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Aqua(hexamethylenetetramine-κN)-bis(methanol)bis(thiocyanato-κN)-nickel(II)

Yan Bai,* Wei-Li Shang, Fu-Lian Zhang, Xiao-Jing Pan and Xiao-Fang Niu

Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, People's Republic of China
Correspondence e-mail: baiyan@henu.edu.cn

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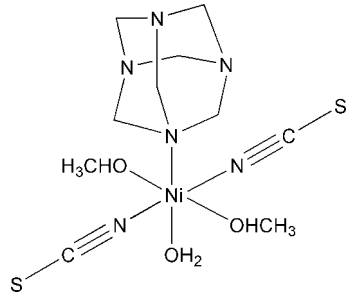
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(N–C) = 0.003 Å; R factor = 0.031; wR factor = 0.077; data-to-parameter ratio = 19.7.

The Ni atom in the title complex, $[Ni(SCN)_2(C_6H_{14}N_4)(CH_4O)_2(H_2O)]$, is six-coordinate in a slightly distorted octahedral environment. The hexamethylenetetramine ligand binds to the Ni atom through only one of its N atoms, *trans* to the coordinated water molecule. The thiocyanate and methanol ligands are also mutually *trans*. In the crystal structure, complex molecules are linked by four different kinds of hydrogen bonds (O—H···S, O—H···N, C—H···N and C—H···O) to form a three-dimensional network structure.

Related literature

For information on the self-assembly of transition-metal complexes, see: Guo *et al.* (2002); Kumar *et al.* (2007); Venkateswaran *et al.* (2007). For complexes of the hexamethylenetetramine (hmt) ligand, see: Liu *et al.* (2006); Zhang *et al.* (1999); Meng *et al.* (2001); Li *et al.* (2002).



Experimental

Crystal data

$[Ni(SCN)_2(C_6H_{14}N_4)(CH_4O)_2(H_2O)]$
M_r = 397.17
Orthorhombic, *Pbca*
a = 14.069 (3) Å
b = 15.312 (3) Å
c = 16.036 (3) Å
V = 3454.6 (12) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.38 mm^{-1}
T = 293 (2) K
0.25 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
20196 measured reflections
3954 independent reflections
3102 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.077
S = 1.01
3954 reflections
201 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WB···S2^{i}	0.85	2.61	3.431 (2)	162
O1—H1A···N6^{i}	0.85	1.93	2.762 (2)	165
O1W—H1WD···N5^{ii}	0.85	2.02	2.836 (2)	162
O2—H2A···N4^{iii}	0.85	2.09	2.839 (2)	148
C3—H3A···N1	0.97	2.50	3.084 (3)	119
C3—H3B···O2	0.97	2.53	3.130 (3)	120
C7—H7A···O1	0.97	2.59	2.962 (3)	103
C10—H10B···N2	0.96	2.52	3.156 (4)	123

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: SJ2363).

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supplementary materials

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Aqua(hexamethylenetetramine-*κN*)bis(methanol)bis(thiocyanato-*κN*)nickel(II)

Y. Bai, W.-L. Shang, F.-L. Zhang, X.-J. Pan and X.-F. Niu

Comment

During the past decade, the self-assembly of transition metal ions and organic molecules has become a powerful methodology for the construction of different supramolecular architectures with unusual and interesting properties either by strong metal-ligand bonding or by weaker bonding forces such as hydrogen bonding and π—π interactions (Guo, *et al.*, 2002; Kumar, Das *et al.*, 2007; Venkateswaran *et al.*, 2007). Among the ligands, hexamethylenetetramine (hmt) as a potential tetradentate ligand or hydrogen bond acceptor seems quite suitable in self-assembly systems. Several groups have reported that Co(II), Mn(II) or Ni(II) complexes with hmt and SCN^- as ligands form two- or three-dimensional networks (Liu *et al.*, 2006; Zhang *et al.*, 1999; Meng *et al.*, 2001; Li *et al.*, 2002). Herein, we present a new hmt complex, (I), of nickel(II) with SCN^-, Fig 1. The title complex, which contains one nickel center, one hmt, two NCS^-, two coordinated methanol molecules and one coordinated water molecule, forms a mononuclear complex (Fig.1). The Ni^{2+} atom has a distorted octahedral coordination geometry. The N atom of hmt and the O atom of the water molecule, the N atoms of the two isothiocyanates and the O atoms of both methanol molecules are each mutually *trans* to each other. Intramolecular C—H···N and C—H···O hydrogen bonds (Table 2) are important factors in the stabilization of the molecule.

