

Tetra- μ_3 -methanolato-tetrakis[(2-formyl-6-methoxyphenolato)methanolnickel(II)]

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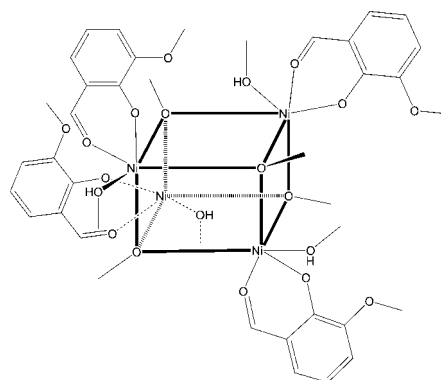
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Key indicators: single-crystal X-ray study; $T = 110$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.032; wR factor = 0.081; data-to-parameter ratio = 19.9.

The molecule of the title compound, $[\text{Ni}_4(\text{CH}_3\text{O})_4(\text{C}_8\text{H}_7\text{O}_3)_4(\text{CH}_4\text{O})_4]$, has S_4 symmetry. Each of the four Ni^{II} atoms occupies every other corner of a cube, with the alternate corners occupied by μ_3 -methanolate bridging groups linking to three Ni^{II} atoms. Each Ni^{II} atom is in an O_6 octahedral coordination environment formed by three O atoms from three μ_3 -methanolate groups, one from methanol, and two others from a bidentate 2-formyl-6-methoxyphenolate ligand. The Ni—O bond distances range from 2.0020 (14) to 2.0938 (14) Å, the *cis* bond angles range from 81.74 (6) to 97.63°, and the *trans* bond angles range from 168.76 (5) to 175.22 (6)°. There are bifurcated hydrogen-bonding interactions between the coordinated methanol OH groups and both the phenolic and methoxy O atoms of an adjoining 2-formyl-6-methoxyphenolate moiety. In addition, there are weak intermolecular C—H \cdots O interactions involving the methoxy O atoms.

Related literature

For literature related to Ni_4 cubane-type clusters, see; Andrew & Blake (1969); Barnes & Hatfield (1971); Bertrand *et al.* (1971, 1978); Brezina *et al.* (1998); Cromie *et al.* (2001); El Fallah *et al.* (1996); Gladfelter *et al.* (1981); Luo *et al.* (2007); Moragues-Canovas *et al.* (2004); Mukherjee *et al.* (2003); Ran *et al.* (2008); Yang *et al.* (2006).



Experimental

Crystal data

$[\text{Ni}_4(\text{CH}_3\text{O})_4(\text{C}_8\text{H}_7\text{O}_3)_4(\text{CH}_4\text{O})_4]$
 $M_r = 1091.69$
 Tetragonal, $I4_1/a$
 $a = 22.2670$ (9) Å
 $c = 9.70106$ (10) Å
 $V = 4810.0$ (3) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.62$ mm⁻¹
 $T = 110$ K
 $0.47 \times 0.28 \times 0.24$ mm

Data collection

Oxford Xcalibur diffractometer with a Ruby (Gemini Mo) detector
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2007)
 $T_{\text{min}} = 0.463$, $T_{\text{max}} = 1.000$

12226 measured reflections
 2962 independent reflections
 2131 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.081$
 $S = 0.99$
 2962 reflections

149 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.32$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2S}-\text{H2S}\cdots\text{O1}^i$	0.84	2.05	2.8062 (19)	150
$\text{O2S}-\text{H2S}\cdots\text{O3}^i$	0.84	2.50	3.181 (2)	139
$\text{C5}-\text{H5A}\cdots\text{O3}^{ii}$	0.95	2.45	3.360 (3)	159
$\text{C1S}-\text{H1SC}\cdots\text{O2S}^{iii}$	0.98	2.47	3.106 (3)	122

Symmetry codes: (i) $-y + \frac{3}{4}, x - \frac{1}{4}, -z + \frac{3}{4}$; (ii) $-y + \frac{1}{4}, x - \frac{1}{4}, z - \frac{1}{4}$; (iii) $y + \frac{1}{4}, -x + \frac{3}{4}, -z + \frac{3}{4}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5390).

