

Ya-Bo Xie,* Xiang-Jie Wang and
Dao WangCollege of Environmental and Energy Engineering,
Beijing University of Technology,
Beijing 100022, People's Republic of China

Correspondence e-mail: xieyabo@bjut.edu.cn

Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$
 R factor = 0.063
 wR factor = 0.111
Data-to-parameter ratio = 15.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetraaquabis[2,3-bis(5-methyl-1,3,4-thia-
diazol-2-ylsulfanylmethyl)quinoxaline]nickel(II)
bis(perchlorate) acetone disolvate

In the centrosymmetric, mononuclear title complex, $[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \cdot 2\text{C}_3\text{H}_6\text{O}$ [$\text{L} = 2,3\text{-bis}(5\text{-methyl-1,3,4-thiadiazol-2-ylsulfanylmethyl)quinoxaline}$, $\text{C}_{16}\text{H}_{14}\text{N}_6\text{S}_4$], the Ni^{II} center adopts a slightly distorted octahedral coordination geometry, formed by two N atoms from two distinct ligands and four O atoms from water molecules. Only one N atom of L takes part in coordinating to the Ni^{II} atom.

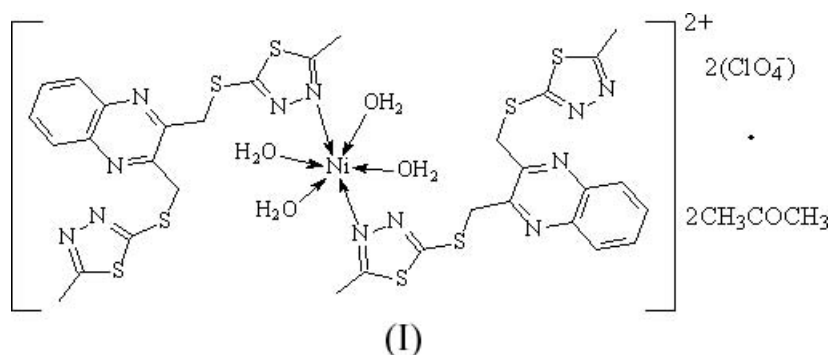
Received 16 September 2005

Accepted 20 September 2005

Online 28 September 2005

Comment

The generation of coordination architectures depends mainly on the combination of two factors, *viz.* the coordination geometry of metal ions and the nature of the ligands (Sun *et al.*, 2002; Goodgame *et al.*, 2002; Hamblin *et al.*, 2002). Multithioether ligands possess unusual potential for structure control in inorganic chemistry, and many crystal structures of complexes with multithioether ligands have been reported (Li *et al.*, 2003; Zheng *et al.*, 2003). The crystal structure of a nickel(II) complex, $[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{COCH}_3$, (I), with a flexible dithioether ligand, namely 2,3-bis(5-methyl-1,3,4-thiadiazol-2-ylsulfanylmethyl)quinoxaline (L), is reported here.



The structure of the title complex consists of a mononuclear $[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_4]^{2+}$ cation, two ClO_4^- anions and two uncoordinated CH_3COCH_3 molecules (Fig. 1). The $[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_4]^{2+}$ cation is centrosymmetric, with the Ni^{II} atom residing on an inversion center. The Ni^{II} atom is coordinated by two N atoms from two distinct ligands (L) and four O atoms from water molecules, giving a slightly distorted octahedral coordination geometry with the *cis* bond angles around the Ni^{II} center in the range $88.16(13)$ to $92.97(12)^\circ$. As shown in Table 1, the Ni—N bond length is $2.129(4)\text{ \AA}$, while the Ni—O bond lengths are unequal with values for Ni1—O1 and Ni1—O2 of $2.089(3)$ and $2.050(3)\text{ \AA}$, respectively. In the title complex, although each ligand has ten potential donors (six N and four S), only one N atom takes part in coordination to the Ni^{II} center. The dihedral angle formed by the two thiadiazole rings of the same ligand is $63.5(3)^\circ$. In the crystal structure O—H...O and O—

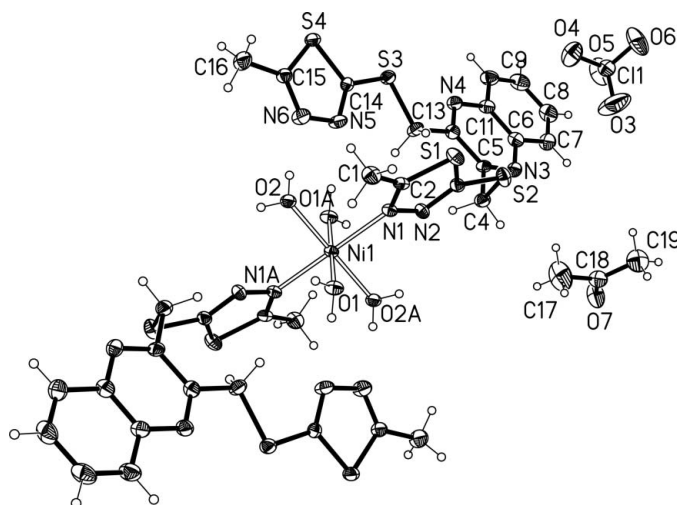


Figure 1

Structure of (I), showing displacement ellipsoids at the 30% probability level [symmetry code: (A) $2 - x, 1 - y, 1 - z$]. The symmetry-related perchlorate ion and acetone molecule are not shown.

