

Hexakis(1*H*-imidazole- κ N³)nickel(II) sulfate dihydrate

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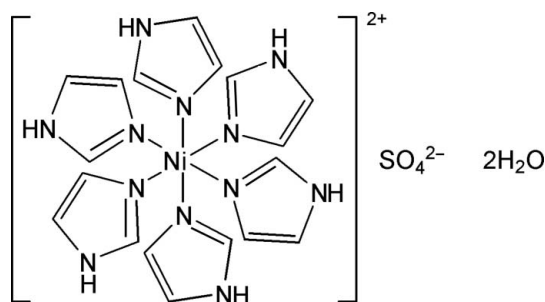
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; disorder in solvent or counterion; R factor = 0.056; wR factor = 0.183; data-to-parameter ratio = 11.6.

The title compound, $[\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6]\text{SO}_4 \cdot 2\text{H}_2\text{O}$, was prepared by hydrothermal synthesis. The Ni^{II} atom lies on a site of $\bar{3}$ point symmetry and is coordinated by six imidazole ligands in a regular octahedral geometry. The sulfate anion is disordered about a site of 32 point symmetry; water molecules lie on sites of 32 point symmetry and on general positions. The coordinated imidazole molecules make $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds with the sulfate anions.

Related literature

The unit-cell dimensions of this compound have been reported previously (Phung *et al.*, 1976), although complete space-group information and atomic coordinates were not given. For examples of other structures containing $[\text{Ni}(\text{C}_3\text{N}_2\text{H}_4)_6]^{2+}$ cations, see: Fu *et al.* (2007); Gao *et al.* (2004); Wang *et al.* (2000).



Experimental

Crystal data

$[\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6]\text{SO}_4 \cdot 2\text{H}_2\text{O}$
 $M_r = 599.29$
 Trigonal, $P\bar{3}1c$
 $a = 9.0029$ (9) Å
 $c = 22.937$ (4) Å
 $V = 1610.0$ (4) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.72$ mm⁻¹
 $T = 293$ (2) K
 $0.13 \times 0.12 \times 0.12$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\text{min}} = 0.913$, $T_{\text{max}} = 0.919$

7600 measured reflections
 949 independent reflections
 794 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.183$
 $S = 1.16$
 949 reflections
 82 parameters
 17 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.49$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H3A} \cdots \text{O1}$	0.86	2.10	2.868 (3)	149
$\text{N1}-\text{H3A} \cdots \text{O2}^{\text{i}}$	0.86	2.09	2.908 (7)	159
$\text{N1}-\text{H3A} \cdots \text{O2}^{\text{ii}}$	0.86	2.44	3.191 (7)	146

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); 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: BI2207).

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supplementary materials

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Hexakis(1*H*-imidazole- κ N³)nickel(II) sulfate dihydrate

X.-C. Sun, G.-P. Zhou, Z.-B. Liu and Y. Xu

Comment

The title compound was obtained during an attempted synthesis of a metal-organic framework (MOF) incorporating Ni^{II} and imidazole. The unit cell has been reported previously (Phung *et al.*, 1976), although complete space group information and atomic coordinates were not given.

The structure comprises discrete [Ni(C₃N₂H₄)₆]²⁺ cations (Figure 1). The Ni^{II} atom lies on a site of $\bar{3}$ point symmetry and is coordinated by six N atoms from six imidazole molecules in a regular octahedral geometry with Ni—N = 2.1216 (17) Å. The Ni—N bond lengths and angles are comparable to those in similar reported Ni^{II} compounds (for example, Fu *et al.*, 2007). The sulfate anion is disordered about a site of 32 point symmetry. As shown in Figure 2, the non-coordinated N atoms of imidazole are involved in hydrogen-bonding interactions with O atoms of the sulfate groups.

Experimental

Light purple block crystals were synthesized hydrothermally from a complex reaction mixture. In a typical synthesis, GeO₂ (0.1054 g), NH₄VO₃ (0.1079) and NiSO₄ (0.5278 g) were dissolved in the mixed solvent of dimethyl formamide (0.5162 g) and water (1.8388 g) followed by addition of imidazole (0.4551 g) with constant stirring. The mixture was kept in a 25 ml Teflon-lined steel autoclave at 443 K for 7 days then slowly cooled to room temperature. The product was filtered, washed with distilled water, and dried at room temperature.

Refinement

H atoms bound to C or N atoms were placed geometrically and allowed to ride with C—H = 0.93 Å or N—H = 0.86 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C/N})$. H atoms of the water molecules were located in difference Fourier maps and refined with O—H distances restrained to be 0.85 (1) Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The displacement parameters of the O atoms of the water molecules were restrained to approximate isotropic behaviour and the S—O distances in the disordered sulfate anion were restrained to be 1.420 (2) Å.

