C21—H21···O4	0.89 (2)	2.59 (3)	3.353 (7)	144 (4)

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

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(Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2472).

References

Barandika, M. G., Cortes, R., Lezama, L., Urtiaga, M. K., Ariortua, M. I. & Rojo, T. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2971–2976.

Barkelew, C. H. & Calvin, M. (1946). *J. Am. Chem. Soc.* **68**, 2257–2267.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Drew, M. G. B., Prasad, R. N. & Sharma, R. P. (1985). *Acta Cryst.* C**41**, 1755–1758.

Du, M., Zhao, X. J., Guo, J. H., Bu, X. H. & Ribas, J. (2005). *Eur. J. Inorg. Chem.* pp. 294–304.

Durmuş, S., Tatar, L., Arıcı, C., Dinçer, N., Atakol, O., Svoboda, I. & Fuess, H. (2005). *Z. Kristallogr.* **220**, 977–982.

Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Fukuhara, C., Tsuneyoshi, K., Matsumato, N., Kida, S., Mikuriya, M. & Mori, M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3437–3479.

Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.

Martell, A. E. & Calvin, M. (1958). *Die Chemie der Metall chelat-Verbindungen*, pp. 197-199. Weinheim/Bergstrasse: Verlag Chemie GmbH.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Reglinski, J., Taylor, M. K. & Kennedy, A. R. (2006). *Inorg. Chem. Commun.* **9**, 736–739.

Ribas, J., Escuer, A., Monfort, M., Vicente, R., Cortes, R., Lezama, L. & Rojo, T. (1999). *Coord. Chem. Rev.* **193–195**, 1027–1068.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Tatar, L. (2002). *Acta Cryst.* E**58**, m231–m233.

Tatar, Y. L. & Atakol, O. (2002). *Cryst. Res. Technol.* **37**, 1352–1359.

supplementary materials

Acta Cryst. (2007). E**63**, m2403-m2404 [**doi:10.1107/S1600536807040184**]

Bis[μ_2-2,2'-dimethyl-*N*,*N*'-bis(2-oxidobenzyl)propane-1,3-diamine]-1κ^4*O*,*N*,*N*',*O*':2κ^2*O*,*O*';2κ^2*O*,*O*':3κ^4*O*,*N*,*N*',*O*'-bis(*N*,*N*'-dimethylformamide)-1κ*O*,3κ*O*-di-μ_2-formato-1:2κ^2*O*:*O*';2:3κ^2*O*:*O*'-trinickel(II)

L. Tatar Yildirim, O. Atakol and G. Kavak

Comment

ONNO type Schiff base ligands have been known since as early as 1946 (Barkelew & Calvin, 1946; Martell *et al.*, 1958). Schiff-bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals (Drew *et al.*, 1985; Fukuhara *et al.*, 1990). Oxygen-bridged polynuclear complexes of the transition series are of interest because of their magnetic properties (Barandika *et al.*, 1999; Ribas *et al.*, 1999; Du *et al.*, 2005). The ONNO type ligand stereochemistry around the metal ions and the structure of the O-atom bridges influence the magnetic exchange interactions. These complexes may be homo or heteronuclear. Polynuclear metal complexes of Schiff-base ligands have been the subject on considerable interest in our laboratory, *e.g.* [$NiZnI_2(LH_2)$(dmf)] (Tatar, 2002), [Ni{$Ni(LH_2)(O_2CMe)$(dmf)}$_2$] (Tatar & Atakol, 2002), [$Ni(LH_2)N_3$(dmf)H_2O and $Ni(DMLH_2)N_3$(dmf)] (Durmuş *et al.*, 2005). Where LH_2 is *N*,*N*'-bis(salicylidene)-1,3-propanediamine.

In this study, bis-*N*,*N*'(salicylidene)-2,2'-dimethyl-1,3-propanediamine was reduced by using $NaBH_4$ in MeOH and we obtained an ONNO type ligand. The title molecule was prepared by initating a reaction between the ONNO ligand and nickel(II)-formato in dmf. The crystal and molecular structure of the title homotrinuclear complex has been determined. Recently details of a similar complex were reported literature (Reglinski *et al.*, 2006).

In the title complex (Fig. 1), the central Ni1 atom, which is located on an inversion centre, has a distorted octahedral coordination environment, formed by four O atoms from two $DMLH_2$ ligands in the equatorial plane [Ni1—O1 = 2.075 (3), Ni1—O2 = 2.076 (3) Å] and two O atoms of two $–O_2CH$ groups located at the axial positions [Ni1—O4 = 2.160 (3) Å]. The bond angles around Ni1 angles range between 99.66 (12) and 80.34 (12)°.

