Acta Cryst E STRUCTURE REPORTS

ISSN 1600-5368

Crystal structure of {μ-6,6′-dimethoxy-2,2′-[ethane-1,2-diylbis(nitrilomethanylylidene)]diphenolato}-(methanol)(nitrato)nickel(II)sodium

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Received 6 August 2014
Accepted 30 September 2014

Edited by M. Zeller, Youngstown State University, USA

Keywords: crystal structure; hydrogen bonds; π–π stacking; Ni^{II}–Na heterometallic complex; Schiff base

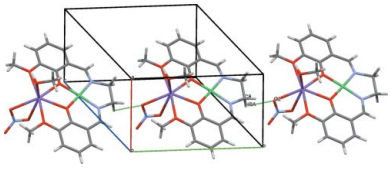
CCDC reference: 1026857
Supporting information: this article has supporting information at journals.iucr.org/e

In the molecular structure of the title compound, [$NaNi(C_{18}H_{18}N_2O_4)(NO_3)(CH_3OH)$], the Ni^{2+} ion has a slightly distorted square-planar coordination environment defined by two N and two O atoms which belong to a Schiff base ligand, *viz.* 6,6′-dimethoxy-2,2′-[ethane-1,2-diylbis(nitrilomethanylylidene)]diphenolate. Seven O atoms form the coordination environment of the Na^+ ion: four from the Schiff base ligand, two from a bidentate chelating nitrate anion and one O atom from a coordinating methanol molecule. In the crystal, the bimetallic complexes are assembled into chains along the *b*-axis direction *via* weak C—H···O hydrogen-bond interactions. Neighbouring chains are in turn connected through bifurcated O—H···O hydrogen bonds that involve the coordinating methanol molecules and the nitrate anions, and through π–π stacking interactions between phenyl rings of neighbouring molecules.

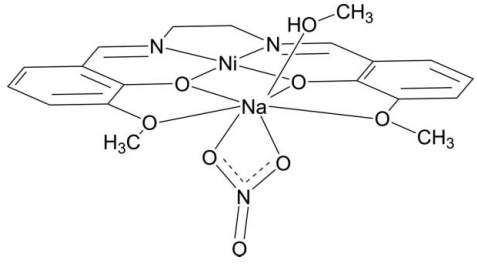
1. Chemical context

Schiff bases are known to be effective ligands able to coordinate a wide range of different metal ions, and they have been widely utilized in the study of biochemical processes (Lindoy *et al.*, 1976; Correia *et al.*, 2005). Compartmental Schiff base ligands, *i.e.* tetra- and hexadentate Schiff base ligands with different 'compartments' for different types of metal ions, have been employed extensively as 'blocking ligands'. Typical examples would be *e.g.* ligands with an N_2O_4 donor set with two Schiff base N-donor sites, two anionic phenolate donor sites, and two additional ether donor sites. The N_2O_2 compartment is generally more favorable for 3*d* metal ions. The additional O-donor atoms provide the opportunity to accommodate a second metal ion, which might be a 3*d*-, 4*f*-, *s*- or *p*-block element, thus allowing the production of di-, tri- or oligonuclear systems (Gheorghe *et al.*, 2006; Costes *et al.*, 2008; Andruh *et al.*, 2009).

Studies on heterometallic complexes began at the end of the 1960s. They are of interest because of their physicochemical properties that arise from the presence of dissimilar metal ions in close proximity. The majority of publications in this field are devoted to the preparation of 3*d*–4*f* heterometallic complexes (Costes *et al.*, 1998; Koner *et al.*, 2005; Sakamoto *et al.*, 2001). Metal salicylaldimines, on the other hand, represent a fascinating group of ligands that are not only effective complexing agents for *p*- and *d*-block elements, but also for alkali metal ions similar to the more well known ligand systems such as crown ethers, cryptands *etc.* Much of the interest concerning



the coordination chemistry of alkali metal ions originates from the development of molecular systems that can mimic naturally occurring molecules that are responsible for the selective transport of these ions, *e.g.* through membranes. Some of the alkali–metal-ion adducts behave as precursors for other potentially interesting molecular species that can be used for small-molecule activation (Gambarotta *et al.*, 1982), electron storage (Gallo *et al.*, 1997) and the production of materials with remarkable magnetic properties, the alkali cation being crucial in determining the three-dimensional network in the solid state (Miyasaka *et al.*, 1996).



