3,5-Lutidine pentaaqua sulfate complexes of first-row transition metals: [M(3,5-lutidine)(H$_2$O)$_5$]SO$_4$, with M = Mn, Co, Ni, and Zn

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The reactions of MnSO$_4$·H$_2$O, CoSO$_4$·7H$_2$O, NiSO$_4$·6H$_2$O and ZnSO$_4$·7H$_2$O with 3,5-lutidine (3,5-dimethylpyridine) yield crystals of pentaaqua(3,5-dimethylpyridine-κN)manganese(II) sulfate, [Mn(C$_7$H$_9$N)(H$_2$O)$_5$]SO$_4$, (1), pentaaqua(3,5-dimethylpyridine-κN)cobalt(II) sulfate, [Co(C$_7$H$_9$N)(H$_2$O)$_5$]SO$_4$, (2), pentaaqua(3,5-dimethylpyridine-κN)nickel(II) sulfate, [Ni(C$_7$H$_9$N)(H$_2$O)$_5$]SO$_4$, (3), and pentaaqua(3,5-dimethylpyridine-κN)zinc(II) sulfate, [Zn(C$_7$H$_9$N)-(H$_2$O)$_5$]SO$_4$, (4), which were characterized by single-crystal X-ray diffraction. The four crystals are isostructural, demonstrating near identical unit-cell parameters and atomic positions. The metal atoms are all octahedrally coordinated, with one lutidine ligand and five water ligands. The sulfate dianion hydrogen bonds with the coordinated water molecules of the dicationic metal complex salts, generating infinite three-dimensional networks.

1. Chemical context

Metal–pyridine sulfate complexes have been reported in the literature since the 1880s (Jørgensen, 1886; Reitzenstein, 1898; Manke, 2021), though an extensive and systematic look at the crystal structures of this class of compounds has never been undertaken. In recent years, our laboratory began looking at the structures of first-row transition-metal–pyridine sulfate complexes, first with the parent pyridine (Park et al., 2019; Pham et al., 2018; Roy et al., 2018) and then with picoline ligands (Park et al., 2022; Pham et al., 2019). In our efforts to examine the structural diversity of this class of compounds, we recently expanded to look at lutidine ligands. Herein we report four isostructural first-row transition-metal complexes of 3,5-lutidine.
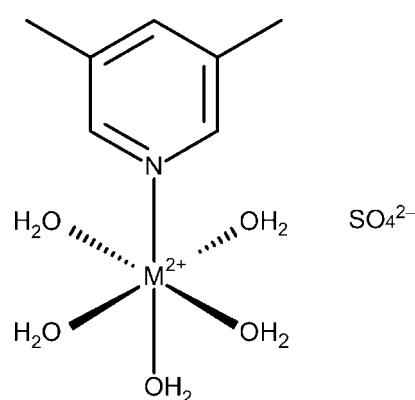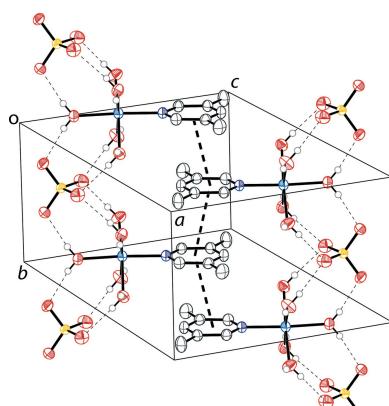
M = Mn (1), Co (2), Ni (3), Zn (4)

Table 1
Selected bond lengths (Å) for compounds (**1**)–(**4**).

Compound	$M-N1$	$S1-O4$	$S1-O5$	$S1-O6$
(**1**)	2.227 (3)	1.462 (2)	1.4650 (17)	1.484 (2)
(**2**)	2.112 (3)	1.462 (3)	1.4618 (17)	1.488 (2)
(**3**)	2.066 (2)	1.464 (2)	1.4588 (14)	1.4895 (19)
(**4**)	2.0924 (19)	1.4641 (19)	1.4596 (13)	1.4886 (18)

2. Structural commentary

The four compounds described herein are isostructural, demonstrating near identical unit-cell parameters and atomic positions (Fig. 1). The asymmetric unit comprises half of the cation and half of the sulfate anion, both ions having crystallographic mirror symmetry. In the cation, the metal atom, the lutidine ligand and the O1 atom of the *trans*-aqua ligand lie in the mirror plane, while two independent aqua ligands are in general positions. In each structure, both methyl groups of the lutidine ligand are rotationally disordered between two mirror-related orientations. In the anion, atoms S1, O4 and O6 lie in the mirror plane, while O5 and O5^{ii} are related by it. Reflection generates the full dicationic complex, which exhibits an octahedral coordination with one lutidine and five water ligands bound to the metal, as well as the full sulfate dianion.

The MO_3N plane formed by the three crystallographically unique water molecules and the lutidine nitrogen atom is rotated by 45.52 (4)° from the plane of the pyridine ring for Mn, 45.79 (4)° for Co, 45.93 (3)° for Ni, and 45.75 (3)° for Zn.
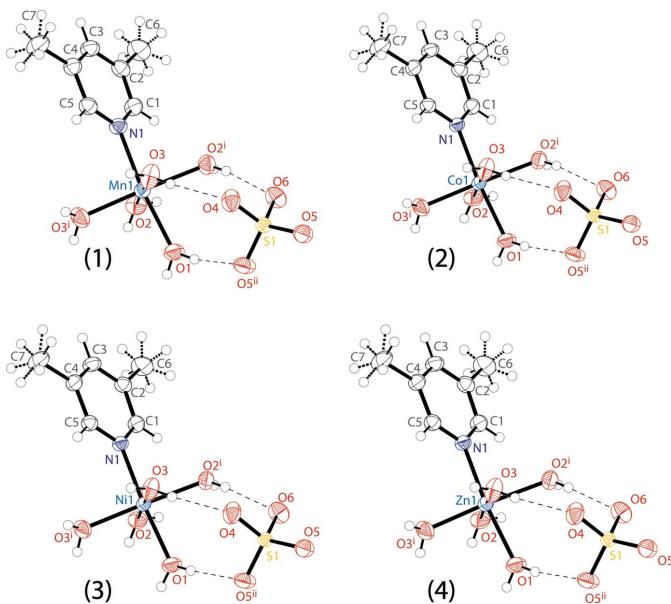

Figure 1
The molecular structures of 3,5-lutidine pentaaqua manganese sulfate (**1**), 3,5-lutidine pentaaqua cobalt sulfate (**2**), 3,5-lutidine pentaaqua nickel sulfate (**3**), and 3,5-lutidine pentaaqua zinc sulfate (**4**) showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. Dashed bonds are used to show the disordered hydrogen atoms on the methyl groups. Symmetry codes: (i) $x, \frac{3}{2} - y, z$; (ii) $x, \frac{1}{2} - y, z$.