The terminal Ni2 atoms also have distorted octahedral coordination environments formed by two O and two N atoms from $DMLH_2$ ligands in the equatorial plane and bond distances ranging between 2.037 (3) − 2.098 (4) Å. The distance of atom Ni2 from the O1/O2/N1/N2 mean plane is 0.0546 (8) Å. The dihedral angle between the planes O1—Ni2—O2 and N1—Ni2—N2 is 4.3 (2)°. The axial positions are occupied by atoms O3 and $O5^i$ [symmetry code: (i) −*x*, −*y*, −*z*] from a dmf molecule and an $–O_2CH$ group, respectively. This coordination involves a fairly long axial Ni2—O3 bond of 2.147 (3) Å. The Ni2 coordination involves bond angles ranging between 81.85 (12) and 93.54 (16)°.

The conformation of the rings in the title molecule were analyzed using *PLATON* (Spek, 2003). The Cremer & Pople puckering parameter (Cremer & Pople, 1975) of Q(2) = 0.262 (2) Å is for the Ni1—O1—Ni2—O2 ring and the dihedral angle between the planes O1—Ni1—O2 and O1—Ni2—O2 is 19.36 (12)°. The six-membered Ni2/N1/C8/C9/C12/N2 ring is in a (C) chair form (Q = 0.607 (6) Å, θ = 3.1 (5)° and φ = 168 (10)°). The Cremer & Pople puckering parameters of the Ni1—O1—Ni2—$O5^i$—$C20^i$—$O4^i$ (symmetry code: (i) −*x*, −*y*, −*z*) ring are Q = 1.045 (3) Å, θ = 128.4 (2), φ = 239.7 (3)

°, showing this six-membered ring is an E (envelope) form. The crystal structure is stabilized by weak C—H···O hydrogen bonds.

Experimental

Bis-*N*,*N*'(salicylidene)-2,2'-dimethyl-1,3-propanediamine was synthesized from salicylaldehyde and 2,2'-dimethyl-1,3-propanediamine in EtOH. This compound was reduced using $NaBH_4$ in MeOH resulting in the formation of bis-*N*,*N*'(2-hydroxybenzyl)-2,2'-dimethyl-1,3-propanediamine. 0.628 g (2 mmol) bis-*N*,*N*'(2-hydroxybenzyl)-2,2'-dimethyl-1,3-propanediamine was dissolved in 50 ml dmf and heated to 383 K. To this solution were added a solution of 0.712 g (3 mmol) $NiCl_2{\cdot}6H_2O$ in 20 ml hot MeOH and a solution of 0.408 g (6 mmol) NaHCOO in 5 ml hot water. This final mixture was left to stand for 2–3 days. After this period, light green crystals were filtered and dried in air. [$C_{46}H_{64}N_6O_{10}Ni_3$] Element Analysis results: Ni, found %: 16.24 (calculated %:16.65); N found %: 7.53 (calculated %: 7.94). The measured dmf mass using thermogravimetrie: % 13.69 (calculated: %13.80).

Refinement

The H atoms of the phenyl rings were positioned geometrically using riding model $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms on all methyl groups excluding C23 were positioned geometrically using a riding-model with $U_{iso}(H) = 1.5U_{eq}(C)$. All other hydrogen atoms were located in a difference map and refined isotropically.

Figures

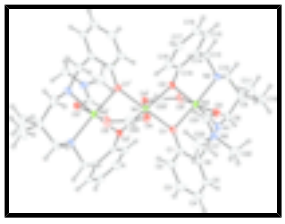


Fig. 1. The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level (symmetry code (i): −*x*, −*y*, −*z*).

Bis[μ$_2$-2,2'-dimethyl-*N*,*N*'-bis(2-oxidobenzyl)propane-1,3-diamine]-1κ^4*O*,*N*,*N*',*O*':2κ^2*O*,*O*';2κ^2*O*,*O*':3κ^4*O*,*N*,*N*',*O*'-bis(N,*N*'- dimethylformamide)-1κ*O*,3κ*O*-di-μ$_2$-formato-1:2κ^2*O*:*O*';2:3κ^2*O*:*O*'- trinickel(II)

Crystal data

$[Ni_3(C_{19}H_{24}N_2O_2)_2(CHO_2)_2(C_3H_7NO)_2]$	F_{000} = 1092
M_r = 1037.10	D_x = 1.440 Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation λ = 1.54184 Å
Hall symbol: -P 2yn	Cell parameters from 15 reflections
a = 10.289 (2) Å	θ = 19.0–23.9º
b = 14.054 (5) Å	μ = 1.88 mm^{-1}
c = 17.005 (4) Å	T = 293 (2) K
β = 103.433 (19)º	Prism, light green