In the case of compartmental Schiff base ligands such as *e.g.* N(imine)$_2$O(phenoxo)$_2$O(methoxy/ethoxy)$_2$, the metal ion may be either retained in the plane of the O$_4$ donor set or sandwiched between two sets of the Schiff base O atoms. The former case is usually characterized by a coordination number of eight from two O(phenoxo)$_2$O(methoxy/ethoxy)$_2$ compartments which belong to different molecules. The latter features a coordination number of six from the O$_4$ compartment of the Schiff base, and two other donors are provided by coordinating solvent molecules and/or anions. The present paper is devoted to the synthesis and structural analysis of an Ni^{2+}-containing complex [NaNi(*L*)(CH$_3$OH)(NO$_3$)], (I), in which the Na^+ ion has a seven-coordination geometry and where H$_2$*L* is the compartmental Schiff base ligand 6,6′-dimethoxy-2,2′-(ethane-1,2-diyldiiminodimethylene)diphenol.

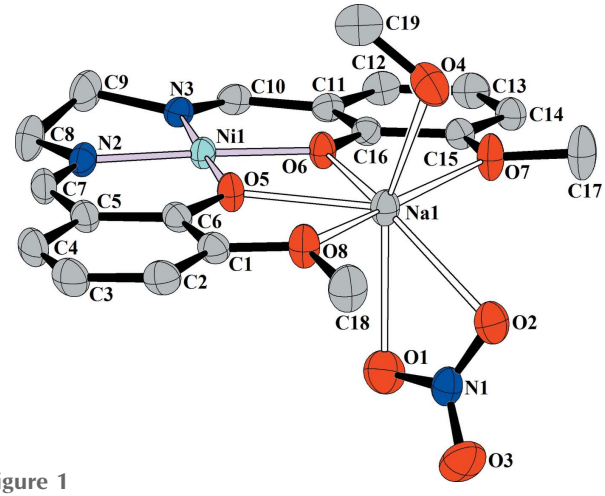


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*O*···O1^{i}	0.82	2.24	2.991 (2)	154
O4—H4*O*···O3^{i}	0.82	2.49	3.181 (2)	143
C8—H8*B*···O2^{ii}	0.97	2.65	3.152 (2)	112

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

2. Structural commentary

The molecular structure of compound (I) with the atom numbering is shown in Fig. 1. Two phenolate O atoms provided by the Schiff base ligand create a double bridge between the Ni^{2+} and Na^+ ions. The coordination environment of the Ni^{2+} ion is square-planar, formed by two imine N atoms and two phenolate O atoms. The Na^+ ion has an unusual seven-coordinated geometry in which the ion sits in the plane of the Schiff base O atoms. Further significant interactions with two nitrate O atoms and one O atom from the coordinating methanol molecule, which are located above and below the plane formed by *L*, complete the coordination sphere. Values for the geometric parameters in (I) are in good agreement with those observed for complexes based on similar Schiff base ligands (Allen *et al.*, 1987; Cunningham *et al.*, 2000; Wang & Shen, 2009; Xiao, 2009). The two phenoxo and two methoxy O atoms of the O(phenoxo)$_2$O(ethoxy)$_2$ moiety adopt a planar geometry as evidenced by the small mean deviation of the O atoms (<0.02 Å), from the O5/O6/O7/O8 least-squares plane. The deviations of the Na^+ and Ni^{2+} ions from the O5/O6/O7/O8 plane [0.166 (1) and 0.008 (2) Å, respectively] indicate that Na and Ni are well incorporated in the O(phenoxo)$_2$O(ethoxy)$_2$ moiety.

3. Supramolecular features

In the crystal structure, the molecules of the title compound form chains along the *b*-axis *via* weak C—H···O hydrogen-bond interactions (Fig. 2, Table 1). The C atom of the ethylene moiety acts as a donor and one O atom of the nitrate anion of the neighboring molecule acts as an acceptor. These chains are further assembled into sheets by a bifurcated O—H···O hydrogen bond (Steiner, 2002), which involves the coordin-

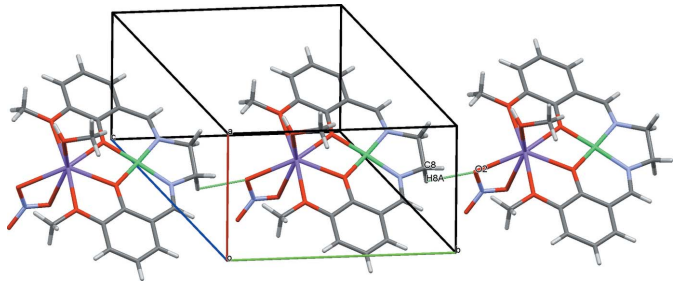


Figure 2
The molecular packing for (I), viewed along the *b* axis. C—H···O interactions are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[NaNi(C_{18}H_{18}N_2O_4)(NO_3)\cdot(CH_4O)]$
M_r	502.09
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, b, c (Å)	7.207 (1), 11.047 (1), 13.619 (1)
α, β, γ (°)	95.30 (1), 99.81 (1), 99.05 (1)
V (Å^3)	1047.2 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.00
Crystal size (mm)	0.4 × 0.2 × 0.2
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)
T_{min}, T_{max}	0.690, 0.825
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12718, 6501, 4324
R_{int}	0.020
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.744
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.081, 0.90
No. of reflections	6501
No. of parameters	292
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.32