Table 2
Hydrogen-bond geometry (Å, °) for (**1**).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···O5^i	0.79 (1)	2.00 (1)	2.775 (2)	166 (3)
O2—H2A···O6^i	0.78 (1)	2.06 (1)	2.832 (3)	172 (3)
O2—H2B···O6^{ii}	0.78 (1)	2.10 (2)	2.850 (3)	162 (4)
O3—H3A···O5^{iii}	0.78 (1)	1.98 (1)	2.752 (2)	177 (4)
O3—H3B···O4	0.78 (1)	1.99 (1)	2.748 (3)	165 (3)

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

Table 3
Hydrogen-bond geometry (Å, °) for (**2**).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···O5^i	0.78 (1)	2.01 (1)	2.782 (2)	173 (3)
O2—H2A···O6^i	0.78 (1)	2.07 (1)	2.840 (3)	169 (3)
O2—H2B···O6^{ii}	0.78 (1)	2.07 (2)	2.822 (3)	161 (4)
O3—H3A···O5^{iii}	0.77 (1)	1.99 (1)	2.764 (2)	174 (3)
O3—H3B···O4	0.78 (1)	1.97 (1)	2.742 (3)	171 (3)

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

Table 4
Hydrogen-bond geometry (Å, °) for (**3**).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···O5^i	0.78 (1)	2.00 (1)	2.7822 (18)	174 (3)
O2—H2A···O6^i	0.78 (1)	2.08 (1)	2.857 (2)	172 (2)
O2—H2B···O6^{ii}	0.79 (1)	2.06 (1)	2.821 (2)	163 (3)
O3—H3A···O5^{iii}	0.77 (1)	2.00 (1)	2.7683 (18)	173 (2)
O3—H3B···O4	0.77 (1)	1.98 (1)	2.745 (2)	172 (2)

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

Table 5
Hydrogen-bond geometry (Å, °) for (**4**).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···O5^i	0.78 (1)	2.01 (1)	2.7892 (17)	172 (3)
O2—H2A···O6^i	0.78 (1)	2.07 (1)	2.845 (2)	173 (2)
O2—H2B···O6^{ii}	0.79 (1)	2.08 (1)	2.833 (2)	162 (3)
O3—H3A···O5^{iii}	0.77 (1)	1.99 (1)	2.7571 (18)	177 (2)
O3—H3B···O4	0.77 (1)	1.97 (1)	2.7395 (19)	172 (2)

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

The $M-N$ distances (Table 1) observed in the complexes are all consistent with the ionic radii for the metals (Shannon, 1976). The full sulfate dianions have three near equivalent S—O bonds (S1—O4, S1—O5 and S1—O5^{ii}) with two metal-bound waters hydrogen bonding to each oxygen atom. There is also one slightly longer S—O bond (S1—O6) with four metal-bound waters hydrogen bonding to the oxygen. All S—O distances are listed in Table 1.

3. Supramolecular features

The ions in all of the compounds described are connected in an extended 3D network through hydrogen bonding. The major hydrogen bonds are between the metal–aqua complexes and the sulfate dianions (Tables 2–5). The extended structure packing of all compounds show π–π stacking between lutidine rings of adjacent complexes. The parameters of the π–π

Table 6
Parameters of π–π interactions (Å).

	(1)	(2)	(3)	(4)
Centroid-to-centroid	3.6461 (6)	3.6485 (6)	3.6337 (5)	3.6370 (5)
Plane-to-plane shift	0.770 (3)	0.829 (3)	0.8599 (19)	0.8290 (19)
Plane-to-centroid	3.5639 (3)	3.5532 (2)	3.53045 (15)	3.54130 (15)

interactions are in Table 6. The crystal packing of the zinc complex is shown in Fig. 2. The crystal packing of the other three compounds is isostructural in nature.

4. Database survey

While there are many examples of metal–pyridine penta-hydrate complexes, there is only one pyridine-based penta-hydrate complex of a transition metal with a sulfate counter-ion, which is the dimer of zinc bridged by 1,2-bis(pyridin-3-ylmethylene)hydrazine (YUMVAG; Lozovan *et al.*, 2020). The other similar structures with sulfur-based anions in the literature include a 3-carboxamidepyridine complex of cobalt with a sulfonate counter-ion (CACFAP; Lian *et al.*, 2010), and a pyridine nickel sulfonate complex with a calixarene tetra-sulfonate counter-anion (VIWHUE: Atwood *et al.*, 1991). The only similar 3,5-lutidine structures are a tetrakis(3,5-lutidine)
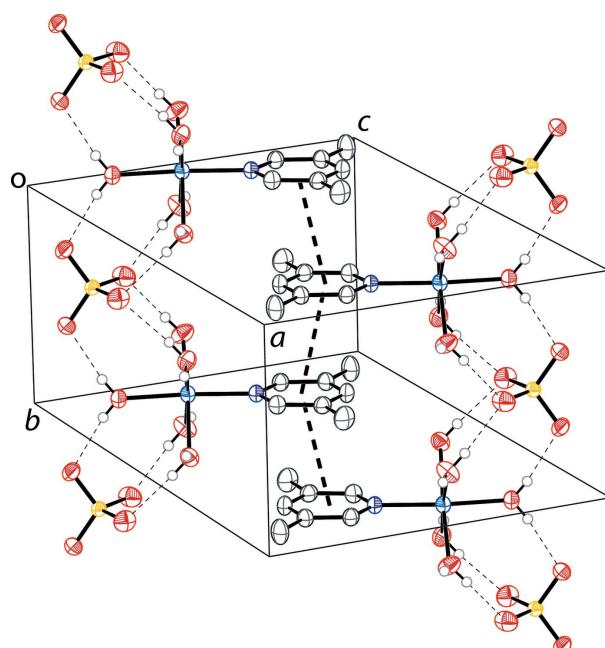

Figure 2
The crystal packing of 3,5-lutidine pentaaqua zinc sulfate (4). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines and π–π interactions are shown as bold dashed lines. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

Table 7
Experimental details.

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	[Mn(C₇H₉N)(H₂O)₅]SO₄	[Co(C₇H₉N)(H₂O)₅]SO₄	[Ni(C₇H₉N)(H₂O)₅]SO₄	[Zn(C₇H₉N)(H₂O)₅]SO₄
M_r	348.23	352.22	352.00	358.66
Crystal system, space group	Orthorhombic, *Pnma*	Orthorhombic, *Pnma*	Orthorhombic, *Pnma*	Orthorhombic, *Pnma*
Temperature (K)	297	297	297	297
a, b, c (Å)	17.1868 (13), 7.1278 (5), 11.4447 (8)	17.1238 (10), 7.1064 (4), 11.2576 (6)	17.1196 (8), 7.0609 (3), 11.2233 (5)	17.1312 (8), 7.0826 (3), 11.2879 (5)
V (Å³)	1402.02 (17)	1369.92 (13)	1356.67 (10)	1369.60 (11)
Z	4	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm⁻¹)	1.13	1.44	1.62	1.99
Crystal size (mm)	0.22 × 0.08 × 0.05	0.08 × 0.08 × 0.06	0.17 × 0.04 × 0.03	0.21 × 0.13 × 0.1
Data collection				
Diffractometer	Bruker D8 Venture CMOS	Bruker D8 Venture CMOS	Bruker D8 Venture CMOS	Bruker D8 Venture CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2021)	Multi-scan (*SADABS*; Bruker, 2021)	Multi-scan (*SADABS*; Bruker, 2021)	Multi-scan (*SADABS*; Bruker, 2021)
T_{min}, T_{max}	0.585, 0.745	0.714, 0.745	0.680, 0.745	0.671, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27161, 1460, 1265	32289, 1367, 1194	36924, 1499, 1386	46710, 1516, 1414
R_{int}	0.074	0.070	0.049	0.042
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.612	0.603	0.625	0.625
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.081, 1.11	0.028, 0.069, 1.12	0.023, 0.060, 1.10	0.021, 0.056, 1.12
No. of reflections	1460	1367	1499	1516
No. of parameters	128	128	128	128
No. of restraints	7	7	7	7
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.39, −0.42	0.43, −0.29	0.44, −0.33	0.40, −0.27

Computer programs: *APEX4* and *SAINT* (Bruker, 2021), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009), and *publCIF* (Westrip, 2010).

copper sulfate complex (IWAWEJ; Bowmaker *et al.*, 2011), and a bis(3,5-lutidine) nickel thiosulfate dimer (BEMNIS; Pladzyk *et al.*, 2012).