V = 2391.7 (11) Å^3	0.2 × 0.2 × 0.1 mm
Z = 2	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	R_{int} = 0.048
Radiation source: fine-focus sealed tube	θ_{max} = 73.9º
Monochromator: graphite	θ_{min} = 4.1º
non–profiled ω scans	h = −12→0
Absorption correction: ψ scan (North *et al.*, 1968)	k = −17→0
T_{min} = 0.720, T_{max} = 0.828	l = −20→21
5007 measured reflections	3 standard reflections
4740 independent reflections	every 120 min
2200 reflections with $I > 2\sigma(I)$	intensity decay: 2%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.056	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.150	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.3344P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(\Delta/\sigma)_{max} < 0.001$
4740 reflections	$\Delta\rho_{max}$ = 0.43 e Å^{-3}
343 parameters	$\Delta\rho_{min}$ = −0.49 e Å^{-3}
6 restraints	Extinction coefficient: ?
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}

Ni1	0	0	0	0.0447 (3)
Ni2	0.00481 (8)	−0.08187 (5)	0.16902 (5)	0.0439 (3)
O1	0.1113 (3)	0.0124 (2)	0.11806 (18)	0.0470 (9)
O3	0.1641 (3)	−0.1840 (2)	0.1868 (2)	0.0510 (9)
O2	−0.0683 (3)	−0.1191 (2)	0.05036 (17)	0.0443 (9)
N2	−0.1059 (4)	−0.1871 (3)	0.2102 (2)	0.0436 (11)
N1	0.0996 (5)	−0.0405 (3)	0.2869 (3)	0.0537 (12)
O4	0.1491 (3)	−0.0798 (2)	−0.0429 (2)	0.0526 (10)
C12	−0.1609 (7)	−0.1579 (5)	0.2788 (4)	0.0598 (17)
C7	0.1727 (8)	0.0507 (4)	0.2844 (4)	0.0646 (19)
C1	0.2388 (6)	0.0303 (3)	0.1530 (3)	0.0480 (14)
C5	0.4122 (7)	0.0612 (4)	0.2736 (4)	0.078 (2)
H5	0.4371	0.0723	0.329	0.093*
C2	0.3375 (6)	0.0313 (4)	0.1086 (4)	0.0641 (16)
H2	0.3148	0.0228	0.0529	0.077*
C6	0.2769 (6)	0.0465 (4)	0.2373 (3)	0.0568 (15)
C18	−0.0554 (5)	−0.2520 (4)	−0.0358 (3)	0.0610 (16)
H18	−0.0156	−0.2155	−0.0693	0.073*
C15	−0.1814 (6)	−0.3629 (4)	0.0580 (3)	0.0604 (16)
H15	−0.2243	−0.4002	0.0894	0.072*
C14	−0.1610 (5)	−0.2665 (4)	0.0757 (3)	0.0477 (14)
C17	−0.0766 (6)	−0.3480 (4)	−0.0512 (3)	0.0668 (17)
H17	−0.0477	−0.3757	−0.0938	0.08*
C19	−0.0936 (5)	−0.2091 (4)	0.0301 (3)	0.0427 (13)
C9	−0.0597 (6)	−0.1276 (4)	0.3550 (3)	0.0614 (16)
O5	0.1429 (4)	−0.0182 (3)	−0.1667 (2)	0.0607 (11)
N3	0.3568 (5)	−0.2094 (3)	0.1475 (3)	0.0568 (12)
C21	0.2270 (6)	−0.1944 (4)	0.1348 (4)	0.0522 (15)
C22	0.4387 (6)	−0.2064 (4)	0.2286 (3)	0.080 (2)
H22A	0.53	−0.2185	0.2274	0.12*
H22B	0.4088	−0.254	0.2608	0.12*
H22C	0.4317	−0.1447	0.2515	0.12*
C13	−0.2127 (5)	−0.2229 (4)	0.1423 (4)	0.0529 (15)
C10	0.0391 (6)	−0.2081 (4)	0.3851 (3)	0.0689 (18)
H10A	0.1026	−0.1879	0.433	0.103*
H10B	0.0853	−0.2242	0.344	0.103*
H10C	−0.0084	−0.2628	0.3974	0.103*
C11	−0.1416 (7)	−0.1071 (4)	0.4189 (4)	0.099 (2)
H11A	−0.0824	−0.0878	0.4687	0.148*
H11B	−0.1884	−0.1637	0.4279	0.148*
H11C	−0.2048	−0.0573	0.3998	0.148*
C3	0.4713 (6)	0.0452 (4)	0.1494 (5)	0.078 (2)
H3	0.5367	0.0444	0.1197	0.094*
C8	0.0105 (7)	−0.0342 (5)	0.3429 (3)	0.0639 (17)
C16	−0.1395 (6)	−0.4034 (4)	−0.0046 (4)	0.0730 (19)
H16	−0.1534	−0.4678	−0.0157	0.088*
C4	0.5093 (7)	0.0599 (4)	0.2304 (5)	0.084 (2)
H4	0.5987	0.0688	0.2559	0.101*
C23	0.4236 (7)	−0.2142 (6)	0.0815 (4)	0.089 (2)