Computer programs: *COLLECT* (Nonius, 1999), *DENZO/SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS97* and *SHELXL2014* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

ating methanol molecule and nitrate units (Fig. 3, Table 1) and through π–π stacking interactions, which exist between phenyl rings of neighbouring molecules, with a separation of 3.5845 (11) Å between the centroids formed by the C atoms of the rings [symmetry code: (iii) $-x+1, -y, -z$]. For the O—H···O hydrogen bond, the O atom of the methanol molecule acts as a donor and the O atoms of the nitrate anion of the neighbouring molecule act as the acceptors.

4. Synthesis and crystallization

A mixture of 6,6′-dimethoxy-2,2′-(ethane-1,2-diyldiimino-dimethylene)diphenol (1 mmol) and nickel nitrate (1 mmol) in methanol (15 ml) was stirred for 30 min at room temperature. Then, sodium nitrate (1mmol) was added, and the mixture was stirred for another 30 min and filtered. The resulting clear orange filtrate was left at ambient temperature for crystallization in air. The red–orange block-shaped crystals were collected by filtration after 6 d, washed with chilled isopropanol and dried on filter paper (yield 0.28 g, 56%).

5. Refinement

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 (aromatic) or 0.99 Å (methylene), with U_{iso}(H) = 1.2U_{eq}(C), C—H = 0.98 Å for methyl H atoms, with U_{iso}(H) = 1.5U_{eq}(C), and O—H = 0.82 Å for the hydroxy group of methanol, with U_{iso}(H) = 1.5U_{eq}(O). Crystal data, data collection and structure refinement details are summarized in Table 2.

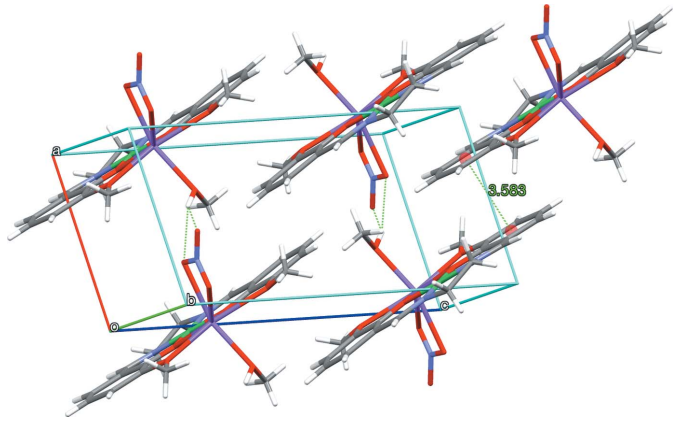


Figure 3
O—H···O and π–π contacts for (I), shown as dashed lines, with ring centroids shown as coloured spheres.

Acknowledgements

The authors are grateful to Dr Y. S. Moroz for his kind assistance in refining the structure.

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supporting information

Acta Cryst. (2014). E**70**, 305-308 [doi:10.1107/S160053681402159X]

Crystal structure of {μ-6,6′-dimethoxy-2,2′-[ethane-1,2-diylbis(nitrilomethanylylidene)]diphenolato}(methanol)(nitrato)nickel(II)sodium

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Computing details

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

{μ-6,6′-Dimethoxy-2,2′-[ethane-1,2-diylbis(nitrilomethanylylidene)]diphenolato}(methanol)(nitrato)nickel(II)sodium