In the crystal structure, molecules interact with each other, forming a three-dimensional supramolecular network through multiform intermolecular hydrogen bonds (Fig. 2 and Table 1). The O_1, O_2 and O_{1w} atoms form three O—H···N hydrogen bonds with the N_6, N_4 and N_5 atoms of the adjacent hmt ligand, respectively. In addition, an O_{1w}—H···S_2 hydrogen bond is also found in the solid state.

Experimental

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The hexamethylenetetramine (0.50 mmol, 0.07 g), KSCN (2 mmol, 0.19 g) and $NiCl_2{\cdot}6H_2O$ (0.50 mmol, 0.12 g) were mixed in methanol (25 ml). The green solution was left for several weeks at room temperature to afford green crystals (yield 68%).

Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.97 Å, $U_{iso} = 1.2U_{eq}$ (C) for CH_2, 0.96 Å, $U_{iso} = 1.5U_{eq}$ (C) for CH_3 atoms and 0.85 Å, $U_{iso} = 1.2U_{eq}$ (O) for the OH groups.

Figures

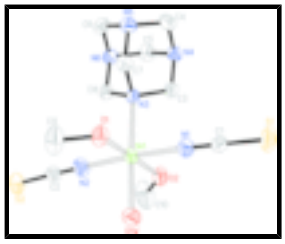

Fig. 1. The molecular structure of the title complex, with displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

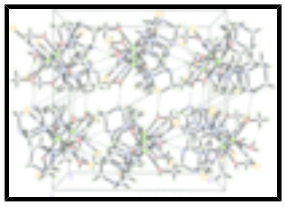

Fig. 2. Perspective view of the three-dimensional showing the intermolecular hydrogen bonds as dashed lines.

Aqua(hexamethylenetetramine-κ*N*)bis(methanol)bis(thiocyanato-κ*N*)nickel(II)

Crystal data

$[Ni(SCN)_2(C_6H_{14}N_4)(CH_4O)_2(H_2O)]$	F_{000} = 1664
M_r = 397.17	D_x = 1.527 Mg m^{-3}
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 5794 reflections
a = 14.069 (3) Å	θ = 2.3–27.0º
b = 15.312 (3) Å	μ = 1.38 mm^{-1}
c = 16.036 (3) Å	*T* = 293 (2) K
V = 3454.6 (12) Å^3	Block, green
Z = 8	0.25 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer	3102 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	R_{int} = 0.037
Monochromator: graphite	θ_{max} = 27.5º
T = 293(2) K	θ_{min} = 2.3º
φ and ω scans	*h* = −17→18
Absorption correction: none	*k* = −19→19
20196 measured reflections	*l* = −15→20
3954 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.077$

$S = 1.02$

3954 reflections

201 parameters

Primary atom site location: structure-invariant direct methods

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 1.4403P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.63$ e Å^{-3}

$\Delta\rho_{min} = -0.53$ e Å^{-3}

Extinction correction: none

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	1.051115 (17)	1.037270 (16)	0.284126 (16)	0.02737 (9)
N1	1.15174 (12)	0.97450 (11)	0.35135 (12)	0.0348 (4)
C1	1.21094 (14)	0.94091 (13)	0.38983 (13)	0.0298 (4)
S1	1.29502 (5)	0.89385 (4)	0.44312 (5)	0.0560 (2)
N2	0.95730 (13)	1.10636 (13)	0.21696 (12)	0.0379 (4)
C2	0.90475 (15)	1.14612 (13)	0.17719 (13)	0.0308 (4)
S2	0.83037 (4)	1.20509 (4)	0.12261 (4)	0.04665 (16)
N3	0.94070 (11)	0.94372 (10)	0.32743 (10)	0.0248 (3)
N4	0.88319 (12)	0.86786 (11)	0.45339 (11)	0.0319 (4)
N5	0.88039 (12)	0.79295 (11)	0.31899 (10)	0.0307 (4)
N6	0.77062 (11)	0.91318 (11)	0.34617 (11)	0.0294 (4)
C3	0.95225 (14)	0.93031 (14)	0.41893 (12)	0.0301 (4)
H3A	1.0160	0.9092	0.4299	0.036*
H3B	0.9450	0.9860	0.4471	0.036*
C4	0.89509 (16)	0.78346 (14)	0.40984 (13)	0.0353 (5)
H4A	0.9585	0.7611	0.4202	0.042*
H4B	0.8498	0.7416	0.4318	0.042*
C5	0.78700 (15)	0.90098 (15)	0.43675 (13)	0.0346 (5)
H5A	0.7784	0.9563	0.4652	0.042*
H5B	0.7406	0.8601	0.4586	0.042*
C6	0.78424 (15)	0.82792 (14)	0.30448 (14)	0.0338 (5)
H6A	0.7376	0.7867	0.3253	0.041*
H6B	0.7740	0.8347	0.2450	0.041*
C7	0.94994 (14)	0.85635 (13)	0.28606 (13)	0.0290 (4)
H7A	0.9404	0.8630	0.2265	0.035*
H7B	1.0137	0.8341	0.2948	0.035*
C8	0.84141 (13)	0.97490 (13)	0.31293 (13)	0.0284 (4)
H8A	0.8330	1.0313	0.3395	0.034*