C20	0.1795 (6)	−0.0748 (4)	−0.1089 (4)	0.0565 (15)
H12B	−0.208 (5)	−0.207 (3)	0.295 (3)	0.061*
H13B	−0.274 (4)	−0.273 (3)	0.163 (2)	0.052*
H12A	−0.221 (5)	−0.099 (4)	0.262 (3)	0.067 (17)*
H8A	−0.066 (4)	0.011 (3)	0.321 (3)	0.052*
H7A	0.097 (5)	0.092 (4)	0.259 (3)	0.070 (19)*
H8B	0.064 (4)	−0.021 (3)	0.3945 (17)	0.067 (18)*
H21	0.188 (4)	−0.190 (3)	0.0823 (13)	0.042 (15)*
H7B	0.206 (5)	0.073 (4)	0.342 (3)	0.09 (2)*
H13A	−0.261 (4)	−0.166 (2)	0.121 (3)	0.075 (19)*
H23B	0.4846	−0.2653	0.0803	0.057 (16)*
H23C	0.4841	−0.1563	0.0878	0.09 (2)*
H23A	0.3565	−0.2136	0.0288	0.12 (3)*
H20	0.246 (4)	−0.114 (3)	−0.113 (3)	0.067 (19)*
H2N	−0.042 (3)	−0.230 (3)	0.227 (3)	0.051 (16)*
H1N	0.153 (5)	−0.090 (3)	0.300 (3)	0.09 (2)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0489 (8)	0.0389 (7)	0.0441 (7)	−0.0022 (6)	0.0061 (6)	0.0071 (6)
Ni2	0.0512 (5)	0.0374 (5)	0.0416 (5)	−0.0010 (4)	0.0078 (4)	0.0018 (4)
O1	0.049 (2)	0.045 (2)	0.043 (2)	−0.0099 (18)	0.0016 (17)	0.0045 (16)
O3	0.054 (2)	0.045 (2)	0.055 (2)	0.0034 (18)	0.0129 (19)	0.0038 (18)
O2	0.058 (2)	0.0333 (19)	0.0393 (19)	−0.0065 (17)	0.0076 (17)	0.0044 (15)
N2	0.046 (3)	0.045 (3)	0.040 (3)	0.004 (2)	0.009 (2)	0.004 (2)
N1	0.079 (4)	0.035 (3)	0.045 (3)	−0.002 (3)	0.010 (3)	0.000 (2)
O4	0.056 (2)	0.051 (2)	0.052 (2)	0.0104 (19)	0.0147 (19)	0.0130 (19)
C12	0.079 (5)	0.051 (4)	0.058 (4)	0.007 (4)	0.034 (4)	0.009 (3)
C7	0.100 (6)	0.038 (3)	0.047 (4)	−0.009 (4)	0.000 (4)	−0.002 (3)
C1	0.054 (4)	0.028 (3)	0.057 (4)	−0.004 (3)	0.003 (3)	0.003 (3)
C5	0.085 (5)	0.050 (4)	0.075 (5)	−0.031 (4)	−0.029 (4)	0.007 (3)
C2	0.055 (4)	0.054 (4)	0.078 (4)	−0.014 (3)	0.006 (4)	−0.001 (3)
C6	0.076 (5)	0.036 (3)	0.052 (4)	−0.012 (3)	0.002 (3)	0.004 (3)
C18	0.072 (4)	0.059 (4)	0.050 (3)	−0.008 (3)	0.009 (3)	−0.004 (3)
C15	0.069 (4)	0.049 (4)	0.051 (4)	−0.017 (3)	−0.010 (3)	0.010 (3)
C14	0.053 (3)	0.043 (3)	0.041 (3)	−0.006 (3)	−0.002 (3)	0.001 (3)
C17	0.085 (5)	0.055 (4)	0.057 (4)	−0.006 (4)	0.010 (3)	−0.015 (3)
C19	0.041 (3)	0.041 (3)	0.040 (3)	−0.001 (3)	−0.004 (2)	0.005 (3)
C9	0.088 (5)	0.056 (4)	0.047 (4)	0.006 (4)	0.029 (3)	−0.003 (3)
O5	0.074 (3)	0.058 (3)	0.056 (2)	0.016 (2)	0.027 (2)	0.015 (2)
N3	0.053 (3)	0.049 (3)	0.062 (3)	0.007 (2)	0.000 (3)	−0.005 (2)
C21	0.057 (4)	0.045 (3)	0.049 (4)	0.006 (3)	−0.001 (3)	−0.001 (3)
C22	0.067 (4)	0.077 (5)	0.081 (5)	−0.001 (4)	−0.016 (4)	−0.008 (4)
C13	0.042 (3)	0.058 (4)	0.057 (4)	−0.013 (3)	0.007 (3)	0.013 (3)
C10	0.095 (5)	0.053 (4)	0.049 (4)	0.003 (4)	−0.003 (3)	0.010 (3)
C11	0.175 (7)	0.073 (5)	0.073 (5)	0.012 (5)	0.076 (5)	0.001 (4)
C3	0.059 (5)	0.058 (4)	0.114 (6)	−0.012 (3)	0.014 (4)	−0.002 (4)