Crystal data

$[NaNi(C_{18}H_{18}N_2O_4)(NO_3)(CH_4O)]$
M_r = 502.09
Triclinic, $P\overline{1}$
a = 7.207 (1) Å
b = 11.047 (1) Å
c = 13.619 (1) Å
α = 95.30 (1)°
β = 99.81 (1)°
γ = 99.05 (1)°
V = 1047.2 (2) Å^3
Z = 2
$F(000)$ = 520
D_x = 1.592 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 12718 reflections
θ = 2.9–31.9°
μ = 1.00 mm^{-1}
T = 293 K
Block, white
0.4 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: sealed X-ray tube
φ scans and ω scans with κ offset
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.690, T_{max} = 0.825
12718 measured reflections
6501 independent reflections
4324 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 31.9°, θ_{min} = 2.9°
h = −8→10
k = −15→15
l = −19→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.081
S = 0.90
6501 reflections
292 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	1.3085 (3)	0.47914 (14)	0.20473 (11)	0.0500 (4)
N2	1.0634 (2)	−0.10231 (12)	0.31510 (10)	0.0414 (3)
N3	0.87587 (19)	−0.13606 (11)	0.13663 (10)	0.0384 (3)
O1	1.3115 (2)	0.36716 (13)	0.19219 (14)	0.0823 (5)
O2	1.1514 (2)	0.51204 (13)	0.20629 (12)	0.0692 (4)
O3	1.4575 (2)	0.55470 (16)	0.21536 (12)	0.0840 (5)
O4	0.7094 (2)	0.36010 (15)	0.29641 (10)	0.0708 (4)
H4O	0.6210	0.3784	0.2582	0.106*
O5	1.04924 (18)	0.14171 (10)	0.31975 (8)	0.0439 (3)
O6	0.87634 (17)	0.10986 (10)	0.14652 (8)	0.0401 (3)
O7	0.7790 (2)	0.29628 (11)	0.06339 (9)	0.0531 (3)
O8	1.1398 (2)	0.36213 (11)	0.41444 (9)	0.0539 (3)
C1	1.2043 (2)	0.27108 (16)	0.46557 (12)	0.0417 (4)
C2	1.3145 (3)	0.28976 (19)	0.56084 (13)	0.0504 (4)
H2	1.3492	0.3688	0.5958	0.060*
C3	1.3734 (3)	0.1895 (2)	0.60439 (14)	0.0592 (5)
H3	1.4487	0.2022	0.6683	0.071*
C4	1.3227 (3)	0.0743 (2)	0.55493 (13)	0.0554 (5)
H4	1.3625	0.0085	0.5856	0.067*
C5	1.2091 (2)	0.05142 (16)	0.45629 (12)	0.0419 (4)
C6	1.1504 (2)	0.15157 (15)	0.41092 (11)	0.0380 (4)
C7	1.1604 (3)	−0.07053 (17)	0.40535 (13)	0.0457 (4)
H7	1.2019	−0.1330	0.4399	0.055*
C8	1.0406 (3)	−0.23159 (17)	0.27149 (14)	0.0585 (5)
H8A	1.0011	−0.2860	0.3189	0.070*
H8B	1.1616	−0.2488	0.2568	0.070*
C9	0.8924 (3)	−0.25411 (15)	0.17663 (15)	0.0578 (5)
H9A	0.9287	−0.3105	0.1274	0.069*
H9B	0.7699	−0.2914	0.1905	0.069*
C10	0.7997 (2)	−0.13762 (15)	0.04360 (13)	0.0411 (4)
H10	0.7711	−0.2136	0.0037	0.049*
C11	0.7552 (2)	−0.03232 (15)	−0.00347 (11)	0.0366 (3)
C12	0.6631 (3)	−0.04768 (17)	−0.10544 (12)	0.0455 (4)