H8B	0.8311	0.9824	0.2535	0.034*
O1	1.08313 (10)	0.95834 (10)	0.18127 (9)	0.0344 (3)
H1A	1.1430	0.9511	0.1796	0.041*
C9	1.05023 (17)	0.9745 (2)	0.09820 (15)	0.0551 (7)
H9A	1.0726	0.9291	0.0619	0.083*
H9B	1.0740	1.0298	0.0793	0.083*
H9C	0.9820	0.9754	0.0977	0.083*
O2	1.02424 (11)	1.12126 (9)	0.38967 (9)	0.0396 (4)
H2A	1.0708	1.1218	0.4234	0.048*
C10	0.9735 (3)	1.20139 (19)	0.39099 (19)	0.0753 (10)
H10A	0.9296	1.2013	0.4369	0.113*
H10B	0.9390	1.2081	0.3397	0.113*
H10C	1.0173	1.2489	0.3973	0.113*
O1W	1.15882 (11)	1.12462 (9)	0.24620 (10)	0.0408 (4)
H1WB	1.1952	1.1361	0.2871	0.049*
H1WD	1.1343	1.1721	0.2292	0.049*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02452 (14)	0.02876 (15)	0.02882 (15)	0.00163 (10)	−0.00440 (10)	0.00596 (10)
N1	0.0296 (10)	0.0369 (10)	0.0378 (10)	0.0010 (8)	−0.0052 (8)	0.0060 (8)
C1	0.0302 (11)	0.0277 (10)	0.0315 (11)	−0.0021 (8)	−0.0029 (9)	−0.0016 (8)
S1	0.0549 (4)	0.0463 (4)	0.0668 (5)	0.0131 (3)	−0.0356 (3)	−0.0032 (3)
N2	0.0335 (10)	0.0405 (10)	0.0398 (11)	0.0044 (8)	−0.0047 (8)	0.0108 (8)
C2	0.0303 (11)	0.0308 (11)	0.0313 (11)	0.0006 (9)	−0.0006 (9)	0.0019 (9)
S2	0.0430 (3)	0.0513 (4)	0.0457 (4)	0.0130 (3)	−0.0128 (3)	0.0088 (3)
N3	0.0241 (8)	0.0275 (8)	0.0228 (8)	0.0004 (6)	−0.0025 (6)	0.0015 (6)
N4	0.0333 (10)	0.0356 (10)	0.0269 (9)	−0.0019 (7)	0.0003 (7)	0.0042 (7)
N5	0.0342 (10)	0.0263 (9)	0.0318 (9)	−0.0009 (7)	0.0025 (7)	−0.0004 (7)
N6	0.0247 (9)	0.0318 (9)	0.0318 (9)	−0.0007 (7)	0.0004 (7)	−0.0013 (7)
C3	0.0296 (11)	0.0368 (11)	0.0239 (10)	−0.0031 (9)	−0.0032 (8)	0.0019 (8)
C4	0.0357 (12)	0.0318 (11)	0.0385 (12)	0.0014 (9)	0.0007 (9)	0.0079 (9)
C5	0.0303 (11)	0.0443 (13)	0.0294 (11)	0.0001 (9)	0.0062 (9)	−0.0017 (9)
C6	0.0310 (11)	0.0348 (11)	0.0356 (12)	−0.0055 (9)	−0.0019 (9)	−0.0024 (9)
C7	0.0296 (10)	0.0289 (10)	0.0285 (10)	0.0022 (8)	0.0041 (8)	−0.0016 (8)
C8	0.0250 (10)	0.0297 (10)	0.0307 (10)	0.0021 (8)	−0.0025 (8)	0.0006 (8)
O1	0.0246 (7)	0.0492 (9)	0.0292 (8)	−0.0004 (6)	−0.0002 (6)	0.0020 (7)
C9	0.0417 (15)	0.091 (2)	0.0326 (13)	0.0067 (14)	−0.0027 (10)	−0.0001 (13)
O2	0.0487 (9)	0.0349 (8)	0.0352 (9)	0.0078 (7)	−0.0121 (7)	−0.0017 (7)
C10	0.115 (3)	0.0549 (18)	0.0561 (18)	0.0408 (18)	−0.0207 (18)	−0.0111 (14)
O1W	0.0380 (9)	0.0340 (8)	0.0504 (10)	−0.0035 (7)	−0.0073 (7)	0.0114 (7)