C8	0.101 (5)	0.057 (4)	0.034 (4)	0.006 (4)	0.016 (4)	−0.003 (3)
C16	0.101 (5)	0.036 (4)	0.066 (4)	−0.007 (3)	−0.012 (4)	−0.002 (3)
C4	0.064 (5)	0.058 (5)	0.113 (6)	−0.020 (4)	−0.016 (4)	0.008 (4)
C23	0.059 (4)	0.121 (7)	0.090 (6)	0.018 (5)	0.025 (4)	−0.030 (4)
C20	0.046 (4)	0.051 (4)	0.075 (5)	0.010 (3)	0.021 (3)	0.003 (4)

Geometric parameters (Å, °)

Ni1—Ni2	3.0857 (14)	C18—H18	0.93
Ni1—O1^{i}	2.075 (3)	C15—C16	1.362 (7)
Ni1—O1	2.075 (3)	C15—C14	1.392 (7)
Ni1—O2	2.076 (3)	C15—H15	0.93
Ni1—O2^{i}	2.076 (3)	C14—C19	1.409 (6)
Ni1—O4	2.160 (3)	C14—C13	1.490 (7)
Ni1—O4^{i}	2.160 (3)	C17—C16	1.375 (7)
Ni2—O1	2.037 (3)	C17—H17	0.93
Ni2—O2	2.051 (3)	C9—C10	1.529 (7)
Ni2—O5^{i}	2.064 (4)	C9—C8	1.534 (8)
Ni2—N2	2.084 (4)	C9—C11	1.550 (7)
Ni2—N1	2.098 (4)	O5—C20	1.253 (6)
Ni2—O3	2.147 (3)	O5—Ni2^{i}	2.064 (4)
O1—C1	1.332 (6)	N3—C21	1.319 (7)
O3—C21	1.221 (6)	N3—C22	1.440 (6)
O2—C19	1.321 (5)	N3—C23	1.447 (7)
N2—C12	1.469 (7)	C21—H21	0.892 (19)
N2—C13	1.485 (6)	C22—H22A	0.96
N2—H2N	0.892 (19)	C22—H22B	0.96
N1—C8	1.470 (7)	C22—H22C	0.96
N1—C7	1.492 (7)	C13—H13B	1.06 (4)
N1—H1N	0.890 (19)	C13—H13A	0.964 (19)
O4—C20	1.235 (6)	C10—H10A	0.96
C12—C9	1.523 (8)	C10—H10B	0.96
C12—H12B	0.93 (5)	C10—H10C	0.96
C12—H12A	1.03 (5)	C11—H11A	0.96
C7—C6	1.480 (8)	C11—H11B	0.96
C7—H7A	0.98 (5)	C11—H11C	0.96
C7—H7B	1.00 (5)	C3—C4	1.357 (8)
C1—C2	1.398 (7)	C3—H3	0.93
C1—C6	1.415 (7)	C8—H8A	1.01 (4)
C5—C4	1.370 (8)	C8—H8B	0.937 (19)
C5—C6	1.402 (8)	C16—H16	0.93
C5—H5	0.93	C4—H4	0.93
C2—C3	1.404 (7)	C23—H23B	0.957 (7)
C2—H2	0.93	C23—H23C	1.014 (8)
C18—C17	1.382 (7)	C23—H23A	0.996 (7)
C18—C19	1.406 (7)	C20—H20	0.886 (19)
O1^{i}—Ni1—O1	180.00 (19)	C17—C18—H18	119.7