5. Synthesis and crystallization

A metal sulfate (44 mg of MnSO$_4$·H$_2$O, 44 mg of CoSO$_4$·7H$_2$O, 217 mg of NiSO$_4$·6H$_2$O, 33 mg of ZnSO$_4$·7H$_2$O) was dissolved in five drops of water and 2.5 mL of 3,5-lutidine. The resulting solution was heated to 338–343 K for twelve hours and allowed to cool slowly to room temperature producing single crystals suitable for X-ray diffraction. The manganese crystals formed as colorless blocks, the cobalt crystals formed as pink blocks, the nickel crystals formed as pale-green plates, and the zinc crystals formed as colorless blocks.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 7. The water hydrogen atoms H1, H2A, H2B, H3A, and H3B were found in difference-Fourier maps. These hydrogen atoms were refined isotropically, using DFIX restraints with O—H distances of 0.78 (1) Å. Isotropic displacement parameters were set to 1.5 U_{eq} of the parent oxygen atom. All other hydrogen atoms were placed in calculated positions [C—H = 0.93 Å (sp^2), 0.96 Å (CH$_3$)]. Isotropic displacement parameters were set to 1.2 U_{eq} of the parent aromatic carbon atoms and 1.5 U_{eq} of the parent methyl atoms.

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Computing details

For all structures, data collection: *APEX4* (Bruker, 2021); cell refinement: *SAINT* (Bruker, 2021); data reduction: *SAINT* (Bruker, 2021); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Pentaaqua(3,5-dimethylpyridine-κN)manganese(II) sulfate (1)

Crystal data

[Mn(C₇H₉N)(H₂O)₅]SO₄	$D_x = 1.650$ Mg m⁻³
$M_r = 348.23$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $Pnma$	Cell parameters from 7487 reflections
$a = 17.1868$ (13) Å	$\theta = 3.0$–25.7°
$b = 7.1278$ (5) Å	$\mu = 1.13$ mm⁻¹
$c = 11.4447$ (8) Å	$T = 297$ K
$V = 1402.02$ (17) Å³	BLOCK, colourless
$Z = 4$	$0.22 \times 0.08 \times 0.05$ mm
$F(000) = 724$	

Data collection

Bruker D8 Venture CMOS diffractometer	1460 independent reflections
φ and ω scans	1265 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2021)	$R_{int} = 0.074$
	$\theta_{max} = 25.8°$, $\theta_{min} = 3.0°$
$T_{min} = 0.585$, $T_{max} = 0.745$	$h = -20 \rightarrow 20$
27161 measured reflections	$k = -8 \rightarrow 8$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.032$	
$wR(F^2) = 0.081$	$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 0.6101P]$
$S = 1.11$	where $P = (F_o^2 + 2F_c^2)/3$
1460 reflections	$(\Delta/\sigma)_{max} < 0.001$
128 parameters	$\Delta\rho_{max} = 0.39$ e Å⁻³
7 restraints	$\Delta\rho_{min} = -0.42$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.38853 (3)	0.750000	0.19452 (4)	0.02628 (16)	
S1	0.33347 (4)	0.250000	−0.03698 (6)	0.02472 (19)	
O1	0.35349 (17)	0.750000	0.0101 (2)	0.0431 (6)	
O2	0.47201 (10)	0.9730 (3)	0.14197 (15)	0.0370 (4)	
O3	0.30623 (11)	0.5330 (3)	0.23922 (17)	0.0442 (4)	
O4	0.29510 (15)	0.250000	0.0770 (2)	0.0442 (6)	
O5	0.31258 (11)	0.0805 (2)	−0.10225 (15)	0.0433 (4)	
O6	0.41874 (13)	0.250000	−0.0163 (2)	0.0414 (6)	
N1	0.44712 (15)	0.750000	0.3681 (2)	0.0305 (6)	
C1	0.52514 (18)	0.750000	0.3748 (3)	0.0335 (7)	
H1A	0.553273	0.750000	0.305376	0.040*	
C2	0.56607 (18)	0.750000	0.4786 (3)	0.0322 (7)	
C3	0.52253 (19)	0.750000	0.5812 (3)	0.0344 (7)	
H3	0.547891	0.750000	0.652995	0.041*	
C4	0.44230 (19)	0.750000	0.5779 (3)	0.0327 (7)	
C5	0.40755 (19)	0.750000	0.4686 (3)	0.0323 (7)	
H5	0.353492	0.750000	0.465014	0.039*	
C6	0.6535 (2)	0.750000	0.4798 (4)	0.0489 (10)	
H6A	0.671766	0.681677	0.546736	0.073*	0.5
H6B	0.672147	0.876855	0.483598	0.073*	0.5
H6C	0.672591	0.691467	0.409899	0.073*	0.5
C7	0.3933 (2)	0.750000	0.6867 (3)	0.0500 (10)	
H7A	0.420061	0.816577	0.747595	0.075*	0.5
H7B	0.384142	0.623070	0.711140	0.075*	0.5
H7C	0.344518	0.810353	0.670925	0.075*	0.5
H1	0.3430 (17)	0.834 (3)	−0.032 (2)	0.054 (9)*	
H2A	0.4583 (16)	1.057 (3)	0.103 (2)	0.056 (10)*	
H2B	0.5081 (14)	0.930 (5)	0.111 (3)	0.084 (13)*	
H3A	0.2719 (12)	0.549 (4)	0.282 (2)	0.062 (10)*	
H3B	0.2951 (17)	0.451 (3)	0.197 (2)	0.062 (10)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0239 (2)	0.0297 (3)	0.0253 (3)	0.000	−0.00054 (17)	0.000
S1	0.0223 (4)	0.0241 (4)	0.0278 (4)	0.000	−0.0028 (3)	0.000
O1	0.0624 (17)	0.0320 (14)	0.0347 (14)	0.000	−0.0176 (12)	0.000
O2	0.0330 (9)	0.0403 (10)	0.0378 (9)	−0.0031 (8)	0.0016 (7)	0.0063 (8)
O3	0.0413 (10)	0.0442 (11)	0.0469 (10)	−0.0143 (9)	0.0136 (8)	−0.0105 (9)

O4	0.0490 (15)	0.0410 (14)	0.0425 (13)	0.000	0.0151 (11)	0.000
O5	0.0548 (11)	0.0305 (9)	0.0447 (9)	0.0012 (8)	−0.0186 (8)	−0.0054 (7)
O6	0.0218 (11)	0.0466 (15)	0.0558 (15)	0.000	−0.0007 (10)	0.000
N1	0.0274 (13)	0.0352 (15)	0.0290 (13)	0.000	−0.0047 (11)	0.000
C1	0.0293 (16)	0.0395 (19)	0.0315 (16)	0.000	0.0012 (13)	0.000
C2	0.0256 (16)	0.0314 (17)	0.0396 (18)	0.000	−0.0050 (13)	0.000
C3	0.0340 (17)	0.0389 (19)	0.0303 (16)	0.000	−0.0080 (13)	0.000
C4	0.0318 (16)	0.0357 (17)	0.0307 (16)	0.000	−0.0015 (13)	0.000
C5	0.0273 (15)	0.0344 (17)	0.0351 (17)	0.000	−0.0038 (13)	0.000
C6	0.0255 (17)	0.064 (3)	0.057 (2)	0.000	−0.0055 (16)	0.000
C7	0.042 (2)	0.076 (3)	0.0317 (18)	0.000	0.0010 (15)	0.000

Geometric parameters (Å, º)