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supplementary materials

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Tetra- μ_3 -methanolato-tetrakis[(2-formyl-6-methoxyphenolato)methanolnickel(II)]

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Comment

Polynuclear nickel(II) complexes have become a focused research area due to their single-molecule magnet properties, biomimetic activity and their flexibility to engender cluster construction. (Yang *et al.*, 2006). The structural and magnetic properties of symmetric Ni₄O₄ cores have been correlated to the Ni—O—Ni angle. It has been shown that the Ni₄O₄ core exhibits ferromagnetic interactions when the Ni—O—Ni angle is less than 98° and antiferromagnetic interactions when the angle is greater than 109° (Andrew & Blake, 1969; Barnes & Hatfield, 1971; Bertrand *et al.*, 1971, 1978; Gladfelder *et al.*, 1981; Mukherjee *et al.*, 2003). Moragues-Canovas *et al.* (2004) have synthesized and studied the low-temperature magnetism of the Ni₄O₄ cubane core complex with four pendant acetonitrile ions and four nitrate ions. Brezina *et al.* (1998), El Fallah *et al.* (1996), Luo *et al.* (2007), Cromie *et al.* (2001), and Ran *et al.* (2008) have synthesized, crystallized and studied their magnetism at low and/or various temperatures and confirmed the ferromagnetism/antiferromagnetism of such cubane Ni₄O₄ core complexes.

In Fig.(1), we report a structure of {Ni-(μ_3 -OCH₃)[*o*-OC₆H₃(CH₃O)CHO](CH₃OH)}₄ which has a Ni₄O₄ cubane-type core centre formed from four μ_3 -methanolate O atoms and four nickels. Each Ni^{II} is in an octahedral O₆ coordination environment completed with three μ_3 -methanolate O atoms, a bidentate 2-formyl-6-methoxyphenolate ligand, and a coordinated methanol molecule. The Ni—O(cubane) bond distances range from 2.0020 (14) to 2.0938 (14) Å, the *cis* bond angles range from 81.74 (6) to 97.63°, and the *trans* bond angles range from 168.76 (5) to 175.22 (6)°. The three Ni—O μ_3 -methanolate bond distances are 2.0350 (13), 2.0568 (13), and 2.0636 (13) Å. All Ni—O distances are within the normal ranges observed in other Ni complexes containing similar ligands. The *o*-vanillin, the methanol, and methanoate cause less distortion about the Ni's due to rigidity and stability established by the cubane Ni₄O₄. As a result, this coordination environment of the Ni is closer to perfect octahedral with the following bond angles: O(1S)#1-Ni—O(1S)#2 81.74 (6)°, O(1S)#2-Ni—O(1S) 82.32 (5)°, O(1S)#1-Ni—O(1S) 82.85 (5)°, Ni#1-O(1S)—Ni 96.50 (5)°, Ni#2-O(1S)—Ni 97.19 (5)°, Ni#2-O(1S)—Ni#1 97.91 (6)°. All the bond angles on the cubane (Ni—O—Ni and O—Ni—O) are close to but less than 98°. There are bifurcated hydrogen-bonding interactions between the coordinated methanol OH and both the phenolic and methoxy O of an adjoining 2-formyl-6-methoxyphenolate moiety. In addition there are weak intermolecular C—H···O interactions involving the methoxy O.

Experimental

The complex was synthesized by reacting 0.53 g (1.45 mmol) of nickel perchlorate [Ni^{II}(ClO₄)₂·6H₂O] in methanol [MeOH] (20 ml) with a mixture of 0.23 g *o*-vanillin (1.46 mmol) and 0.26 g of 2-benzylaminopyridine (2-BAP) (1.46 mmol). The secondary amine and the aldehyde were initially mixed in 30 ml of methanol and refluxed with stirring overnight between 50 C and 60 C. The nickel salt solution and the ligands were then mixed and stirred overnight at room temperature (23°-25°), followed by reduced pressure (vacuum) evaporated to obtain a green oily (semi-solid). A portion of the washed product (about 0.025 g) was dissolved in 50/50 MeOH/Propanol. This solution obtained was filtered and layered with diethyl ether.