H12	0.6384	−0.1255	−0.1424	0.055*
C13	0.6106 (3)	0.04949 (18)	−0.14969 (12)	0.0489 (4)
H13	0.5500	0.0374	−0.2167	0.059*
C14	0.6459 (2)	0.16813 (16)	−0.09638 (12)	0.0419 (4)
H14	0.6087	0.2342	−0.1276	0.050*
C15	0.7366 (2)	0.18574 (15)	0.00292 (11)	0.0372 (4)
C16	0.7923 (2)	0.08597 (14)	0.05155 (11)	0.0340 (3)
C17	0.7114 (4)	0.39946 (18)	0.02595 (15)	0.0719 (7)
H17A	0.7727	0.4218	−0.0287	0.108*
H17B	0.7399	0.4676	0.0784	0.108*
H17C	0.5755	0.3791	0.0027	0.108*
C18	1.2117 (4)	0.48674 (18)	0.45544 (16)	0.0714 (7)
H18A	1.1842	0.5002	0.5217	0.107*
H18B	1.1519	0.5405	0.4136	0.107*
H18C	1.3475	0.5039	0.4587	0.107*
C19	0.6357 (4)	0.2606 (2)	0.34481 (17)	0.0756 (7)
H19A	0.6104	0.1856	0.2994	0.113*
H19B	0.5192	0.2755	0.3650	0.113*
H19C	0.7275	0.2531	0.4029	0.113*
Ni1	0.96567 (3)	0.00143 (2)	0.22924 (2)	0.03524 (7)
Na1	0.97774 (10)	0.30835 (6)	0.23162 (5)	0.04288 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0603 (11)	0.0439 (9)	0.0431 (8)	0.0079 (8)	0.0013 (7)	0.0085 (7)
N2	0.0517 (9)	0.0324 (7)	0.0464 (8)	0.0153 (6)	0.0169 (7)	0.0103 (6)
N3	0.0379 (8)	0.0283 (7)	0.0493 (8)	0.0060 (5)	0.0091 (6)	0.0051 (6)
O1	0.0755 (12)	0.0449 (9)	0.1300 (14)	0.0208 (8)	0.0217 (10)	0.0081 (9)
O2	0.0728 (11)	0.0523 (9)	0.0915 (11)	0.0276 (8)	0.0203 (8)	0.0175 (7)
O3	0.0702 (12)	0.0779 (11)	0.0851 (11)	−0.0239 (9)	−0.0063 (8)	0.0156 (9)
O4	0.0659 (10)	0.0912 (11)	0.0610 (9)	0.0337 (9)	0.0065 (7)	0.0143 (8)
O5	0.0570 (8)	0.0342 (6)	0.0367 (6)	0.0132 (5)	−0.0063 (5)	0.0041 (5)
O6	0.0512 (7)	0.0295 (6)	0.0350 (6)	0.0094 (5)	−0.0055 (5)	0.0019 (4)
O7	0.0809 (10)	0.0335 (6)	0.0400 (6)	0.0180 (6)	−0.0087 (6)	0.0025 (5)
O8	0.0715 (9)	0.0379 (7)	0.0434 (7)	0.0095 (6)	−0.0106 (6)	−0.0001 (5)
C1	0.0384 (10)	0.0475 (10)	0.0373 (8)	0.0068 (7)	0.0027 (7)	0.0043 (7)
C2	0.0466 (11)	0.0605 (12)	0.0384 (9)	0.0031 (9)	0.0000 (8)	0.0025 (8)
C3	0.0523 (13)	0.0792 (15)	0.0418 (10)	0.0118 (10)	−0.0052 (8)	0.0112 (10)
C4	0.0549 (13)	0.0717 (14)	0.0440 (10)	0.0226 (10)	0.0022 (8)	0.0227 (9)
C5	0.0403 (10)	0.0495 (10)	0.0397 (9)	0.0145 (8)	0.0076 (7)	0.0131 (7)
C6	0.0339 (9)	0.0467 (10)	0.0344 (8)	0.0092 (7)	0.0049 (6)	0.0089 (7)
C7	0.0502 (11)	0.0501 (11)	0.0467 (10)	0.0230 (8)	0.0145 (8)	0.0231 (8)
C8	0.0886 (16)	0.0380 (10)	0.0563 (11)	0.0250 (10)	0.0168 (10)	0.0146 (8)
C9	0.0685 (14)	0.0264 (9)	0.0742 (13)	0.0049 (8)	0.0038 (10)	0.0070 (8)
C10	0.0410 (10)	0.0290 (8)	0.0507 (10)	0.0018 (7)	0.0107 (7)	−0.0052 (7)
C11	0.0338 (9)	0.0360 (8)	0.0386 (8)	0.0031 (6)	0.0076 (6)	0.0006 (6)
C12	0.0492 (11)	0.0443 (10)	0.0379 (9)	0.0016 (8)	0.0075 (7)	−0.0079 (7)

C13	0.0497 (11)	0.0615 (12)	0.0309 (8)	0.0046 (9)	0.0022 (7)	0.0003 (8)
C14	0.0421 (10)	0.0480 (10)	0.0357 (8)	0.0098 (7)	0.0044 (7)	0.0083 (7)
C15	0.0378 (9)	0.0377 (9)	0.0352 (8)	0.0079 (7)	0.0036 (6)	0.0043 (6)
C16	0.0326 (9)	0.0327 (8)	0.0346 (8)	0.0039 (6)	0.0041 (6)	0.0009 (6)
C17	0.111 (2)	0.0414 (11)	0.0596 (12)	0.0280 (11)	−0.0082 (12)	0.0091 (9)
C18	0.0865 (18)	0.0455 (12)	0.0671 (13)	0.0025 (11)	−0.0136 (12)	−0.0035 (10)
C19	0.0713 (17)	0.0801 (17)	0.0719 (15)	0.0061 (13)	0.0154 (12)	0.0002 (13)
Ni1	0.03972 (13)	0.02768 (11)	0.03891 (12)	0.00921 (8)	0.00475 (8)	0.00648 (8)
Na1	0.0529 (4)	0.0312 (3)	0.0421 (3)	0.0085 (3)	0.0013 (3)	0.0039 (3)