Geometric parameters (Å, °)

Ni1—N2	2.005 (2)	C3—H3B	0.9700
Ni1—N1	2.022 (2)	C4—H4A	0.9700
Ni1—O1	2.094 (2)	C4—H4B	0.9700
Ni1—O1W	2.111 (2)	C5—H5A	0.9700

Ni1—O2	2.159 (2)	C5—H5B	0.9700
Ni1—N3	2.224 (2)	C6—H6A	0.9700
N1—C1	1.157 (3)	C6—H6B	0.9700
C1—S1	1.627 (2)	C7—H7A	0.9700
N2—C2	1.151 (3)	C7—H7B	0.9700
C2—S2	1.636 (2)	C8—H8A	0.9700
N3—C3	1.490 (2)	C8—H8B	0.9700
N3—C8	1.494 (2)	O1—C9	1.432 (3)
N3—C7	1.499 (2)	O1—H1A	0.8500
N4—C5	1.470 (3)	C9—H9A	0.9600
N4—C3	1.471 (3)	C9—H9B	0.9600
N4—C4	1.479 (3)	C9—H9C	0.9600
N5—C6	1.473 (3)	O2—C10	1.420 (3)
N5—C7	1.476 (3)	O2—H2A	0.8500
N5—C4	1.479 (3)	C10—H10A	0.9600
N6—C8	1.473 (2)	C10—H10B	0.9600
N6—C6	1.479 (3)	C10—H10C	0.9600
N6—C5	1.482 (3)	O1W—H1WB	0.8500
C3—H3A	0.9700	O1W—H1WD	0.8500
N2—Ni1—N1	176.16 (7)	N4—C5—N6	111.39 (16)
N2—Ni1—O1	91.32 (7)	N4—C5—H5A	109.4
N1—Ni1—O1	89.71 (7)	N6—C5—H5A	109.4
N2—Ni1—O1W	89.05 (7)	N4—C5—H5B	109.4
N1—Ni1—O1W	87.26 (7)	N6—C5—H5B	109.4
O1—Ni1—O1W	89.10 (6)	H5A—C5—H5B	108.0
N2—Ni1—O2	89.51 (7)	N5—C6—N6	111.62 (16)
N1—Ni1—O2	89.31 (7)	N5—C6—H6A	109.3
O1—Ni1—O2	177.47 (6)	N6—C6—H6A	109.3
O1W—Ni1—O2	88.52 (6)	N5—C6—H6B	109.3
N2—Ni1—N3	92.74 (7)	N6—C6—H6B	109.3
N1—Ni1—N3	90.94 (7)	H6A—C6—H6B	108.0
O1—Ni1—N3	91.40 (6)	N5—C7—N3	111.79 (15)
O1W—Ni1—N3	178.13 (6)	N5—C7—H7A	109.3
O2—Ni1—N3	90.95 (6)	N3—C7—H7A	109.3
C1—N1—Ni1	177.90 (17)	N5—C7—H7B	109.3
N1—C1—S1	179.4 (2)	N3—C7—H7B	109.3
C2—N2—Ni1	178.66 (19)	H7A—C7—H7B	107.9
N2—C2—S2	178.3 (2)	N6—C8—N3	111.76 (15)
C3—N3—C8	107.41 (15)	N6—C8—H8A	109.3
C3—N3—C7	107.66 (15)	N3—C8—H8A	109.3
C8—N3—C7	107.29 (15)	N6—C8—H8B	109.3
C3—N3—Ni1	108.66 (11)	N3—C8—H8B	109.3
C8—N3—Ni1	113.48 (11)	H8A—C8—H8B	107.9
C7—N3—Ni1	112.09 (11)	C9—O1—Ni1	124.31 (15)
C5—N4—C3	108.40 (16)	C9—O1—H1A	108.3
C5—N4—C4	108.67 (17)	Ni1—O1—H1A	108.3
C3—N4—C4	108.42 (16)	O1—C9—H9A	109.5
C6—N5—C7	108.24 (16)	O1—C9—H9B	109.5
C6—N5—C4	108.65 (16)	H9A—C9—H9B	109.5