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Greenish X-ray quality crystals were obtained after five days of slow diffusion of the diethyl ether into the MeOH/Propanol solvent.

Refinement

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with a C—H distance of $0.95 U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and 0.98 \AA for CH_3 [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$]. The H atoms attached to O were idealized with an O—H distance of 0.84 \AA .

Figures

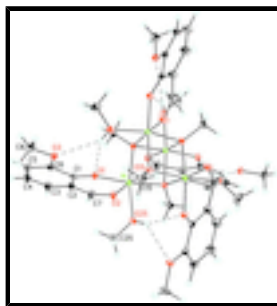


Fig. 1. Diagram showing the pseudo-cubic $\{\text{Ni}-(\mu_3\text{-OCH}_3)[o\text{-OC}_6\text{H}_3(\text{CH}_3\text{O})\text{CHO}](\text{CH}_3\text{OH})\}_4$ cluster with unique part labelled. The bifurcated intramolecular hydrogen bonds are shown by dashed lines.



Fig. 2. The molecular packing for $\{\text{Ni}-(\mu_3\text{-OCH}_3)[o\text{-OC}_6\text{H}_3(\text{CH}_3\text{O})\text{CHO}](\text{CH}_3\text{OH})\}_4$ viewed down the c axis. Intra- and intermolecular interactions are shown by dashed lines.

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Crystal data

$[\text{Ni}_4(\text{CH}_3\text{O})_4(\text{C}_8\text{H}_7\text{O}_3)_4(\text{CH}_4\text{O})_4]$

$M_r = 1091.69$

Tetragonal, $I4_1/a$

Hall symbol: $-I 4ad$

$a = 22.2670 (9) \text{ \AA}$

$c = 9.70106 (10) \text{ \AA}$

$V = 4810.0 (3) \text{ \AA}^3$

$Z = 4$

$F(000) = 2272$

$D_x = 1.508 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 4573 reflections

$\theta = 5.0\text{--}29.3^\circ$

$\mu = 1.62 \text{ mm}^{-1}$

$T = 110 \text{ K}$

Prism, green

$0.47 \times 0.28 \times 0.24 \text{ mm}$

Data collection

Oxford Xcalibur
diffractometer with a Ruby (Gemini Mo) detector

2962 independent reflections

Radiation source: Enhance (Mo) X-ray Source

2131 reflections with $I > 2\sigma(I)$

graphite $R_{\text{int}} = 0.035$
 Detector resolution: 10.5081 pixels mm^{-1} $\theta_{\text{max}} = 29.4^\circ$, $\theta_{\text{min}} = 4.9^\circ$
 ω scans $h = -21 \rightarrow 30$
 Absorption correction: multi-scan $k = -30 \rightarrow 22$
 (*CrysAlis PRO*; Oxford Diffraction, 2007)
 $T_{\text{min}} = 0.463$, $T_{\text{max}} = 1.000$ $l = -13 \rightarrow 12$
 12226 measured reflections

Refinement

Refinement on F^2 Primary atom site location: structure-invariant direct methods
 Least-squares matrix: full Secondary atom site location: difference Fourier map
 $R[F^2 > 2\sigma(F^2)] = 0.032$ Hydrogen site location: inferred from neighbouring sites
 $wR(F^2) = 0.081$ H-atom parameters constrained
 $S = 0.99$ $w = 1/[\sigma^2(F_o^2) + (0.0454P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 2962 reflections $(\Delta/\sigma)_{\text{max}} = 0.001$
 149 parameters $\Delta\rho_{\text{max}} = 0.32 \text{ e } \text{\AA}^{-3}$
 0 restraints $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni	0.478914 (11)	0.183990 (11)	0.26340 (2)	0.02258 (10)
O1	0.39721 (6)	0.14647 (6)	0.26250 (13)	0.0269 (3)
O2	0.48379 (6)	0.17818 (7)	0.05257 (15)	0.0344 (4)
O3	0.28657 (6)	0.11763 (6)	0.31043 (15)	0.0336 (3)
O1S	0.48109 (6)	0.19293 (6)	0.47507 (13)	0.0232 (3)
O2S	0.52889 (7)	0.10453 (6)	0.27601 (15)	0.0351 (4)
H2S	0.5524	0.1035	0.3436	0.042*
C1	0.36431 (9)	0.13635 (8)	0.1537 (2)	0.0264 (4)
C2	0.38418 (10)	0.14135 (10)	0.0123 (2)	0.0326 (5)
C3	0.34410 (11)	0.12800 (11)	-0.0989 (2)	0.0439 (6)
H3A	0.3580	0.1314	-0.1911	0.053*