Figures

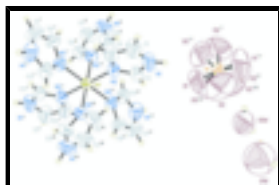


Fig. 1. The molecular structure of title compound showing displacement ellipsoids at the 70% probability level for non-H atoms.

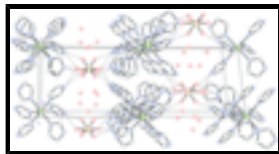


Fig. 2. Unit-cell contents for title compound. Dashed lines denote hydrogen bonds.

Hexakis(1*H*-imidazole- κ N³)nickel(II) sulfate dihydrate

Crystal data

$[\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6]\text{SO}_4 \cdot 2\text{H}_2\text{O}$	$Z = 2$
$M_r = 599.29$	$F_{000} = 624$
Trigonal, $P\bar{3}1c$	$D_x = 1.236 \text{ Mg m}^{-3}$
Hall symbol: $-P\ 3\ 2c$	Mo $K\alpha$ radiation
$a = 9.0029 (9) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 9.0029 (9) \text{ \AA}$	Cell parameters from 7600 reflections
$c = 22.937 (4) \text{ \AA}$	$\theta = 2.6\text{--}25.0^\circ$
$\alpha = 90^\circ$	$\mu = 0.72 \text{ mm}^{-1}$
$\beta = 90^\circ$	$T = 293 (2) \text{ K}$
$\gamma = 120^\circ$	Block, blue
$V = 1610.0 (4) \text{ \AA}^3$	$0.13 \times 0.12 \times 0.12 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	949 independent reflections
Radiation source: fine-focus sealed tube	794 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.023$
$T = 293(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
ω scans	$\theta_{\text{min}} = 2.6^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -10 \rightarrow 9$
$T_{\text{min}} = 0.913$, $T_{\text{max}} = 0.919$	$k = -10 \rightarrow 9$
7600 measured reflections	$l = -15 \rightarrow 27$

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
$wR(F^2) = 0.183$	$w = 1/[\sigma^2(F_o^2) + (0.13P)^2 + 0.1485P]$
$S = 1.16$	where $P = (F_o^2 + 2F_c^2)/3$
949 reflections	$(\Delta/\sigma)_{\text{max}} = 0.032$
	$\Delta\rho_{\text{max}} = 0.49 \text{ e \AA}^{-3}$

82 parameters $\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$
 17 restraints Extinction correction: none
 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ni1	0.0000	0.0000	0.0000	0.04666 (14)	
S1	0.3333	-0.3333	-0.2500	0.0660 (3)	
N1	0.3116 (2)	-0.0743 (2)	-0.12231 (8)	0.0878 (5)	
H3A	0.3235	-0.1243	-0.1524	0.105*	
N2	0.18871 (19)	-0.00718 (14)	-0.05341 (7)	0.0557 (4)	
C1	0.4392 (3)	0.0428 (3)	-0.08892 (12)	0.0901 (8)	
H1A	0.5562	0.0872	-0.0945	0.108*	
C2	0.3650 (2)	0.0825 (3)	-0.04641 (10)	0.0746 (6)	
H4A	0.4229	0.1592	-0.0163	0.090*	
C3	0.1628 (2)	-0.0995 (2)	-0.10058 (8)	0.0693 (5)	
H6A	0.0557	-0.1725	-0.1167	0.083*	
O1	0.3333	-0.3333	-0.18837 (15)	0.108 (2)	0.50
O2	0.3702 (8)	-0.4468 (6)	-0.2181 (3)	0.211 (2)	0.50
O1W	0.0000	-1.0000	-0.2500	0.313 (5)	0.50
H1W	0.0255 (4)	-1.0713 (3)	-0.2645 (3)	0.375*	0.17
O2W	0.3549 (10)	-0.7269 (11)	-0.2078 (5)	0.137 (3)	0.25
H2WB	0.460 (2)	-0.647 (6)	-0.211 (6)	0.165*	0.25
H2WA	0.271 (3)	-0.799 (6)	-0.2284 (17)	0.165*	0.25