Geometric parameters (Å, º)

N1—O3	1.230 (2)	C4—C5	1.427 (2)
N1—O1	1.2372 (19)	C4—H4	0.9300
N1—O2	1.246 (2)	C5—C6	1.403 (2)
N1—Na1	2.8961 (19)	C5—C7	1.420 (2)
N2—C7	1.293 (2)	C7—H7	0.9300
N2—C8	1.468 (2)	C8—C9	1.503 (3)
N2—Ni1	1.8433 (13)	C8—H8A	0.9700
N3—C10	1.290 (2)	C8—H8B	0.9700
N3—C9	1.473 (2)	C9—H9A	0.9700
N3—Ni1	1.8371 (13)	C9—H9B	0.9700
O1—Na1	2.5512 (19)	C10—C11	1.432 (2)
O2—Na1	2.4806 (16)	C10—H10	0.9300
O4—C19	1.412 (3)	C11—C16	1.408 (2)
O4—Na1	2.3837 (17)	C11—C12	1.416 (2)
O4—H4O	0.8151	C12—C13	1.352 (3)
O5—C6	1.3139 (18)	C12—H12	0.9300
O5—Ni1	1.8396 (11)	C13—C14	1.402 (2)
O5—Na1	2.3644 (12)	C13—H13	0.9300
O6—C16	1.3148 (17)	C14—C15	1.380 (2)
O6—Ni1	1.8339 (10)	C14—H14	0.9300
O6—Na1	2.3288 (12)	C15—C16	1.413 (2)
O7—C15	1.3689 (19)	C17—H17A	0.9600
O7—C17	1.412 (2)	C17—H17B	0.9600
O7—Na1	2.4666 (13)	C17—H17C	0.9600
O8—C1	1.371 (2)	C18—H18A	0.9600
O8—C18	1.418 (2)	C18—H18B	0.9600
O8—Na1	2.5364 (13)	C18—H18C	0.9600
C1—C2	1.380 (2)	C19—Na1	3.125 (3)
C1—C6	1.416 (2)	C19—H19A	0.9600
C2—C3	1.394 (3)	C19—H19B	0.9600
C2—H2	0.9300	C19—H19C	0.9600
C3—C4	1.349 (3)	Ni1—Na1	3.3749 (7)
C3—H3	0.9300		
O3—N1—O1	120.31 (19)	O6—C16—C11	123.80 (14)
O3—N1—O2	121.67 (18)	O6—C16—C15	117.42 (13)

O1—N1—O2	118.02 (17)	C11—C16—C15	118.78 (13)
O3—N1—Na1	166.28 (12)	O7—C17—H17A	109.5
O1—N1—Na1	61.59 (11)	O7—C17—H17B	109.5
O2—N1—Na1	58.35 (10)	H17A—C17—H17B	109.5
C7—N2—C8	118.06 (14)	O7—C17—H17C	109.5
C7—N2—Ni1	126.55 (12)	H17A—C17—H17C	109.5
C8—N2—Ni1	115.16 (11)	H17B—C17—H17C	109.5
C10—N3—C9	118.99 (14)	O8—C18—H18A	109.5
C10—N3—Ni1	126.49 (11)	O8—C18—H18B	109.5
C9—N3—Ni1	114.51 (11)	H18A—C18—H18B	109.5
N1—O1—Na1	93.16 (12)	O8—C18—H18C	109.5
N1—O2—Na1	96.34 (11)	H18A—C18—H18C	109.5
C19—O4—Na1	108.10 (13)	H18B—C18—H18C	109.5
C19—O4—H4O	108.2	O4—C19—Na1	46.47 (10)
Na1—O4—H4O	119.0	O4—C19—H19A	109.5
C6—O5—Ni1	127.75 (10)	Na1—C19—H19A	79.9
C6—O5—Na1	125.60 (10)	O4—C19—H19B	109.5
Ni1—O5—Na1	106.12 (5)	Na1—C19—H19B	155.4
C16—O6—Ni1	127.73 (10)	H19A—C19—H19B	109.5
C16—O6—Na1	123.96 (9)	O4—C19—H19C	109.5
Ni1—O6—Na1	107.75 (5)	Na1—C19—H19C	87.4
C15—O7—C17	118.69 (13)	H19A—C19—H19C	109.5
C15—O7—Na1	118.60 (9)	H19B—C19—H19C	109.5
C17—O7—Na1	122.69 (10)	O6—Ni1—N3	95.02 (5)
C1—O8—C18	118.12 (13)	O6—Ni1—O5	83.21 (5)
C1—O8—Na1	118.85 (9)	N3—Ni1—O5	178.04 (5)
C18—O8—Na1	120.66 (11)	O6—Ni1—N2	177.63 (6)
O8—C1—C2	125.03 (16)	N3—Ni1—N2	87.08 (6)
O8—C1—C6	113.83 (13)	O5—Ni1—N2	94.71 (6)
C2—C1—C6	121.13 (16)	O6—Ni1—Na1	41.09 (3)
C1—C2—C3	119.59 (18)	N3—Ni1—Na1	135.99 (4)
C1—C2—H2	120.2	O5—Ni1—Na1	42.30 (3)
C3—C2—H2	120.2	N2—Ni1—Na1	136.74 (5)
C4—C3—C2	120.82 (16)	O6—Na1—O5	62.62 (4)
C4—C3—H3	119.6	O6—Na1—O4	105.64 (6)
C2—C3—H3	119.6	O5—Na1—O4	102.21 (5)
C3—C4—C5	121.15 (18)	O6—Na1—O7	64.88 (4)
C3—C4—H4	119.4	O5—Na1—O7	127.21 (5)
C5—C4—H4	119.4	O4—Na1—O7	86.56 (5)
C6—C5—C7	121.30 (15)	O6—Na1—O2	139.36 (6)
C6—C5—C4	118.75 (17)	O5—Na1—O2	136.66 (5)
C7—C5—C4	119.95 (16)	O4—Na1—O2	103.03 (6)
O5—C6—C5	123.93 (15)	O7—Na1—O2	88.99 (5)
O5—C6—C1	117.52 (14)	O6—Na1—O8	125.89 (5)
C5—C6—C1	118.55 (14)	O5—Na1—O8	63.39 (4)
N2—C7—C5	125.72 (15)	O4—Na1—O8	82.22 (5)
N2—C7—H7	117.1	O7—Na1—O8	166.29 (5)
C5—C7—H7	117.1	O2—Na1—O8	85.91 (5)