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C4	0.28728 (11)	0.11077 (11)	-0.0753 (2)	0.0471 (6)
H4A	0.2614	0.1016	-0.1502	0.057*
C5	0.26610 (10)	0.10643 (10)	0.0628 (3)	0.0390 (6)
H5A	0.2258	0.0944	0.0795	0.047*
C6	0.30315 (9)	0.11932 (9)	0.1725 (2)	0.0294 (5)
C7	0.44257 (10)	0.16174 (11)	-0.0244 (2)	0.0386 (6)
H7A	0.4510	0.1629	-0.1203	0.046*
C8	0.22877 (10)	0.09432 (13)	0.3404 (3)	0.0530 (7)
H8A	0.1984	0.1170	0.2889	0.080*
H8B	0.2209	0.0980	0.4394	0.080*
H8C	0.2271	0.0519	0.3136	0.080*
C1S	0.46424 (10)	0.14354 (9)	0.5602 (2)	0.0316 (5)
H1SA	0.4799	0.1497	0.6535	0.047*
H1SB	0.4809	0.1064	0.5220	0.047*
H1SC	0.4204	0.1406	0.5635	0.047*
C2S	0.51222 (14)	0.04601 (11)	0.2403 (3)	0.0646 (9)
H2SA	0.5060	0.0223	0.3242	0.097*
H2SB	0.5441	0.0276	0.1848	0.097*
H2SC	0.4749	0.0471	0.1869	0.097*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni	0.02257 (15)	0.02712 (16)	0.01804 (14)	-0.00098 (11)	0.00057 (10)	-0.00374 (10)
O1	0.0258 (7)	0.0310 (8)	0.0241 (7)	-0.0014 (6)	-0.0011 (6)	-0.0027 (6)
O2	0.0285 (8)	0.0531 (10)	0.0218 (7)	-0.0090 (7)	0.0017 (6)	-0.0082 (7)
O3	0.0251 (7)	0.0362 (8)	0.0394 (8)	-0.0014 (6)	0.0064 (7)	0.0024 (7)
O1S	0.0285 (7)	0.0219 (7)	0.0193 (7)	-0.0004 (6)	0.0021 (5)	0.0019 (5)
O2S	0.0365 (8)	0.0299 (8)	0.0388 (9)	0.0023 (7)	-0.0096 (7)	-0.0111 (7)
C1	0.0269 (10)	0.0214 (10)	0.0309 (11)	-0.0003 (8)	-0.0010 (9)	-0.0038 (8)
C2	0.0297 (11)	0.0402 (12)	0.0281 (11)	-0.0042 (10)	0.0004 (9)	-0.0072 (9)
C3	0.0423 (14)	0.0598 (16)	0.0296 (12)	-0.0085 (12)	-0.0021 (10)	-0.0117 (11)
C4	0.0391 (14)	0.0616 (17)	0.0407 (14)	-0.0098 (12)	-0.0123 (11)	-0.0104 (12)
C5	0.0239 (11)	0.0391 (13)	0.0541 (15)	-0.0040 (9)	-0.0052 (10)	-0.0025 (12)
C6	0.0278 (11)	0.0254 (10)	0.0349 (12)	0.0017 (9)	0.0020 (9)	-0.0007 (9)
C7	0.0370 (13)	0.0560 (15)	0.0228 (11)	-0.0058 (12)	0.0034 (9)	-0.0085 (10)
C8	0.0245 (12)	0.0724 (18)	0.0621 (17)	-0.0014 (12)	0.0080 (12)	0.0126 (14)
C1S	0.0412 (12)	0.0259 (11)	0.0276 (11)	-0.0004 (10)	0.0049 (10)	0.0053 (9)
C2S	0.0657 (19)	0.0344 (15)	0.094 (2)	-0.0018 (13)	-0.0241 (16)	-0.0189 (15)