Mn1—O1	2.195 (2)	N1—C5	1.336 (4)
Mn1—O2^{i}	2.2240 (17)	C1—H1A	0.9300
Mn1—O2	2.2240 (17)	C1—C2	1.381 (5)
Mn1—O3	2.1575 (17)	C2—C3	1.392 (5)
Mn1—O3^{i}	2.1575 (17)	C2—C6	1.504 (4)
Mn1—N1	2.227 (3)	C3—H3	0.9300
S1—O4	1.462 (2)	C3—C4	1.379 (5)
S1—O5^{ii}	1.4650 (17)	C4—C5	1.386 (4)
S1—O5	1.4650 (17)	C4—C7	1.503 (5)
S1—O6	1.484 (2)	C5—H5	0.9300
O1—H1	0.786 (10)	C6—H6A	0.9600
O1—H1^{i}	0.786 (10)	C6—H6B	0.9600
O2—H2A	0.781 (10)	C6—H6C	0.9600
O2—H2B	0.776 (10)	C7—H7A	0.9600
O3—H3A	0.775 (10)	C7—H7B	0.9600
O3—H3B	0.779 (10)	C7—H7C	0.9600
N1—C1	1.343 (4)		
O1—Mn1—O2^{i}	85.24 (7)	C1—N1—Mn1	120.2 (2)
O1—Mn1—O2	85.24 (7)	C5—N1—Mn1	122.5 (2)
O1—Mn1—N1	169.05 (11)	C5—N1—C1	117.3 (3)
O2^{i}—Mn1—O2	91.24 (10)	N1—C1—H1A	118.0
O2^{i}—Mn1—N1	87.11 (7)	N1—C1—C2	123.9 (3)
O2—Mn1—N1	87.11 (7)	C2—C1—H1A	118.0
O3^{i}—Mn1—O1	92.76 (8)	C1—C2—C3	116.9 (3)
O3—Mn1—O1	92.76 (8)	C1—C2—C6	121.1 (3)
O3—Mn1—O2	177.99 (7)	C3—C2—C6	122.0 (3)
O3^{i}—Mn1—O2	88.55 (7)	C2—C3—H3	119.5
O3—Mn1—O2^{i}	88.55 (7)	C4—C3—C2	120.9 (3)
O3^{i}—Mn1—O2^{i}	177.99 (7)	C4—C3—H3	119.5
O3—Mn1—O3^{i}	91.59 (11)	C3—C4—C5	117.1 (3)
O3—Mn1—N1	94.87 (7)	C3—C4—C7	122.5 (3)
O3^{i}—Mn1—N1	94.87 (7)	C5—C4—C7	120.4 (3)
O4—S1—O5^{ii}	110.15 (9)	N1—C5—C4	123.9 (3)

O4—S1—O5	110.15 (10)	N1—C5—H5	118.1
O4—S1—O6	107.66 (15)	C4—C5—H5	118.1
O5—S1—O5ii	111.09 (14)	C2—C6—H6A	109.5
O5—S1—O6	108.85 (9)	C2—C6—H6B	109.5
O5ii—S1—O6	108.86 (9)	C2—C6—H6C	109.5
Mn1—O1—H1i	130 (2)	H6A—C6—H6B	109.5
Mn1—O1—H1	130 (2)	H6A—C6—H6C	109.5
H1—O1—H1i	99 (4)	H6B—C6—H6C	109.5
Mn1—O2—H2A	120 (2)	C4—C7—H7A	109.5
Mn1—O2—H2B	111 (3)	C4—C7—H7B	109.5
H2A—O2—H2B	106.7 (17)	C4—C7—H7C	109.5
Mn1—O3—H3A	123 (2)	H7A—C7—H7B	109.5
Mn1—O3—H3B	123 (2)	H7A—C7—H7C	109.5
H3A—O3—H3B	108.1 (17)	H7B—C7—H7C	109.5
Mn1—N1—C1—C2	180.000 (1)	C2—C3—C4—C5	0.000 (1)
Mn1—N1—C5—C4	180.000 (1)	C2—C3—C4—C7	180.000 (1)
N1—C1—C2—C3	0.000 (1)	C3—C4—C5—N1	0.000 (1)
N1—C1—C2—C6	180.000 (1)	C5—N1—C1—C2	0.000 (1)
C1—N1—C5—C4	0.000 (1)	C6—C2—C3—C4	180.000 (1)
C1—C2—C3—C4	0.000 (1)	C7—C4—C5—N1	180.000 (1)

Symmetry codes: (i) x, $-y+3/2$, z; (ii) x, $-y+1/2$, z.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O5iii	0.79 (1)	2.00 (1)	2.775 (2)	166 (3)
O2—H2A···O6iii	0.78 (1)	2.06 (1)	2.832 (3)	172 (3)
O2—H2B···O6iv	0.78 (1)	2.10 (2)	2.850 (3)	162 (4)
O3—H3A···O5v	0.78 (1)	1.98 (1)	2.752 (2)	177 (4)
O3—H3B···O4	0.78 (1)	1.99 (1)	2.748 (3)	165 (3)

Symmetry codes: (iii) x, $y+1$, z; (iv) $-x+1$, $-y+1$, $-z$; (v) $-x+1/2$, $y+1/2$, $z+1/2$.

Pentaaqua(3,5-dimethylpyridine-κN)cobalt(II) sulfate (2)

Crystal data

[Co(C7H9N)(H2O)5]SO4	D_x = 1.708 Mg m^{-3}
M_r = 352.22	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, $Pnma$	Cell parameters from 6866 reflections
a = 17.1238 (10) Å	θ = 3.0–25.3°
b = 7.1064 (4) Å	μ = 1.44 mm^{-1}
c = 11.2576 (6) Å	T = 297 K
V = 1369.92 (13) Å^3	BLOCK, pink
Z = 4	0.08 × 0.08 × 0.06 mm
$F(000)$ = 732	

Data collection

Bruker D8 Venture CMOS diffractometer	1367 independent reflections
φ and ω scans	1194 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2021)	$R_{int} = 0.070$
	$\theta_{max} = 25.4°$, $\theta_{min} = 3.0°$
$T_{min} = 0.714$, $T_{max} = 0.745$	$h = -20 \rightarrow 20$
32289 measured reflections	$k = -8 \rightarrow 8$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.028$	
$wR(F^2) = 0.069$	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.9563P]$
$S = 1.12$	where $P = (F_o^2 + 2F_c^2)/3$
1367 reflections	$(\Delta/\sigma)_{max} < 0.001$
128 parameters	$\Delta\rho_{max} = 0.43$ e Å^{-3}
7 restraints	$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Co1	0.38970 (2)	0.750000	0.19737 (4)	0.02337 (15)	
S1	0.33394 (4)	0.250000	−0.03379 (7)	0.02209 (19)	
O1	0.35093 (18)	0.750000	0.0198 (2)	0.0394 (6)	
O2	0.46967 (11)	0.9655 (3)	0.14383 (16)	0.0336 (4)	
O3	0.31132 (11)	0.5387 (3)	0.24411 (17)	0.0384 (4)	
O4	0.29778 (16)	0.250000	0.0839 (2)	0.0427 (7)	
O5	0.31138 (11)	0.0802 (2)	−0.09856 (16)	0.0406 (5)	
O6	0.42011 (14)	0.250000	−0.0164 (2)	0.0396 (6)	
N1	0.44535 (16)	0.750000	0.3648 (2)	0.0251 (6)	
C1	0.5235 (2)	0.750000	0.3707 (3)	0.0293 (7)	
H1A	0.551507	0.750000	0.299987	0.035*	
C2	0.56474 (19)	0.750000	0.4765 (3)	0.0279 (7)	
C3	0.5217 (2)	0.750000	0.5803 (3)	0.0315 (8)	
H3	0.547380	0.750000	0.653096	0.038*	
C4	0.4411 (2)	0.750000	0.5776 (3)	0.0297 (7)	
C5	0.40575 (19)	0.750000	0.4670 (3)	0.0268 (7)	
H5	0.351489	0.750000	0.463642	0.032*	
C6	0.6528 (2)	0.750000	0.4759 (4)	0.0439 (10)	
H6A	0.671655	0.688585	0.546196	0.066*	0.5
H6B	0.671452	0.877337	0.474120	0.066*	0.5
H6C	0.671263	0.684078	0.406972	0.066*	0.5
C7	0.3926 (2)	0.750000	0.6890 (3)	0.0465 (10)	