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.05113 (18)	0.05113 (18)	0.0377 (3)	0.02556 (9)	0.000	0.000
S1	0.0785 (4)	0.0785 (4)	0.0412 (5)	0.0392 (2)	0.000	0.000
N1	0.1061 (8)	0.1020 (9)	0.0739 (10)	0.0660 (7)	0.0246 (9)	-0.0081 (8)
N2	0.0600 (7)	0.0609 (6)	0.0504 (8)	0.0334 (5)	0.0035 (7)	-0.0022 (5)
C1	0.0703 (9)	0.1121 (11)	0.0945 (17)	0.0506 (9)	0.0056 (11)	-0.0219 (12)
C2	0.0606 (7)	0.0906 (11)	0.0753 (12)	0.0398 (7)	0.0016 (9)	-0.0088 (10)

supplementary materials

C3	0.0742 (8)	0.0729 (9)	0.0624 (11)	0.0380 (6)	0.0110 (8)	-0.0046 (8)
O1	0.135 (3)	0.135 (3)	0.054 (3)	0.0674 (15)	0.000	0.000
O2	0.317 (4)	0.165 (3)	0.196 (5)	0.155 (2)	-0.079 (4)	0.024 (3)
O1W	0.315 (6)	0.315 (6)	0.307 (8)	0.158 (3)	0.000	0.000
O2W	0.155 (4)	0.141 (4)	0.143 (5)	0.095 (3)	0.018 (4)	0.003 (4)

Geometric parameters (Å, °)

Ni1—N2 ⁱ	2.1216 (17)	N1—C1	1.344 (3)
Ni1—N2 ⁱⁱ	2.1216 (17)	N1—H3A	0.860
Ni1—N2 ⁱⁱⁱ	2.1216 (17)	N2—C3	1.312 (2)
Ni1—N2	2.1216 (17)	N2—C2	1.384 (2)
Ni1—N2 ^{iv}	2.1216 (17)	C1—C2	1.328 (3)
Ni1—N2 ^v	2.1216 (17)	C1—H1A	0.930
S1—O1 ^{vi}	1.414 (3)	C2—H4A	0.930
S1—O1	1.414 (3)	C3—H6A	0.930
S1—O2 ^{vii}	1.423 (6)	O1—O2 ^{ix}	1.400 (7)
S1—O2 ^{viii}	1.423 (6)	O1—O2 ^{viii}	1.400 (7)
S1—O2 ^{ix}	1.423 (6)	O1—O2	1.400 (7)
S1—O2 ^x	1.423 (6)	O2—O2 ^{vi}	1.616 (13)
S1—O2	1.423 (6)	O1W—H1W	0.850 (3)
S1—O2 ^{vi}	1.423 (6)	O2W—H2WB	0.855 (18)
N1—C3	1.338 (3)	O2W—H2WA	0.853 (19)
N2 ⁱ —Ni1—N2 ⁱⁱ	180.00 (11)	O2 ^{ix} —S1—O2	96.0 (4)
N2 ⁱ —Ni1—N2 ⁱⁱⁱ	89.99 (7)	O2 ^x —S1—O2	103.2 (4)
N2 ⁱⁱ —Ni1—N2 ⁱⁱⁱ	90.01 (7)	O1 ^{vi} —S1—O2 ^{vi}	59.1 (3)
N2 ⁱ —Ni1—N2	89.99 (7)	O1—S1—O2 ^{vi}	120.9 (3)
N2 ⁱⁱ —Ni1—N2	90.01 (7)	O2 ^{vii} —S1—O2 ^{vi}	96.0 (4)
N2 ⁱⁱⁱ —Ni1—N2	89.99 (7)	O2 ^{viii} —S1—O2 ^{vi}	103.2 (4)
N2 ⁱ —Ni1—N2 ^{iv}	90.01 (7)	O2 ^{ix} —S1—O2 ^{vi}	156.7 (5)
N2 ⁱⁱ —Ni1—N2 ^{iv}	89.99 (7)	O2 ^x —S1—O2 ^{vi}	96.0 (4)
N2 ⁱⁱⁱ —Ni1—N2 ^{iv}	90.01 (7)	O2—S1—O2 ^{vi}	69.2 (6)
N2—Ni1—N2 ^{iv}	180.00 (9)	C3—N1—C1	108.16 (18)
N2 ⁱ —Ni1—N2 ^v	90.01 (7)	C3—N1—H3A	125.9
N2 ⁱⁱ —Ni1—N2 ^v	89.99 (7)	C1—N1—H3A	125.9
N2 ⁱⁱⁱ —Ni1—N2 ^v	180.00 (10)	C3—N2—C2	104.71 (17)
N2—Ni1—N2 ^v	90.01 (7)	C3—N2—Ni1	127.15 (12)
N2 ^{iv} —Ni1—N2 ^v	89.99 (7)	C2—N2—Ni1	128.14 (14)
O1 ^{vi} —S1—O1	180.0	C2—C1—N1	106.35 (19)
O1 ^{vi} —S1—O2 ^{vii}	59.1 (3)	C2—C1—H1A	126.8
O1—S1—O2 ^{vii}	120.9 (3)	N1—C1—H1A	126.8
O1 ^{vi} —S1—O2 ^{viii}	120.9 (3)	C1—C2—N2	110.03 (19)
O1—S1—O2 ^{viii}	59.1 (3)	C1—C2—H4A	125.0