Geometric parameters (\AA , $^\circ$)

Ni—O1	2.0020 (14)	C2—C3	1.431 (3)
Ni—O1S ⁱ	2.0350 (13)	C3—C4	1.342 (3)
Ni—O2	2.0522 (15)	C3—H3A	0.9500
Ni—O1S ⁱⁱ	2.0568 (13)	C4—C5	1.424 (3)
Ni—O1S	2.0636 (13)	C4—H4A	0.9500
Ni—O2S	2.0938 (14)	C5—C6	1.377 (3)

O1—C1	1.305 (2)	C5—H5A	0.9500
O2—C7	1.239 (3)	C7—H7A	0.9500
O3—C6	1.389 (2)	C8—H8A	0.9800
O3—C8	1.418 (3)	C8—H8B	0.9800
O1S—C1S	1.425 (2)	C8—H8C	0.9800
O1S—Ni ⁱⁱ	2.0350 (13)	C1S—H1SA	0.9800
O1S—Ni ⁱ	2.0568 (13)	C1S—H1SB	0.9800
O2S—C2S	1.398 (3)	C1S—H1SC	0.9800
O2S—H2S	0.8400	C2S—H2SA	0.9800
C1—C6	1.425 (3)	C2S—H2SB	0.9800
C1—C2	1.445 (3)	C2S—H2SC	0.9800
C2—C7	1.423 (3)		
O1—Ni—O1S ⁱ	172.97 (5)	C4—C3—C2	121.3 (2)
O1—Ni—O2	91.00 (5)	C4—C3—H3A	119.4
O1S ⁱ —Ni—O2	92.41 (5)	C2—C3—H3A	119.4
O1—Ni—O1S ⁱⁱ	91.71 (5)	C3—C4—C5	119.5 (2)
O1S ⁱ —Ni—O1S ⁱⁱ	81.74 (6)	C3—C4—H4A	120.3
O2—Ni—O1S ⁱⁱ	97.63 (6)	C5—C4—H4A	120.3
O1—Ni—O1S	93.78 (5)	C6—C5—C4	120.98 (19)
O1S ⁱ —Ni—O1S	82.85 (5)	C6—C5—H5A	119.5
O2—Ni—O1S	175.22 (6)	C4—C5—H5A	119.5
O1S ⁱⁱ —Ni—O1S	82.32 (5)	C5—C6—O3	125.44 (18)
O1—Ni—O2S	97.51 (6)	C5—C6—C1	121.94 (19)
O1S ⁱ —Ni—O2S	88.72 (5)	O3—C6—C1	112.62 (17)
O2—Ni—O2S	88.67 (6)	O2—C7—C2	128.4 (2)
O1S ⁱⁱ —Ni—O2S	168.76 (5)	O2—C7—H7A	115.8
O1S—Ni—O2S	90.63 (5)	C2—C7—H7A	115.8
C1—O1—Ni	125.87 (12)	O3—C8—H8A	109.5
C7—O2—Ni	125.47 (14)	O3—C8—H8B	109.5
C6—O3—C8	116.67 (18)	H8A—C8—H8B	109.5
C1S—O1S—Ni ⁱⁱ	119.50 (11)	O3—C8—H8C	109.5
C1S—O1S—Ni ⁱ	120.73 (12)	H8A—C8—H8C	109.5
Ni ⁱⁱ —O1S—Ni ⁱ	97.91 (6)	H8B—C8—H8C	109.5
C1S—O1S—Ni	119.72 (12)	O1S—C1S—H1SA	109.5
Ni ⁱⁱ —O1S—Ni	97.19 (5)	O1S—C1S—H1SB	109.5
Ni ⁱ —O1S—Ni	96.50 (5)	H1SA—C1S—H1SB	109.5
C2S—O2S—Ni	129.19 (15)	O1S—C1S—H1SC	109.5
C2S—O2S—H2S	109.5	H1SA—C1S—H1SC	109.5
Ni—O2S—H2S	113.6	H1SB—C1S—H1SC	109.5
O1—C1—C6	118.61 (18)	O2S—C2S—H2SA	109.5
O1—C1—C2	125.64 (18)	O2S—C2S—H2SB	109.5
C6—C1—C2	115.75 (18)	H2SA—C2S—H2SB	109.5
C7—C2—C3	116.59 (19)	O2S—C2S—H2SC	109.5
C7—C2—C1	122.81 (19)	H2SA—C2S—H2SC	109.5
C3—C2—C1	120.55 (19)	H2SB—C2S—H2SC	109.5