H7A	0.420270	0.814262	0.751028	0.070*	0.5
H7B	0.382469	0.622638	0.712901	0.070*	0.5
H7C	0.343972	0.813100	0.674071	0.070*	0.5
H1	0.3369 (18)	0.838 (3)	−0.016 (2)	0.058 (10)*	
H2A	0.4543 (17)	1.052 (3)	0.108 (2)	0.058 (11)*	
H2B	0.5060 (14)	0.928 (5)	0.108 (3)	0.079 (14)*	
H3A	0.2753 (11)	0.555 (4)	0.284 (2)	0.046 (9)*	
H3B	0.3023 (16)	0.457 (3)	0.201 (2)	0.053 (10)*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0234 (2)	0.0267 (2)	0.0200 (2)	0.000	−0.00065 (17)	0.000
S1	0.0216 (4)	0.0213 (4)	0.0233 (4)	0.000	−0.0020 (3)	0.000
O1	0.0592 (18)	0.0293 (15)	0.0298 (14)	0.000	−0.0181 (13)	0.000
O2	0.0318 (10)	0.0375 (10)	0.0316 (9)	−0.0022 (8)	0.0004 (8)	0.0067 (9)
O3	0.0381 (11)	0.0389 (11)	0.0382 (10)	−0.0127 (9)	0.0118 (9)	−0.0095 (9)
O4	0.0531 (17)	0.0397 (15)	0.0354 (14)	0.000	0.0166 (12)	0.000
O5	0.0531 (11)	0.0261 (10)	0.0427 (10)	−0.0013 (8)	−0.0190 (9)	−0.0058 (8)
O6	0.0228 (12)	0.0426 (15)	0.0532 (16)	0.000	−0.0015 (11)	0.000
N1	0.0255 (14)	0.0280 (15)	0.0218 (13)	0.000	−0.0028 (11)	0.000
C1	0.0298 (18)	0.0311 (18)	0.0270 (17)	0.000	0.0007 (14)	0.000
C2	0.0270 (17)	0.0258 (17)	0.0309 (18)	0.000	−0.0047 (14)	0.000
C3	0.0344 (19)	0.036 (2)	0.0245 (16)	0.000	−0.0085 (14)	0.000
C4	0.0341 (18)	0.0292 (18)	0.0258 (17)	0.000	0.0003 (14)	0.000
C5	0.0248 (16)	0.0290 (17)	0.0266 (17)	0.000	−0.0031 (13)	0.000
C6	0.0238 (19)	0.060 (3)	0.048 (2)	0.000	−0.0031 (16)	0.000
C7	0.043 (2)	0.070 (3)	0.0268 (19)	0.000	0.0016 (17)	0.000

Geometric parameters (Å, º)

Co1—O1	2.106 (3)	N1—C5	1.335 (4)
Co1—O2	2.1408 (18)	C1—H1A	0.9300
Co1—O2^i	2.1408 (18)	C1—C2	1.384 (5)
Co1—O3	2.0813 (18)	C2—C3	1.382 (5)
Co1—O3^i	2.0813 (18)	C2—C6	1.507 (5)
Co1—N1	2.112 (3)	C3—H3	0.9300
S1—O4	1.462 (3)	C3—C4	1.380 (5)
S1—O5^{ii}	1.4618 (17)	C4—C5	1.385 (5)
S1—O5	1.4618 (17)	C4—C7	1.504 (5)
S1—O6	1.488 (2)	C5—H5	0.9300
O1—H1^i	0.778 (10)	C6—H6A	0.9600
O1—H1	0.778 (10)	C6—H6B	0.9600
O2—H2A	0.782 (10)	C6—H6C	0.9600
O2—H2B	0.784 (10)	C7—H7A	0.9600
O3—H3A	0.774 (10)	C7—H7B	0.9600
O3—H3B	0.776 (10)	C7—H7C	0.9600
N1—C1	1.339 (4)		

O1—Co1—O2ⁱ	86.24 (8)	C1—N1—Co1	119.7 (2)
O1—Co1—O2	86.24 (8)	C5—N1—Co1	122.7 (2)
O1—Co1—N1	171.55 (11)	C5—N1—C1	117.7 (3)
O2—Co1—O2ⁱ	91.32 (11)	N1—C1—H1A	118.2
O3—Co1—O1	92.10 (8)	N1—C1—C2	123.6 (3)
O3ⁱ—Co1—O1	92.10 (8)	C2—C1—H1A	118.2
O3ⁱ—Co1—O2	88.15 (8)	C1—C2—C6	120.5 (3)
O3—Co1—O2ⁱ	88.15 (8)	C3—C2—C1	117.1 (3)
O3ⁱ—Co1—O2ⁱ	178.29 (8)	C3—C2—C6	122.5 (3)
O3—Co1—O2	178.29 (8)	C2—C3—H3	119.5
O3—Co1—O3ⁱ	92.32 (11)	C4—C3—C2	121.0 (3)
O3ⁱ—Co1—N1	93.74 (8)	C4—C3—H3	119.5
O3—Co1—N1	93.74 (8)	C3—C4—C5	117.2 (3)
N1—Co1—O2	87.86 (7)	C3—C4—C7	122.3 (3)
N1—Co1—O2ⁱ	87.86 (7)	C5—C4—C7	120.5 (3)
O4—S1—O6	107.51 (16)	N1—C5—C4	123.6 (3)
O5ⁱⁱ—S1—O4	109.87 (10)	N1—C5—H5	118.2
O5—S1—O4	109.87 (10)	C4—C5—H5	118.2
O5ⁱⁱ—S1—O5	111.27 (14)	C2—C6—H6A	109.5
O5ⁱⁱ—S1—O6	109.12 (10)	C2—C6—H6B	109.5
O5—S1—O6	109.12 (10)	C2—C6—H6C	109.5
Co1—O1—H1	126 (2)	H6A—C6—H6B	109.5
Co1—O1—H1ⁱ	126 (2)	H6A—C6—H6C	109.5
H1—O1—H1ⁱ	106 (5)	H6B—C6—H6C	109.5
Co1—O2—H2A	120 (2)	C4—C7—H7A	109.5
Co1—O2—H2B	114 (3)	C4—C7—H7B	109.5
H2A—O2—H2B	105.7 (16)	C4—C7—H7C	109.5
Co1—O3—H3A	124 (2)	H7A—C7—H7B	109.5
Co1—O3—H3B	121 (2)	H7A—C7—H7C	109.5
H3A—O3—H3B	108.7 (17)	H7B—C7—H7C	109.5
Co1—N1—C1—C2	180.000 (1)	C2—C3—C4—C5	0.000 (1)
Co1—N1—C5—C4	180.000 (1)	C2—C3—C4—C7	180.000 (1)
N1—C1—C2—C3	0.000 (1)	C3—C4—C5—N1	0.000 (1)
N1—C1—C2—C6	180.000 (1)	C5—N1—C1—C2	0.000 (1)
C1—N1—C5—C4	0.000 (1)	C6—C2—C3—C4	180.000 (1)
C1—C2—C3—C4	0.000 (1)	C7—C4—C5—N1	180.000 (1)

Symmetry codes: (i) x, $-y+3/2$, z; (ii) x, $-y+1/2$, z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O5ⁱⁱⁱ	0.78 (1)	2.01 (1)	2.782 (2)	173 (3)
O2—H2A···O6ⁱⁱⁱ	0.78 (1)	2.07 (1)	2.840 (3)	169 (3)
O2—H2B···O6ⁱᵛ	0.78 (1)	2.07 (2)	2.822 (3)	161 (4)

O3—H3A⋯O5^v	0.77 (1)	1.99 (1)	2.764 (2)	174 (3)
O3—H3B⋯O4	0.78 (1)	1.97 (1)	2.742 (3)	171 (3)

Symmetry codes: (iii) $x, y+1, z$; (iv) $-x+1, -y+1, -z$; (v) $-x+1/2, y+1/2, z+1/2$.