O2 ^{vii} —S1—O2 ^{viii}	69.2 (6)	N2—C2—H4A	125.0
O1 ^{vi} —S1—O2 ^{ix}	120.9 (3)	N2—C3—N1	110.71 (16)
O1—S1—O2 ^{ix}	59.1 (3)	N2—C3—H6A	124.6
O2 ^{vii} —S1—O2 ^{ix}	103.2 (4)	N1—C3—H6A	124.6
O2 ^{viii} —S1—O2 ^{ix}	96.0 (4)	O2 ^{ix} —O1—O2 ^{viii}	98.2 (3)
O1 ^{vi} —S1—O2 ^x	59.1 (3)	O2 ^{ix} —O1—O2	98.2 (3)
O1—S1—O2 ^x	120.9 (3)	O2 ^{viii} —O1—O2	98.2 (3)
O2 ^{vii} —S1—O2 ^x	96.0 (4)	O2 ^{ix} —O1—S1	60.8 (3)
O2 ^{viii} —S1—O2 ^x	156.7 (5)	O2 ^{viii} —O1—S1	60.8 (3)
O2 ^{ix} —S1—O2 ^x	69.2 (6)	O2—O1—S1	60.8 (3)
O1 ^{vi} —S1—O2	120.9 (3)	O1—O2—S1	60.1 (3)
O1—S1—O2	59.1 (3)	O1—O2—O2 ^{vi}	109.6 (3)
O2 ^{vii} —S1—O2	156.7 (5)	S1—O2—O2 ^{vi}	55.4 (3)
O2 ^{viii} —S1—O2	96.0 (4)	H2WB—O2W—H2WA	141 (10)

Symmetry codes: (i) $-x+y, -x, z$; (ii) $x-y, x, -z$; (iii) $-y, x-y, z$; (iv) $-x, -y, -z$; (v) $y, -x+y, -z$; (vi) $-y, -x, -z-1/2$; (vii) $x, x-y-1, -z-1/2$; (viii) $-y, x-y-1, z$; (ix) $-x+y+1, -x, z$; (x) $-x+y+1, y, -z-1/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H3A \cdots O1	0.86	2.10	2.868 (3)	149
N1—H3A \cdots O2 ^{viii}	0.86	2.09	2.908 (7)	159
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Symmetry codes: (viii) $-y, x-y-1, z$; (ix) $-x+y+1, -x, z$.

Fig. 1

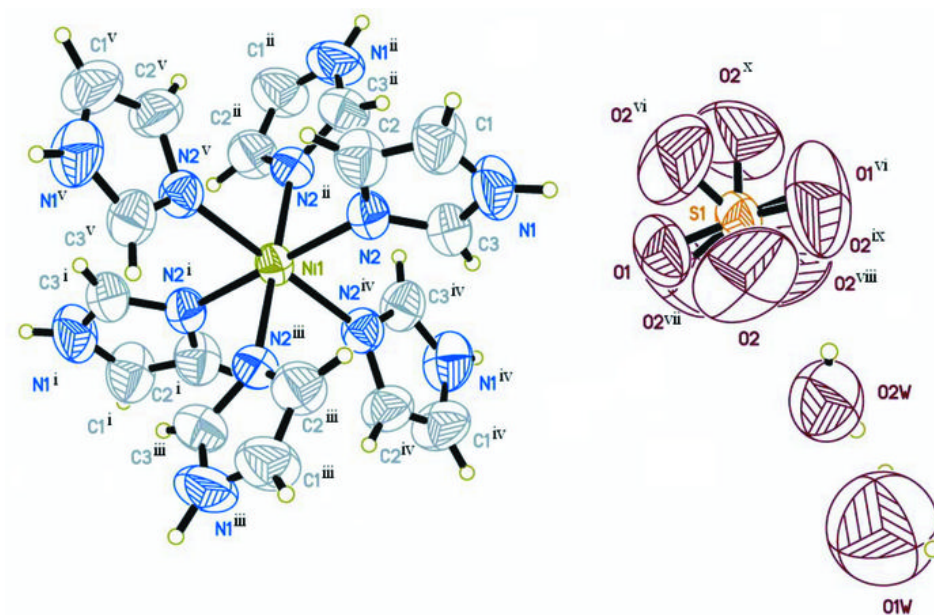


Fig. 2