supplementary materials

O1S ⁱ —Ni—O1—C1	109.0 (4)	O1S ⁱ —Ni—O2S—C2S	-161.5 (2)
O2—Ni—O1—C1	-10.03 (15)	O2—Ni—O2S—C2S	-69.1 (2)
O1S ⁱⁱ —Ni—O1—C1	87.64 (15)	O1S ⁱⁱ —Ni—O2S—C2S	166.6 (3)
O1S—Ni—O1—C1	170.05 (15)	O1S—Ni—O2S—C2S	115.7 (2)
O2S—Ni—O1—C1	-98.82 (15)	Ni—O1—C1—C6	-168.91 (13)
O1—Ni—O2—C7	6.22 (19)	Ni—O1—C1—C2	10.5 (3)
O1S ⁱ —Ni—O2—C7	-167.63 (19)	O1—C1—C2—C7	-3.7 (3)
O1S ⁱⁱ —Ni—O2—C7	-85.64 (19)	C6—C1—C2—C7	175.7 (2)
O1S—Ni—O2—C7	-174.7 (6)	O1—C1—C2—C3	178.9 (2)
O2S—Ni—O2—C7	103.71 (19)	C6—C1—C2—C3	-1.7 (3)
O1—Ni—O1S—C1S	46.98 (14)	C7—C2—C3—C4	-177.3 (2)
O1S ⁱ —Ni—O1S—C1S	-139.22 (15)	C1—C2—C3—C4	0.2 (4)
O2—Ni—O1S—C1S	-132.1 (7)	C2—C3—C4—C5	0.8 (4)
O1S ⁱⁱ —Ni—O1S—C1S	138.20 (15)	C3—C4—C5—C6	-0.3 (3)
O2S—Ni—O1S—C1S	-50.59 (14)	C4—C5—C6—O3	178.63 (19)
O1—Ni—O1S—Ni ⁱⁱ	-83.07 (6)	C4—C5—C6—C1	-1.3 (3)
O1S ⁱ —Ni—O1S—Ni ⁱⁱ	90.730 (9)	C8—O3—C6—C5	7.4 (3)
O2—Ni—O1S—Ni ⁱⁱ	97.9 (7)	C8—O3—C6—C1	-172.74 (18)
O1S ⁱⁱ —Ni—O1S—Ni ⁱⁱ	8.15 (6)	O1—C1—C6—C5	-178.32 (19)
O2S—Ni—O1S—Ni ⁱⁱ	179.37 (6)	C2—C1—C6—C5	2.2 (3)
O1—Ni—O1S—Ni ⁱ	178.07 (5)	O1—C1—C6—O3	1.8 (2)
O1S ⁱ —Ni—O1S—Ni ⁱ	-8.13 (6)	C2—C1—C6—O3	-177.69 (17)
O2—Ni—O1S—Ni ⁱ	-1.0 (7)	Ni—O2—C7—C2	-2.4 (4)
O1S ⁱⁱ —Ni—O1S—Ni ⁱ	-90.708 (8)	C3—C2—C7—O2	176.9 (2)
O2S—Ni—O1S—Ni ⁱ	80.51 (6)	C1—C2—C7—O2	-0.6 (4)
O1—Ni—O2S—C2S	21.8 (2)		