H \cdots N intramolecular and intermolecular hydrogen bonds stabilize the packing (see Table 2).

Experimental

The reaction of 2,3-bis(bromomethyl)quinoxaline (0.01 mol, 3.16 g) with 5-methyl-2-sulfanyl-1,3,4-thiadiazole (0.021 mol, 2.78 g), in the presence of KOH (0.021 mol, 1.47 g, 80%), gave the ligand *L* in good yield (3.51 g, 84%). Analysis calculated for $C_{16}H_{14}N_6S_4$: C 45.91, H 3.37, N 20.08%; found: C 45.74, H 3.49, N 20.28%; 1H NMR ($CDCl_3$): 2.72 (*s*, 6H, CH_3), 5.10 (*s*, 4H, SCH_2), 7.73–8.07 (*m*, 4H, Ar–H). The title complex was synthesized by carefully layering a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (36.6 mg, 0.1 mmol) in CH_3COCH_3 on top of a solution of *L* (42.0 mg, 0.1 mmol) in chloroform in a test-tube. After about three days at room temperature, blue–green single crystals suitable for X-ray investigation appeared at the boundary between acetone and chloroform with a yield of 22%. IR (KBr, cm^{-1}): 3441 (*s*), 1629 (*w*), 1571 (*w*), 1490 (*m*), 1339 (*m*), 1296 (*m*), 1133 (*m*), 1018 (*m*), 838 (*vs*), 770 (*s*), 556 (*s*).

Crystal data

$[Ni(C_{16}H_{14}N_6S_4)_2(H_2O)_4](ClO_4)_2 \cdot 2C_3H_6O$	$Z = 1$
$M_r = 1282.97$	$D_x = 1.548 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.300$ (7) Å	Cell parameters from 776 reflections
$b = 12.223$ (9) Å	$\theta = 2.4\text{--}26.3^\circ$
$c = 13.964$ (10) Å	$\mu = 0.82 \text{ mm}^{-1}$
$\alpha = 81.108$ (13) $^\circ$	$T = 293$ (2) K
$\beta = 86.415$ (12) $^\circ$	Block, blue–green
$\gamma = 79.596$ (13) $^\circ$	$0.20 \times 0.16 \times 0.12 \text{ mm}$
$V = 1375.8$ (18) Å 3	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	5461 independent reflections
φ and ω scans	3264 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$R_{int} = 0.034$
$T_{min} = 0.789$, $T_{max} = 0.910$	$\theta_{max} = 26.5^\circ$
7534 measured reflections	$h = -10 \rightarrow 10$
	$k = -7 \rightarrow 17$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.111$
 $S = 1.07$
 5461 reflections
 344 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 1.5535P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.85 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.58 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, $^\circ$).

Ni1–N1	2.129 (4)	Ni1–O2	2.050 (3)
Ni1–O1	2.089 (3)		
N1 ⁱ –Ni1–N1	180	O2–Ni1–O1	92.97 (12)
O1–Ni1–N1 ⁱ	88.16 (13)	O2–Ni1–N1 ⁱ	90.37 (13)
O1 ⁱ –Ni1–O1	180	O2–Ni1–N1	89.63 (13)
O2–Ni1–O1 ⁱ	87.03 (12)	O2 ⁱ –Ni1–O2	180

Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, $^\circ$).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> –H \cdots <i>A</i>
O1–H11 \cdots N5 ⁱ	0.88	2.02	2.899 (5)	171
O1–H11 \cdots N6 ⁱ	0.88	2.52	3.323 (5)	152
O1–H12 \cdots O5 ⁱⁱ	0.87	1.87	2.734 (5)	174
O2–H21 \cdots O7 ⁱⁱⁱ	0.85	2.07	2.825 (5)	147
O2–H22 \cdots N6	0.85	1.99	2.835 (5)	172

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

H atoms bonded to C atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C–H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ [$1.5U_{eq}(C)$ for methyl H atoms] of the carrier atom. The H atoms of the water molecules were located in Fourier difference maps and refined with isotropic displacement parameters set at 1.2 times those of the parent O atoms.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT and SHELXTL (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

The authors thank Beijing University of Technology for supporting this work and Dr Jianrong Li of Nankai University for structural analysis.

References

- Bruker (1998). SMART (Version 5.051), SAINT (Version 5.01), SADABS (Version 2.03) and SHELXTL (Version 6.1). Bruker AXS Inc., Madison, Wisconsin, USA.
- Goodgame, D. M. L., Grachvogel, D. A. & Williams, D. J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2259–2260.
- Hamblin, J., Childs, L. J., Alcock, N. W. & Hannon, M. J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 164–169.
- Li, J.-R., Zhang, R.-H. & Bu, X.-H. (2003). *Cryst. Growth Des.* **3**, 829–835.
- Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.
- Sun, W. Y., Kusukawa, T. & Fujita, M. (2002). *J. Am. Chem. Soc.* **124**, 11570–11571.
- Zheng, Y., Du, M., Li, J. R., Zhang, R. H. & Bu, X. H. (2003). *Dalton Trans.* pp. 1509–1514.