N2—C8—C9	109.13 (14)	O6—Na1—O1	102.51 (5)
N2—C8—H8A	109.9	O5—Na1—O1	95.38 (5)
C9—C8—H8A	109.9	O4—Na1—O1	151.34 (6)
N2—C8—H8B	109.9	O7—Na1—O1	100.68 (6)
C9—C8—H8B	109.9	O2—Na1—O1	50.02 (5)
H8A—C8—H8B	108.3	O8—Na1—O1	85.75 (6)
N3—C9—C8	109.49 (14)	O6—Na1—N1	124.94 (5)
N3—C9—H9A	109.8	O5—Na1—N1	114.82 (5)
C8—C9—H9A	109.8	O4—Na1—N1	126.53 (6)
N3—C9—H9B	109.8	O7—Na1—N1	98.99 (5)
C8—C9—H9B	109.8	O2—Na1—N1	25.31 (4)
H9A—C9—H9B	108.2	O8—Na1—N1	81.61 (5)
N3—C10—C11	125.54 (14)	O1—Na1—N1	25.25 (4)
N3—C10—H10	117.2	O6—Na1—C19	88.26 (6)
C11—C10—H10	117.2	O5—Na1—C19	77.74 (6)
C16—C11—C12	119.08 (15)	O4—Na1—C19	25.43 (6)
C16—C11—C10	120.98 (14)	O7—Na1—C19	95.80 (6)
C12—C11—C10	119.84 (14)	O2—Na1—C19	126.74 (6)
C13—C12—C11	120.74 (15)	O8—Na1—C19	77.25 (6)
C13—C12—H12	119.6	O1—Na1—C19	162.98 (6)
C11—C12—H12	119.6	N1—Na1—C19	146.80 (6)
C12—C13—C14	121.20 (15)	O6—Na1—Ni1	31.17 (3)
C12—C13—H13	119.4	O5—Na1—Ni1	31.58 (3)
C14—C13—H13	119.4	O4—Na1—Ni1	108.42 (5)
C15—C14—C13	119.21 (16)	O7—Na1—Ni1	96.03 (3)
C15—C14—H14	120.4	O2—Na1—Ni1	148.38 (4)
C13—C14—H14	120.4	O8—Na1—Ni1	94.97 (3)
O7—C15—C14	125.11 (15)	O1—Na1—Ni1	98.44 (4)
O7—C15—C16	113.90 (12)	N1—Na1—Ni1	123.52 (4)
C14—C15—C16	120.99 (15)	C19—Na1—Ni1	83.90 (5)
O3—N1—O1—Na1	164.40 (14)	C12—C13—C14—C15	0.3 (3)
O2—N1—O1—Na1	−15.51 (17)	C17—O7—C15—C14	6.0 (3)
O3—N1—O2—Na1	−163.87 (15)	Na1—O7—C15—C14	−172.37 (14)
O1—N1—O2—Na1	16.04 (18)	C17—O7—C15—C16	−173.20 (18)
C18—O8—C1—C2	9.2 (3)	Na1—O7—C15—C16	8.43 (19)
Na1—O8—C1—C2	171.84 (14)	C13—C14—C15—O7	−179.79 (16)
C18—O8—C1—C6	−169.82 (18)	C13—C14—C15—C16	−0.6 (3)
Na1—O8—C1—C6	−7.19 (19)	Ni1—O6—C16—C11	0.5 (2)
O8—C1—C2—C3	−179.16 (17)	Na1—O6—C16—C11	170.80 (12)
C6—C1—C2—C3	−0.2 (3)	Ni1—O6—C16—C15	−179.59 (11)
C1—C2—C3—C4	−0.6 (3)	Na1—O6—C16—C15	−9.3 (2)
C2—C3—C4—C5	0.6 (3)	C12—C11—C16—O6	179.76 (15)
C3—C4—C5—C6	0.1 (3)	C10—C11—C16—O6	3.2 (3)
C3—C4—C5—C7	178.98 (19)	C12—C11—C16—C15	−0.2 (2)
Ni1—O5—C6—C5	−1.7 (2)	C10—C11—C16—C15	−176.70 (15)
Na1—O5—C6—C5	−172.10 (12)	O7—C15—C16—O6	−0.1 (2)
Ni1—O5—C6—C1	177.62 (12)	C14—C15—C16—O6	−179.34 (15)