Pentaaqua(3,5-dimethylpyridine-κN)nickel(II) sulfate (3)

Crystal data

[Ni(C_7H_9N)(H_2O)$_5$]SO_4
$M_r = 352.00$
Orthorhombic, *Pnma*
$a = 17.1196 (8)$ Å
$b = 7.0609 (3)$ Å
$c = 11.2233 (5)$ Å
$V = 1356.67 (10)$ Å^3
$Z = 4$
$F(000) = 736$

$D_x = 1.723$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9899 reflections
$\theta = 3.0–26.3°$
$\mu = 1.62$ mm^{-1}
$T = 297$ K
BLOCK, green
$0.17 \times 0.04 \times 0.03$ mm

Data collection

Bruker D8 Venture CMOS
    diffractometer
φ and ω scans
Absorption correction: multi-scan
    (SADABS; Bruker, 2021)
$T_{min} = 0.680$, $T_{max} = 0.745$
36924 measured reflections

1499 independent reflections
1386 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 26.4°$, $\theta_{min} = 3.6°$
$h = -21 \rightarrow 20$
$k = -8 \rightarrow 8$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.060$
$S = 1.10$
1499 reflections
128 parameters
7 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent
    and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 0.6821P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.39091 (2)	0.750000	0.19852 (3)	0.02146 (11)	
S1	0.33343 (3)	0.250000	−0.03397 (5)	0.02160 (14)	
O1	0.35007 (14)	0.750000	0.02346 (18)	0.0384 (5)	
O2	0.46878 (7)	0.9627 (2)	0.14536 (12)	0.0309 (3)	
O3	0.31406 (8)	0.5401 (2)	0.24601 (12)	0.0354 (3)	
O4	0.29830 (12)	0.250000	0.08496 (18)	0.0424 (5)	
O5	0.31029 (8)	0.0794 (2)	−0.09827 (12)	0.0410 (3)	

O6	0.41976 (10)	0.250000	−0.01750 (19)	0.0394 (5)	
N1	0.44466 (12)	0.750000	0.36335 (17)	0.0241 (4)	
C1	0.52308 (14)	0.750000	0.3692 (2)	0.0277 (5)	
H1A	0.551105	0.750000	0.298181	0.033*	
C2	0.56433 (14)	0.750000	0.4753 (2)	0.0272 (5)	
C3	0.52130 (15)	0.750000	0.5799 (2)	0.0304 (6)	
H3	0.546992	0.750000	0.652878	0.036*	
C4	0.44033 (15)	0.750000	0.5768 (2)	0.0282 (5)	
C5	0.40464 (14)	0.750000	0.4658 (2)	0.0260 (5)	
H5	0.350357	0.750000	0.462450	0.031*	
C6	0.65243 (15)	0.750000	0.4748 (3)	0.0409 (7)	
H6A	0.671277	0.686857	0.544900	0.061*	0.5
H6B	0.671120	0.878180	0.474031	0.061*	0.5
H6C	0.670966	0.684963	0.405226	0.061*	0.5
C7	0.39189 (17)	0.750000	0.6886 (2)	0.0429 (7)	
H7A	0.418880	0.818472	0.750001	0.064*	0.5
H7B	0.383346	0.621918	0.714204	0.064*	0.5
H7C	0.342529	0.809610	0.673085	0.064*	0.5
H1	0.3354 (14)	0.840 (3)	−0.011 (2)	0.057 (8)*	
H2A	0.4540 (12)	1.048 (2)	0.1067 (18)	0.045 (7)*	
H2B	0.5056 (10)	0.923 (3)	0.1115 (19)	0.062 (9)*	
H3A	0.2777 (9)	0.557 (3)	0.2854 (16)	0.041 (6)*	
H3B	0.3050 (12)	0.460 (3)	0.2012 (16)	0.048 (7)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02095 (16)	0.02450 (18)	0.01894 (17)	0.000	−0.00045 (11)	0.000
S1	0.0213 (3)	0.0206 (3)	0.0229 (3)	0.000	−0.0023 (2)	0.000
O1	0.0564 (13)	0.0289 (11)	0.0300 (10)	0.000	−0.0187 (9)	0.000
O2	0.0301 (7)	0.0325 (7)	0.0300 (7)	−0.0018 (6)	0.0016 (5)	0.0060 (6)
O3	0.0348 (7)	0.0370 (8)	0.0343 (7)	−0.0105 (6)	0.0108 (6)	−0.0078 (7)
O4	0.0527 (12)	0.0386 (12)	0.0357 (11)	0.000	0.0161 (9)	0.000
O5	0.0544 (8)	0.0269 (7)	0.0417 (8)	0.0008 (6)	−0.0201 (6)	−0.0060 (6)
O6	0.0232 (9)	0.0435 (12)	0.0515 (12)	0.000	0.0003 (8)	0.000
N1	0.0243 (9)	0.0260 (11)	0.0221 (10)	0.000	−0.0029 (8)	0.000
C1	0.0252 (11)	0.0302 (14)	0.0277 (13)	0.000	0.0008 (10)	0.000
C2	0.0244 (12)	0.0273 (13)	0.0299 (13)	0.000	−0.0044 (10)	0.000
C3	0.0330 (13)	0.0339 (14)	0.0242 (12)	0.000	−0.0086 (10)	0.000
C4	0.0323 (12)	0.0280 (13)	0.0243 (12)	0.000	0.0004 (10)	0.000
C5	0.0251 (11)	0.0271 (13)	0.0258 (12)	0.000	−0.0022 (9)	0.000
C6	0.0219 (12)	0.0562 (19)	0.0444 (17)	0.000	−0.0065 (11)	0.000
C7	0.0392 (15)	0.064 (2)	0.0251 (14)	0.000	0.0012 (11)	0.000

Geometric parameters (Å, º)