C7—N5—C4	108.93 (16)	O1—C9—H9C	109.5
C8—N6—C6	108.37 (16)	H9A—C9—H9C	109.5
C8—N6—C5	109.29 (16)	H9B—C9—H9C	109.5
C6—N6—C5	108.14 (16)	C10—O2—Ni1	127.92 (15)
N4—C3—N3	112.79 (16)	C10—O2—H2A	111.7
N4—C3—H3A	109.0	Ni1—O2—H2A	111.7
N3—C3—H3A	109.0	O2—C10—H10A	109.5
N4—C3—H3B	109.0	O2—C10—H10B	109.5
N3—C3—H3B	109.0	H10A—C10—H10B	109.5
H3A—C3—H3B	107.8	O2—C10—H10C	109.5
N5—C4—N4	111.32 (16)	H10A—C10—H10C	109.5
N5—C4—H4A	109.4	H10B—C10—H10C	109.5
N4—C4—H4A	109.4	Ni1—O1W—H1WB	109.9
N5—C4—H4B	109.4	Ni1—O1W—H1WD	110.0
N4—C4—H4B	109.4	H1WB—O1W—H1WD	108.3
H4A—C4—H4B	108.0		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1WB···S2^{i}	0.85	2.61	3.431 (2)	162
O1—H1A···N6^{i}	0.85	1.93	2.762 (2)	165
O1W—H1WD···N5^{ii}	0.85	2.02	2.836 (2)	162
O2—H2A···N4^{iii}	0.85	2.09	2.839 (2)	148
C3—H3A···N1	0.97	2.50	3.084 (3)	119
C3—H3B···O2	0.97	2.53	3.130 (3)	120
C7—H7A···O1	0.97	2.59	2.962 (3)	103
C10—H10B···N2	0.96	2.52	3.156 (4)	123

Symmetry codes: (i) *x*+1/2, *y*, −*z*+1/2; (ii) −*x*+2, *y*+1/2, −*z*+1/2; (iii) −*x*+2, −*y*+2, −*z*+1.

Fig. 1

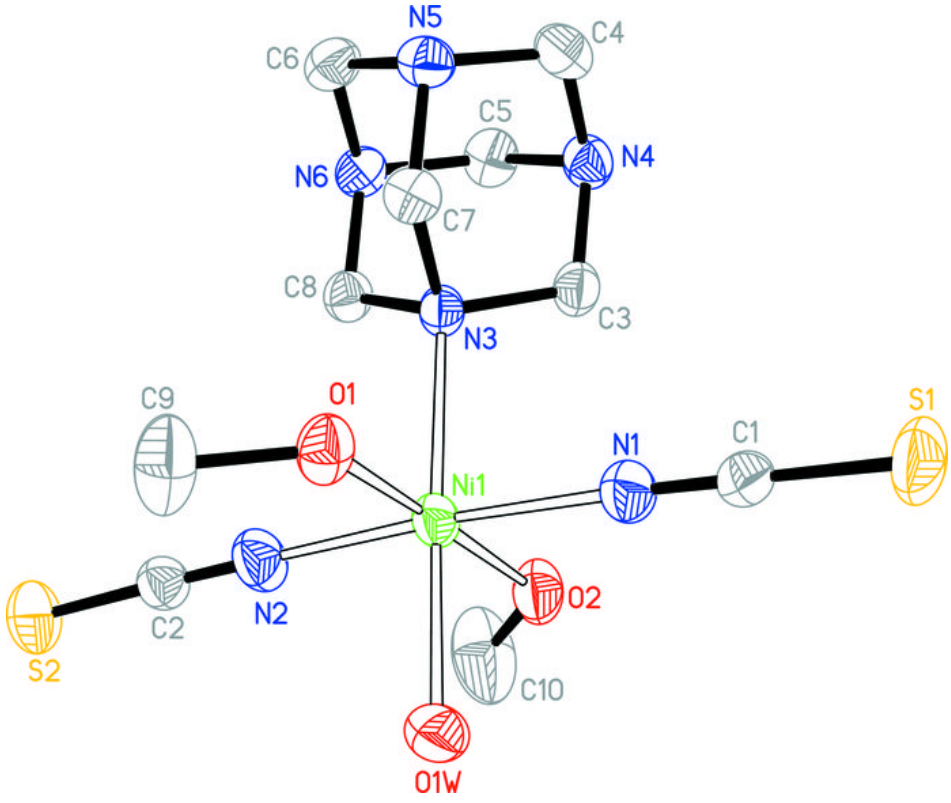

Fig. 2