Na1—O5—C6—C1	7.2 (2)	O7—C15—C16—C11	179.82 (15)
C7—C5—C6—O5	−0.5 (3)	C14—C15—C16—C11	0.6 (2)
C4—C5—C6—O5	178.43 (16)	C16—O6—Ni1—N3	−4.68 (14)
C7—C5—C6—C1	−179.72 (16)	Na1—O6—Ni1—N3	−176.25 (6)
C4—C5—C6—C1	−0.8 (3)	C16—O6—Ni1—O5	176.15 (14)
O8—C1—C6—O5	0.7 (2)	Na1—O6—Ni1—O5	4.58 (6)
C2—C1—C6—O5	−178.41 (16)	C16—O6—Ni1—Na1	171.57 (17)
O8—C1—C6—C5	179.98 (15)	C10—N3—Ni1—O6	7.18 (15)
C2—C1—C6—C5	0.9 (3)	C9—N3—Ni1—O6	−171.60 (13)
C8—N2—C7—C5	174.90 (17)	C10—N3—Ni1—N2	−171.71 (15)
Ni1—N2—C7—C5	0.6 (3)	C9—N3—Ni1—N2	9.50 (13)
C6—C5—C7—N2	1.0 (3)	C10—N3—Ni1—Na1	3.64 (18)
C4—C5—C7—N2	−177.89 (17)	C9—N3—Ni1—Na1	−175.15 (10)
C7—N2—C8—C9	168.53 (17)	C6—O5—Ni1—O6	−176.40 (15)
Ni1—N2—C8—C9	−16.6 (2)	Na1—O5—Ni1—O6	−4.48 (6)
C10—N3—C9—C8	160.57 (16)	C6—O5—Ni1—N2	2.46 (15)
Ni1—N3—C9—C8	−20.5 (2)	Na1—O5—Ni1—N2	174.39 (6)
N2—C8—C9—N3	22.7 (2)	C6—O5—Ni1—Na1	−171.92 (17)
C9—N3—C10—C11	173.00 (16)	C7—N2—Ni1—N3	178.85 (16)
Ni1—N3—C10—C11	−5.7 (3)	C8—N2—Ni1—N3	4.44 (14)
N3—C10—C11—C16	−0.5 (3)	C7—N2—Ni1—O5	−1.95 (16)
N3—C10—C11—C12	−177.00 (17)	C8—N2—Ni1—O5	−176.35 (13)
C16—C11—C12—C13	−0.2 (3)	C7—N2—Ni1—Na1	3.57 (19)
C10—C11—C12—C13	176.39 (16)	C8—N2—Ni1—Na1	−170.84 (11)
C11—C12—C13—C14	0.1 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*O*···O1^{i}	0.82	2.24	2.991 (2)	154
O4—H4*O*···O3^{i}	0.82	2.49	3.181 (2)	143
C8—H8*B*···O2^{ii}	0.97	2.65	3.152 (2)	112

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