O1^{i}—Ni1—O2	99.66 (12)	C19—C18—H18	119.7
O1—Ni1—O2	80.34 (12)	C16—C15—C14	121.1 (5)
O1^{i}—Ni1—O2^{i}	80.34 (12)	C16—C15—H15	119.5
O1—Ni1—O2^{i}	99.66 (12)	C14—C15—H15	119.5
O2—Ni1—O2^{i}	180.00 (17)	C15—C14—C19	120.4 (5)
O1^{i}—Ni1—O4	84.56 (13)	C15—C14—C13	120.1 (5)
O1—Ni1—O4	95.44 (13)	C19—C14—C13	119.5 (5)
O2—Ni1—O4	93.19 (13)	C16—C17—C18	121.2 (6)
O2^{i}—Ni1—O4	86.81 (13)	C16—C17—H17	119.4
O1^{i}—Ni1—O4^{i}	95.44 (13)	C18—C17—H17	119.4
O1—Ni1—O4^{i}	84.56 (13)	O2—C19—C18	123.0 (5)
O2—Ni1—O4^{i}	86.81 (13)	O2—C19—C14	119.8 (5)
O2^{i}—Ni1—O4^{i}	93.19 (13)	C18—C19—C14	117.2 (5)
O4—Ni1—O4^{i}	180.0 (2)	C12—C9—C10	110.4 (5)
O1—Ni2—O2	81.85 (12)	C12—C9—C8	112.1 (5)
O1—Ni2—O5^{i}	90.88 (14)	C10—C9—C8	112.4 (5)
O2—Ni2—O5^{i}	93.16 (14)	C12—C9—C11	105.8 (5)
O1—Ni2—N2	173.93 (15)	C10—C9—C11	109.3 (5)
O2—Ni2—N2	92.58 (14)	C8—C9—C11	106.6 (5)
O5^{i}—Ni2—N2	91.84 (16)	C20—O5—Ni2^{i}	122.2 (4)
O1—Ni2—N1	92.84 (16)	C21—N3—C22	119.8 (5)
O2—Ni2—N1	173.67 (17)	C21—N3—C23	121.7 (5)
O5^{i}—Ni2—N1	90.35 (18)	C22—N3—C23	117.8 (5)
N2—Ni2—N1	92.58 (17)	O3—C21—N3	126.0 (6)
O1—Ni2—O3	91.51 (13)	O3—C21—H21	122 (3)
O2—Ni2—O3	93.54 (13)	N3—C21—H21	112 (3)
O5^{i}—Ni2—O3	173.15 (14)	N3—C22—H22A	109.5
N2—Ni2—O3	86.41 (16)	N3—C22—H22B	109.5
N1—Ni2—O3	83.12 (17)	H22A—C22—H22B	109.5
C1—O1—Ni2	120.3 (3)	N3—C22—H22C	109.5
C1—O1—Ni1	135.4 (3)	H22A—C22—H22C	109.5
Ni2—O1—Ni1	97.26 (13)	H22B—C22—H22C	109.5
C21—O3—Ni2	119.6 (4)	N2—C13—C14	113.5 (4)
C19—O2—Ni2	120.4 (3)	N2—C13—H13B	111 (2)
C19—O2—Ni1	136.8 (3)	C14—C13—H13B	109 (2)
Ni2—O2—Ni1	96.77 (13)	N2—C13—H13A	104 (3)
C12—N2—C13	111.1 (4)	C14—C13—H13A	108 (3)
C12—N2—Ni2	114.2 (3)	H13B—C13—H13A	112 (4)
C13—N2—Ni2	110.1 (3)	C9—C10—H10A	109.5
C12—N2—H2N	109 (3)	C9—C10—H10B	109.5
C13—N2—H2N	112 (3)	H10A—C10—H10B	109.5
Ni2—N2—H2N	100 (3)	C9—C10—H10C	109.5
C8—N1—C7	111.2 (5)	H10A—C10—H10C	109.5
C8—N1—Ni2	114.5 (4)	H10B—C10—H10C	109.5
C7—N1—Ni2	109.7 (3)	C9—C11—H11A	109.5
C8—N1—H1N	110 (4)	C9—C11—H11B	109.5