Symmetry codes: (i) $-y+3/4, x-1/4, -z+3/4$; (ii) $y+1/4, -x+3/4, -z+3/4$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2S—H2S \cdots O1 ⁱ	0.84	2.05	2.8062 (19)	150
O2S—H2S \cdots O3 ⁱ	0.84	2.50	3.181 (2)	139
C5—H5A \cdots O3 ⁱⁱⁱ	0.95	2.45	3.360 (3)	159
C1S—H1SC \cdots O2S ⁱⁱ	0.98	2.47	3.106 (3)	122

Symmetry codes: (i) $-y+3/4, x-1/4, -z+3/4$; (iii) $-y+1/4, x-1/4, z-1/4$; (ii) $y+1/4, -x+3/4, -z+3/4$.

Fig. 1

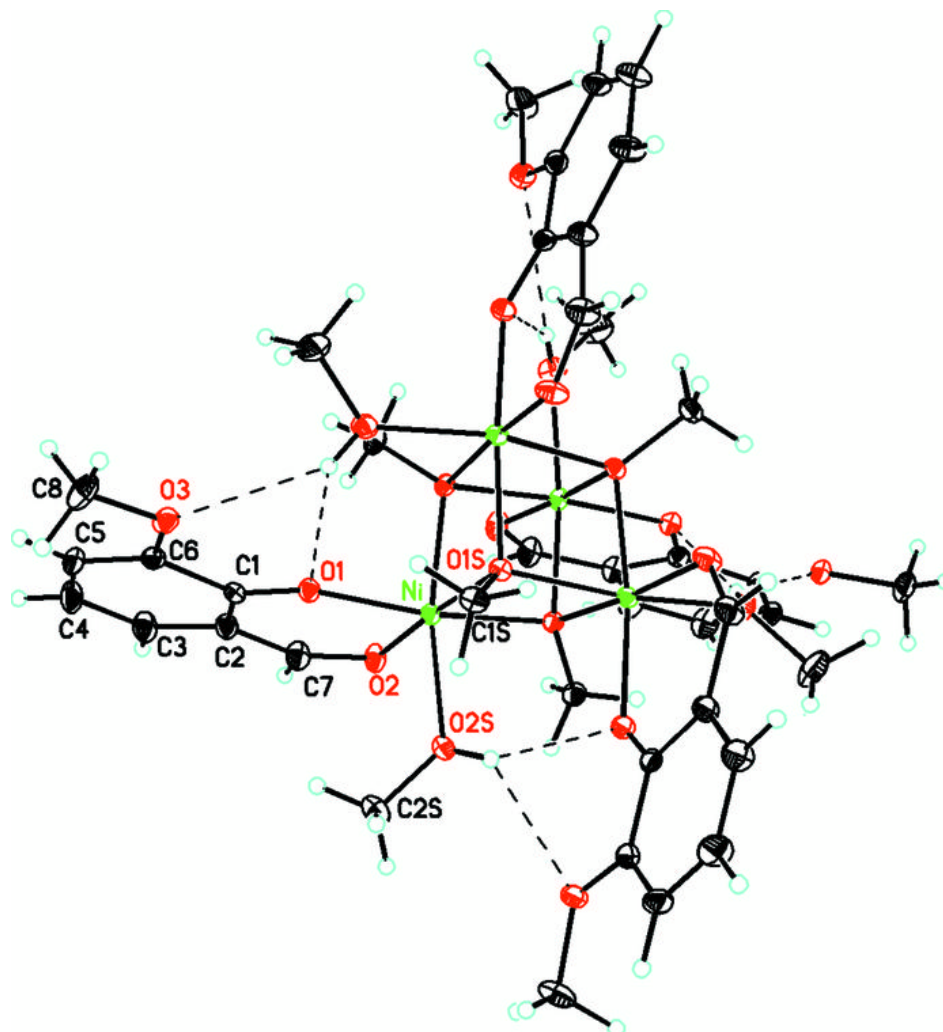


Fig. 2