Ni1—O1	2.0855 (19)	N1—C5	1.339 (3)
Ni1—O2	2.0949 (13)	C1—H1A	0.9300

Ni1—O2[i]	2.0949 (13)	C1—C2	1.384 (3)
Ni1—O3	2.0522 (13)	C2—C3	1.386 (4)
Ni1—O3[i]	2.0522 (13)	C2—C6	1.508 (3)
Ni1—N1	2.066 (2)	C3—H3	0.9300
S1—O4	1.464 (2)	C3—C4	1.387 (4)
S1—O5[ii]	1.4588 (14)	C4—C5	1.387 (3)
S1—O5	1.4588 (14)	C4—C7	1.505 (4)
S1—O6	1.4895 (19)	C5—H5	0.9300
O1—H1[i]	0.782 (10)	C6—H6A	0.9600
O1—H1	0.782 (10)	C6—H6B	0.9600
O2—H2A	0.782 (9)	C6—H6C	0.9600
O2—H2B	0.787 (9)	C7—H7A	0.9600
O3—H3A	0.773 (9)	C7—H7B	0.9600
O3—H3B	0.774 (9)	C7—H7C	0.9600
N1—C1	1.344 (3)		
O1—Ni1—O2[i]	86.85 (6)	C1—N1—Ni1	119.23 (17)
O1—Ni1—O2	86.85 (6)	C5—N1—Ni1	122.77 (16)
O2[i]—Ni1—O2	91.60 (8)	C5—N1—C1	118.0 (2)
O3[i]—Ni1—O1	91.70 (6)	N1—C1—H1A	118.3
O3—Ni1—O1	91.70 (6)	N1—C1—C2	123.4 (2)
O3[i]—Ni1—O2	87.95 (6)	C2—C1—H1A	118.3
O3—Ni1—O2	178.51 (6)	C1—C2—C3	117.2 (2)
O3—Ni1—O2[i]	87.95 (6)	C1—C2—C6	120.5 (2)
O3[i]—Ni1—O2[i]	178.51 (6)	C3—C2—C6	122.3 (2)
O3—Ni1—O3[i]	92.46 (8)	C2—C3—H3	119.7
O3[i]—Ni1—N1	93.04 (6)	C2—C3—C4	120.7 (2)
O3—Ni1—N1	93.04 (6)	C4—C3—H3	119.7
N1—Ni1—O1	173.14 (9)	C3—C4—C5	117.6 (2)
N1—Ni1—O2	88.38 (5)	C3—C4—C7	122.0 (2)
N1—Ni1—O2[i]	88.37 (5)	C5—C4—C7	120.4 (2)
O4—S1—O6	107.12 (13)	N1—C5—C4	123.1 (2)
O5[ii]—S1—O4	109.84 (8)	N1—C5—H5	118.5
O5—S1—O4	109.85 (8)	C4—C5—H5	118.5
O5[ii]—S1—O5	111.30 (11)	C2—C6—H6A	109.5
O5—S1—O6	109.32 (8)	C2—C6—H6B	109.5
O5[ii]—S1—O6	109.32 (8)	C2—C6—H6C	109.5
Ni1—O1—H1	124.8 (19)	H6A—C6—H6B	109.5
Ni1—O1—H1[i]	124.8 (19)	H6A—C6—H6C	109.5
H1—O1—H1[i]	108 (4)	H6B—C6—H6C	109.5
Ni1—O2—H2A	120.2 (17)	C4—C7—H7A	109.5
Ni1—O2—H2B	113.1 (19)	C4—C7—H7B	109.5
H2A—O2—H2B	105.3 (15)	C4—C7—H7C	109.5
Ni1—O3—H3A	123.6 (16)	H7A—C7—H7B	109.5
Ni1—O3—H3B	119.3 (16)	H7A—C7—H7C	109.5
H3A—O3—H3B	108.9 (15)	H7B—C7—H7C	109.5
Ni1—N1—C1—C2	180.000 (1)	C2—C3—C4—C5	0.000 (1)

Ni1—N1—C5—C4	180.000 (1)	C2—C3—C4—C7	180.000 (1)
N1—C1—C2—C3	0.000 (1)	C3—C4—C5—N1	0.000 (1)
N1—C1—C2—C6	180.000 (1)	C5—N1—C1—C2	0.000 (1)
C1—N1—C5—C4	0.000 (1)	C6—C2—C3—C4	180.000 (1)
C1—C2—C3—C4	0.000 (1)	C7—C4—C5—N1	180.000 (1)

Symmetry codes: (i) x, $-y+3/2$, z; (ii) x, $-y+1/2$, z.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O5[iii]	0.78 (1)	2.00 (1)	2.7822 (18)	174 (3)
O2—H2A⋯O6[iii]	0.78 (1)	2.08 (1)	2.857 (2)	172 (2)
O2—H2B⋯O6[iv]	0.79 (1)	2.06 (1)	2.821 (2)	163 (3)
O3—H3A⋯O5[v]	0.77 (1)	2.00 (1)	2.7683 (18)	173 (2)
O3—H3B⋯O4	0.77 (1)	1.98 (1)	2.745 (2)	172 (2)

Symmetry codes: (iii) x, $y+1$, z; (iv) $-x+1$, $-y+1$, $-z$; (v) $-x+1/2$, $y+1/2$, $z+1/2$.

Pentaaqua(3,5-dimethylpyridine-κN)zinc(II) sulfate (4)

Crystal data

[Zn(C$_7$H$_9$N)(H$_2$O)$_5$]SO$_4$	$D_x = 1.739$ Mg m^{-3}
$M_r = 358.66$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $Pnma$	Cell parameters from 9907 reflections
$a = 17.1312$ (8) Å	$\theta = 3.0$–$26.1°$
$b = 7.0826$ (3) Å	$\mu = 1.99$ mm^{-1}
$c = 11.2879$ (5) Å	$T = 297$ K
$V = 1369.60$ (11) Å^3	BLOCK, colourless
$Z = 4$	$0.21 \times 0.13 \times 0.1$ mm
$F(000) = 744$	

Data collection

Bruker D8 Venture CMOS diffractometer	1516 independent reflections
φ and ω scans	1414 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2021)	$R_{int} = 0.042$
	$\theta_{max} = 26.4°$, $\theta_{min} = 3.0°$
$T_{min} = 0.671$, $T_{max} = 0.745$	$h = -21 \rightarrow 21$
46710 measured reflections	$k = -8 \rightarrow 8$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.021$	
$wR(F^2) = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 0.6476P]$
$S = 1.12$	where $P = (F_o^2 + 2F_c^2)/3$
1516 reflections	$(\Delta/\sigma)_{max} < 0.001$
128 parameters	$\Delta\rho_{max} = 0.40$ e Å^{-3}
7 restraints	$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Zn1	0.38941 (2)	0.750000	0.20029 (2)	0.02445 (10)	
S1	0.33349 (3)	0.250000	−0.03485 (5)	0.02238 (13)	
O1	0.35283 (14)	0.750000	0.02014 (17)	0.0411 (5)	
O2	0.46998 (8)	0.9672 (2)	0.14481 (11)	0.0334 (3)	
O3	0.31084 (8)	0.5381 (2)	0.24347 (13)	0.0393 (3)	
O4	0.29751 (12)	0.250000	0.08280 (17)	0.0435 (5)	
O5	0.31108 (8)	0.07969 (19)	−0.09923 (12)	0.0418 (3)	
O6	0.41959 (10)	0.250000	−0.01709 (19)	0.0403 (5)	
N1	0.44544 (12)	0.750000	0.36501 (17)	0.0258 (4)	
C1	0.52356 (14)	0.750000	0.3709 (2)	0.0292 (5)	
H1A	0.551519	0.750000	0.300258	0.035*	
C2	0.56501 (14)	0.750000	0.4762 (2)	0.0296 (5)	
C3	0.52173 (15)	0.750000	0.5806 (2)	0.0314 (5)	
H3	0.547367	0.750000	0.653242	0.038*	
C4	0.44114 (15)	0.750000	0.5775 (2)	0.0290 (5)	
C5	0.40543 (14)	0.750000	0.4668 (2)	0.0273 (5)	
H5	0.351191	0.750000	0.463327	0.033*	
C6	0.65285 (15)	0.750000	0.4765 (3)	0.0440 (7)	
H6A	0.671449	0.681907	0.544387	0.066*	0.5
H6B	0.671527	0.877698	0.479610	0.066*	0.5
H6C	0.671616	0.690396	0.405608	0.066*	0.5
C7	0.39253 (17)	0.750000	0.6883 (2)	0.0438 (7)	
H7A	0.419605	0.817081	0.749703	0.066*	0.5
H7B	0.383455	0.622262	0.713159	0.066*	0.5
H7C	0.343476	0.810656	0.672744	0.066*	0.5
H1	0.3379 (13)	0.836 (2)	−0.0171 (18)	0.052 (7)*	
H2A	0.4540 (12)	1.049 (3)	0.1049 (18)	0.050 (7)*	
H2B	0.5065 (11)	0.928 (4)	0.1108 (19)	0.068 (9)*	
H3A	0.2758 (10)	0.550 (3)	0.2857 (16)	0.050 (7)*	
H3B	0.3024 (13)	0.458 (3)	0.1986 (16)	0.049 (7)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02442 (15)	0.02788 (16)	0.02103 (15)	0.000	−0.00072 (10)	0.000
S1	0.0220 (3)	0.0216 (3)	0.0235 (3)	0.000	−0.0025 (2)	0.000
O1	0.0616 (13)	0.0301 (11)	0.0317 (10)	0.000	−0.0188 (9)	0.000
O2	0.0320 (7)	0.0367 (7)	0.0314 (6)	−0.0012 (6)	0.0013 (5)	0.0063 (6)
O3	0.0387 (7)	0.0406 (8)	0.0387 (7)	−0.0129 (6)	0.0121 (6)	−0.0103 (7)