C7—N1—H1N	113 (4)	H11A—C11—H11B	109.5
Ni2—N1—H1N	98 (4)	C9—C11—H11C	109.5
C20—O4—Ni1	128.8 (4)	H11A—C11—H11C	109.5
N2—C12—C9	116.1 (5)	H11B—C11—H11C	109.5
N2—C12—H12B	111 (3)	C4—C3—C2	122.7 (6)
C9—C12—H12B	104 (3)	C4—C3—H3	118.6
N2—C12—H12A	108 (3)	C2—C3—H3	118.6
C9—C12—H12A	105 (3)	N1—C8—C9	114.8 (5)
H12B—C12—H12A	111 (4)	N1—C8—H8A	110 (3)
C6—C7—N1	114.5 (5)	C9—C8—H8A	104 (3)
C6—C7—H7A	113 (3)	N1—C8—H8B	108 (3)
N1—C7—H7A	100 (3)	C9—C8—H8B	104 (3)
C6—C7—H7B	114 (3)	H8A—C8—H8B	117 (4)
N1—C7—H7B	107 (3)	C15—C16—C17	119.4 (5)
H7A—C7—H7B	108 (4)	C15—C16—H16	120.3
O1—C1—C2	121.7 (5)	C17—C16—H16	120.3
O1—C1—C6	119.6 (5)	C3—C4—C5	118.2 (6)
C2—C1—C6	118.7 (5)	C3—C4—H4	120.9
C4—C5—C6	122.3 (6)	C5—C4—H4	120.9
C4—C5—H5	118.8	N3—C23—H23B	118.9 (7)
C6—C5—H5	118.8	N3—C23—H23C	105.7 (6)
C1—C2—C3	119.1 (6)	H23B—C23—H23C	102.5 (6)
C1—C2—H2	120.4	N3—C23—H23A	110.0 (6)
C3—C2—H2	120.4	H23B—C23—H23A	107.9 (7)
C5—C6—C1	118.9 (6)	H23C—C23—H23A	111.6 (8)
C5—C6—C7	121.7 (6)	O4—C20—O5	131.0 (6)
C1—C6—C7	119.4 (5)	O4—C20—H20	113 (3)
C17—C18—C19	120.6 (5)	O5—C20—H20	116 (3)
O2—Ni2—O1—C1	−140.1 (4)	Ni1—O1—C1—C2	−10.3 (7)
$O5^{i}$—Ni2—O1—C1	126.8 (4)	Ni2—O1—C1—C6	−45.5 (6)
N1—Ni2—O1—C1	36.4 (4)	Ni1—O1—C1—C6	171.2 (3)
O3—Ni2—O1—C1	−46.8 (4)	O1—C1—C2—C3	−176.5 (5)
O2—Ni1—O1—C1	133.9 (4)	C6—C1—C2—C3	2.1 (8)
$O2^{i}$—Ni1—O1—C1	−46.1 (4)	C4—C5—C6—C1	−0.4 (9)
O4—Ni1—O1—C1	41.6 (4)	C4—C5—C6—C7	−178.3 (6)
$O4^{i}$—Ni1—O1—C1	−138.4 (4)	O1—C1—C6—C5	177.3 (5)
O1—Ni2—O3—C21	−39.4 (4)	C2—C1—C6—C5	−1.2 (8)
O2—Ni2—O3—C21	42.5 (4)	O1—C1—C6—C7	−4.7 (7)
N2—Ni2—O3—C21	134.9 (4)	C2—C1—C6—C7	176.8 (5)
N1—Ni2—O3—C21	−132.1 (4)	N1—C7—C6—C5	−117.1 (6)
O1—Ni2—O2—C19	142.4 (4)	N1—C7—C6—C1	65.0 (7)
$O5^{i}$—Ni2—O2—C19	−127.1 (4)	C16—C15—C14—C19	−1.4 (8)
N2—Ni2—O2—C19	−35.1 (4)	C16—C15—C14—C13	177.4 (5)
O3—Ni2—O2—C19	51.4 (4)	C19—C18—C17—C16	2.4 (9)
$O1^{i}$—Ni1—O2—C19	43.8 (4)	Ni2—O2—C19—C18	−134.9 (4)
O1—Ni1—O2—C19	−136.2 (4)	Ni1—O2—C19—C18	10.8 (7)
O4—Ni1—O2—C19	−41.2 (4)	Ni2—O2—C19—C14	44.6 (6)

O4^{i}—Ni1—O2—C19	138.8 (4)	Ni1—O2—C19—C14	−169.6 (3)
O1^{i}—Ni1—O2—Ni2	−165.45 (13)	C17—C18—C19—O2	175.7 (5)
O1—Ni1—O2—Ni2	14.55 (13)	C17—C18—C19—C14	−3.9 (8)
O4—Ni1—O2—Ni2	109.53 (14)	C15—C14—C19—O2	−176.2 (4)
O4^{i}—Ni1—O2—Ni2	−70.47 (14)	C13—C14—C19—O2	5.0 (7)
O2—Ni2—N2—C12	−141.5 (4)	C15—C14—C19—C18	3.4 (7)
O5^{i}—Ni2—N2—C12	−48.3 (4)	C13—C14—C19—C18	−175.4 (5)
N1—Ni2—N2—C12	42.1 (4)	N2—C12—C9—C10	−58.2 (7)
O3—Ni2—N2—C12	125.1 (4)	N2—C12—C9—C8	67.9 (7)
O2—Ni2—N2—C13	−15.8 (4)	N2—C12—C9—C11	−176.3 (5)
O5^{i}—Ni2—N2—C13	77.5 (4)	Ni2—O3—C21—N3	141.5 (5)
N1—Ni2—N2—C13	167.9 (4)	C22—N3—C21—O3	−5.4 (9)
O3—Ni2—N2—C13	−109.2 (4)	C23—N3—C21—O3	−175.5 (6)
O1—Ni2—N1—C8	139.8 (4)	C12—N2—C13—C14	−171.7 (5)
O5^{i}—Ni2—N1—C8	48.9 (4)	Ni2—N2—C13—C14	60.8 (5)
N2—Ni2—N1—C8	−42.9 (4)	C15—C14—C13—N2	115.8 (5)
O3—Ni2—N1—C8	−129.0 (4)	C19—C14—C13—N2	−65.4 (6)
O1—Ni2—N1—C7	14.0 (4)	C1—C2—C3—C4	−1.4 (9)
O5^{i}—Ni2—N1—C7	−76.9 (4)	C7—N1—C8—C9	−174.9 (5)
N2—Ni2—N1—C7	−168.7 (4)	Ni2—N1—C8—C9	60.1 (6)
O3—Ni2—N1—C7	105.2 (4)	C12—C9—C8—N1	−67.7 (7)
O1^{i}—Ni1—O4—C20	37.4 (5)	C10—C9—C8—N1	57.3 (7)
O1—Ni1—O4—C20	−142.6 (5)	C11—C9—C8—N1	177.0 (5)
O2—Ni1—O4—C20	136.8 (5)	C14—C15—C16—C17	−0.2 (9)
O2^{i}—Ni1—O4—C20	−43.2 (5)	C18—C17—C16—C15	−0.2 (9)
C13—N2—C12—C9	175.0 (5)	C2—C3—C4—C5	−0.1 (10)
Ni2—N2—C12—C9	−59.7 (6)	C6—C5—C4—C3	1.1 (10)
C8—N1—C7—C6	172.7 (5)	Ni1—O4—C20—O5	7.0 (10)
Ni2—N1—C7—C6	−59.6 (6)	Ni2^{i}—O5—C20—O4	−6.5 (9)
Ni2—O1—C1—C2	133.0 (4)		

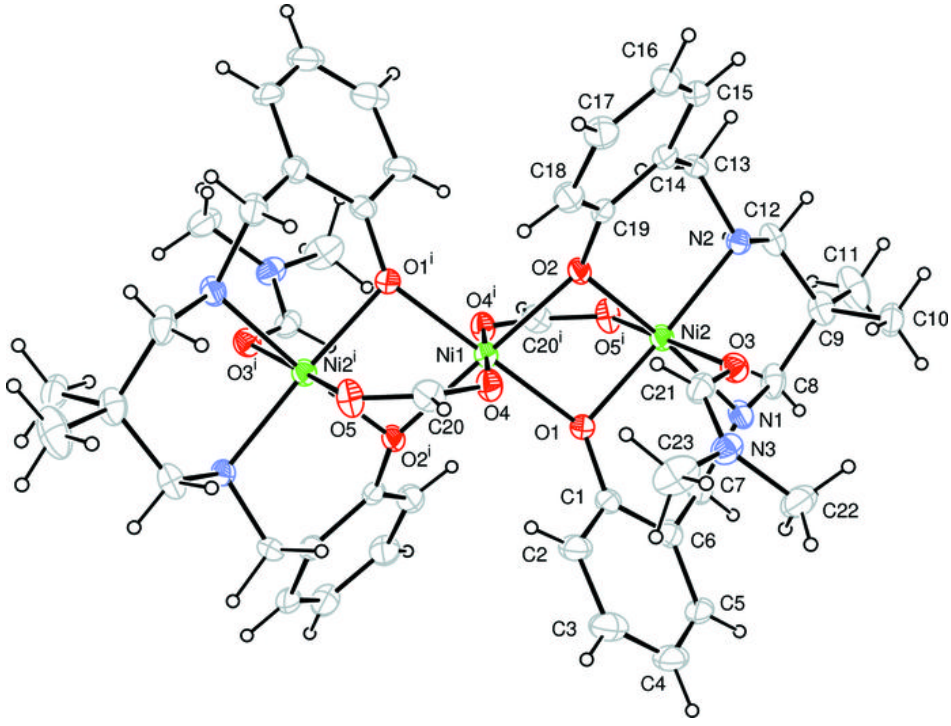
Symmetry codes: (i) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O4	0.93	2.52	3.242 (7)	135
C8—H8A···O5^{ii}	1.01 (5)	2.56 (5)	3.133 (6)	116 (3)
C12—H12A···O5^{ii}	1.04 (6)	2.56 (5)	3.156 (8)	116 (4)
C18—H18···O4	0.93	2.52	3.228 (6)	133
C21—H21···O4	0.89 (2)	2.59 (3)	3.353 (7)	144 (4)

Symmetry codes: (ii) −*x*, −*y*, −*z*.

Fig. 1


C16
C17
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O1i
O4i
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C20i
O5i
Ni2
O3
C9
O3i
Ni2i
Ni1
C21
C8
O5
C20
O4
O1
N1
O2i
C23
N3
C1
C7
C22
C2
C6
C5
C3
C4