O4	0.0544 (12)	0.0396 (11)	0.0366 (10)	0.000	0.0167 (9)	0.000
O5	0.0541 (8)	0.0274 (7)	0.0438 (7)	0.0002 (6)	−0.0201 (6)	−0.0064 (6)
O6	0.0229 (9)	0.0446 (11)	0.0533 (12)	0.000	0.0002 (8)	0.000
N1	0.0275 (10)	0.0274 (10)	0.0226 (9)	0.000	−0.0034 (8)	0.000
C1	0.0259 (12)	0.0339 (13)	0.0278 (12)	0.000	0.0004 (9)	0.000
C2	0.0265 (12)	0.0284 (12)	0.0340 (13)	0.000	−0.0046 (10)	0.000
C3	0.0331 (13)	0.0351 (14)	0.0259 (12)	0.000	−0.0085 (10)	0.000
C4	0.0318 (12)	0.0310 (13)	0.0242 (11)	0.000	0.0001 (10)	0.000
C5	0.0237 (11)	0.0304 (13)	0.0277 (12)	0.000	−0.0018 (9)	0.000
C6	0.0236 (13)	0.0580 (19)	0.0504 (17)	0.000	−0.0049 (11)	0.000
C7	0.0399 (15)	0.066 (2)	0.0251 (13)	0.000	0.0028 (11)	0.000

Geometric parameters (Å, º)

Zn1—O1	2.1279 (19)	N1—C5	1.337 (3)
Zn1—O2	2.1598 (13)	C1—H1A	0.9300
Zn1—O2ⁱ	2.1598 (13)	C1—C2	1.385 (3)
Zn1—O3	2.0742 (13)	C2—C3	1.392 (4)
Zn1—O3ⁱ	2.0742 (13)	C2—C6	1.505 (3)
Zn1—N1	2.0924 (19)	C3—H3	0.9300
S1—O4	1.4641 (19)	C3—C4	1.381 (4)
S1—O5ⁱⁱ	1.4596 (13)	C4—C5	1.392 (3)
S1—O5	1.4596 (13)	C4—C7	1.502 (3)
S1—O6	1.4886 (18)	C5—H5	0.9300
O1—H1ⁱ	0.784 (10)	C6—H6A	0.9600
O1—H1	0.784 (10)	C6—H6B	0.9600
O2—H2A	0.784 (9)	C6—H6C	0.9600
O2—H2B	0.785 (9)	C7—H7A	0.9600
O3—H3A	0.771 (9)	C7—H7B	0.9600
O3—H3B	0.773 (9)	C7—H7C	0.9600
N1—C1	1.340 (3)		
O1—Zn1—O2ⁱ	84.90 (6)	C1—N1—Zn1	120.14 (16)
O1—Zn1—O2	84.90 (6)	C5—N1—Zn1	121.87 (16)
O2ⁱ—Zn1—O2	90.87 (8)	C5—N1—C1	118.0 (2)
O3ⁱ—Zn1—O1	91.92 (6)	N1—C1—H1A	118.2
O3—Zn1—O1	91.92 (6)	N1—C1—C2	123.7 (2)
O3ⁱ—Zn1—O2	88.13 (6)	C2—C1—H1A	118.2
O3—Zn1—O2	176.74 (5)	C1—C2—C3	117.0 (2)
O3—Zn1—O2ⁱ	88.13 (6)	C1—C2—C6	120.9 (2)
O3ⁱ—Zn1—O2ⁱ	176.74 (5)	C3—C2—C6	122.1 (2)
O3—Zn1—O3ⁱ	92.71 (8)	C2—C3—H3	119.6
O3ⁱ—Zn1—N1	95.10 (6)	C4—C3—C2	120.7 (2)
O3—Zn1—N1	95.10 (6)	C4—C3—H3	119.6
N1—Zn1—O1	169.82 (9)	C3—C4—C5	117.5 (2)
N1—Zn1—O2	87.97 (5)	C3—C4—C7	122.2 (2)
N1—Zn1—O2ⁱ	87.97 (5)	C5—C4—C7	120.3 (2)
O4—S1—O6	107.16 (12)	N1—C5—C4	123.1 (2)

O5ⁱⁱ—S1—O4	109.93 (8)	N1—C5—H5	118.4
O5—S1—O4	109.93 (8)	C4—C5—H5	118.4
O5ⁱⁱ—S1—O5	111.46 (11)	C2—C6—H6A	109.5
O5—S1—O6	109.12 (7)	C2—C6—H6B	109.5
O5ⁱⁱ—S1—O6	109.12 (7)	C2—C6—H6C	109.5
Zn1—O1—H1	127.5 (18)	H6A—C6—H6B	109.5
Zn1—O1—H1ⁱ	127.5 (18)	H6A—C6—H6C	109.5
H1—O1—H1ⁱ	102 (4)	H6B—C6—H6C	109.5
Zn1—O2—H2A	118.1 (17)	C4—C7—H7A	109.5
Zn1—O2—H2B	114 (2)	C4—C7—H7B	109.5
H2A—O2—H2B	105.0 (14)	C4—C7—H7C	109.5
Zn1—O3—H3A	125.1 (17)	H7A—C7—H7B	109.5
Zn1—O3—H3B	119.8 (16)	H7A—C7—H7C	109.5
H3A—O3—H3B	109.6 (16)	H7B—C7—H7C	109.5
Zn1—N1—C1—C2	180.000 (1)	C2—C3—C4—C5	0.000 (1)
Zn1—N1—C5—C4	180.000 (1)	C2—C3—C4—C7	180.000 (1)
N1—C1—C2—C3	0.000 (1)	C3—C4—C5—N1	0.000 (1)
N1—C1—C2—C6	180.000 (1)	C5—N1—C1—C2	0.000 (1)
C1—N1—C5—C4	0.000 (1)	C6—C2—C3—C4	180.000 (1)
C1—C2—C3—C4	0.000 (1)	C7—C4—C5—N1	180.000 (1)

Symmetry codes: (i) *x*, −*y*+3/2, *z*; (ii) *x*, −*y*+1/2, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O5ⁱⁱⁱ	0.78 (1)	2.01 (1)	2.7892 (17)	172 (3)
O2—H2*A*···O6ⁱⁱⁱ	0.78 (1)	2.07 (1)	2.845 (2)	173 (2)
O2—H2*B*···O6^{iv}	0.79 (1)	2.08 (1)	2.833 (2)	162 (3)
O3—H3*A*···O5^v	0.77 (1)	1.99 (1)	2.7571 (18)	177 (2)
O3—H3*B*···O4	0.77 (1)	1.97 (1)	2.7395 (19)	172 (2)

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