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STRUCTURAL CHEMISTRY

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A nickel(II) coordination complex, bis[2,6-bis(1H-benzimidazol-2-yl-κN^3)pyridine-κN]nickel(II) sulfate, [Ni($C_{19}H_{13}N_5$)$_2$]SO$_4$ or [Ni(H$_2L$)$_2$]SO$_4$, having four peripheral tetrahedrally oriented N—H donor units, combines with sulfate bridges to create hydrogen-bonded structures of varied dimensionality. The three crystal structures reported herein in the space groups $P2_12_12_1$, $I\bar{4}$ and $Pccn$ are defined solely by strong charge-assisted N—H$\cdots$O hydrogen bonds and contain disordered guests (water and dimethylformamide) that vary in size, shape and degree of hydrophilicity. Two of the compounds are channelled solids with three-dimensional structures, while the third is one-dimensional in nature. In spite of their differences, all three present a striking resemblance to the previously reported anhydrous relative [Guo *et al.* (2011). *Chin. J. Inorg. Chem.* **27**, 1517–1520], which is considered as the reference framework from which all three title compounds are derived. The hydrogen-bonded frameworks are described and compared using crystallographic and topological approaches.

1. Introduction

In the process of looking for adequate metal–organic nodes for hydrogen-bonded frameworks, we came across a family of complexes we had worked with some time ago (Harvey *et al.*, 2003, 2013), formulated as M(H$_2L$)$_2$ [H$_2L$ is 2,6-bis(1H-benzimidazol-2-yl)pyridine and M is a transition metal], where the two identical H$_2L$ ligands bind the metal in an orthogonal fashion relative to each other, giving the bulky M(H$_2L$)$_2$ group a 'pseudo-spherical' shape, with four active N—H donor groups pointing outwards in an approximate tetrahedral geometry around the metal atom (Fig. 1*a*). The bulky group looked promising as a 'tetrahedral hydrogen-bonding donor' acting as a nodal centre in an eventual hydrogen-bond network (Fig. 1*b*), in which case, a linker could be chosen with similar acceptor capabilities which are able to expand by self-organization into a porous three-dimensional array. The simplest example we could think of was sulfate (SO$_4^{2-}$), with a similar tetrahedral distribution of hydrogen-bonding acceptors. The feasibility of this approach was assessed with respect to other complex structures already reported in the literature, *viz.* the interpenetrating network in a hydrogen-bonded chromium sulfate biimidazolate described by Larsson & Öhrström (2003), and we decided to attempt the synthesis of the corresponding M(H$_2L$)$_2$ sulfates in the hope of obtaining

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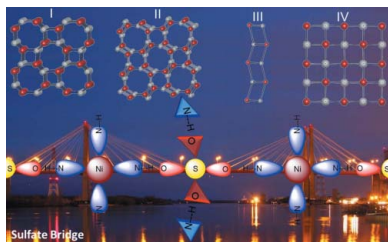
some kind of 'diamond-like' hydrogen-bonded structure. Investigation of the $M(H_2L)_2SO_4$ system proved fruitful in that it provided a number of compounds, not only with the expected geometry, as hydrogen-bonded porous networks, but also in their properties to fine tune their geometry by adequately choosing the solvates, which end up acting as efficient crystallization templates. We report herein the results of these attempts with Ni^{2+} as the cation and dimethylform-amide/water as the solvents.

$\cdot SO_4^{2-} \cdot nH_2O \cdot mC_3H_7NO$
(I)/(II)/(III)
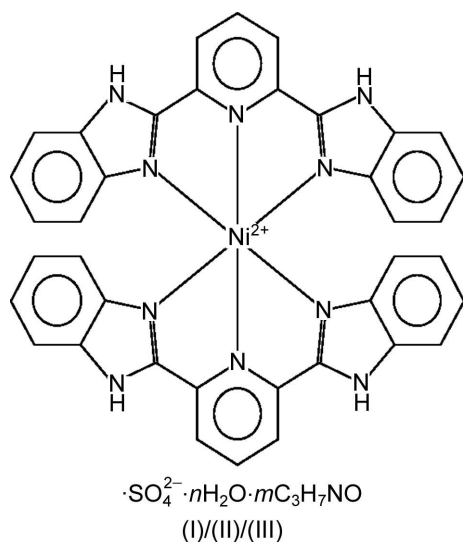
The three phases of bis[2,6-bis(1H-benzimidazol-2-yl-κN^3)-pyridine-κN]nickel(II) sulfate reported herein (see Scheme), with space groups $P2_12_12_1$ for (I), $I\bar{4}$ for (II) and $Pccn$ for (III), are formulated as $[Ni(H_2L)_2]SO_4 \cdot nH_2O \cdot m$DMF (DMF is dimethylformamide), with n and m undeterminable by conventional X-ray diffraction (XRD) methods (see *Refinement* section for details). A search in the Cambridge Structural Database (CSD, Version 5.37 and updates; Groom *et al.*, 2016) for pre-existing members of the $[Ni(H_2L)_2]^{2+}(SO_4)^{2-}$ family resulted in only an unsolvated member [Guo *et al.*, 2011; CSD refcode OYAKEF, hereinafter (IV)], which will be included as a reference in our discussion.

2. Experimental

2.1. Synthesis and crystallization

All reagents used were commercially available and used without further purification. Compound (I) was obtained by dissolution of NiSO$_4$·6H$_2$O (CAS Number 10101-97-0, Sigma–Aldrich) and H$_2$L (CAS Number 28020-73-7, Sigma–Aldrich) in DMF in a 1:2 molar ratio up to a final concentration of 0.010 M of the Ni^{2+} cation. Compounds (II) and (III) were synthesized in a similar fashion, by mixing equal volumes of equimolar solutions (0.010 M) of NiSO$_4$·6H$_2$O in water and H$_2$L in DMF. Upon mixing, the immediate precipitation of a preliminary poorly crystallized phase occurred, which was discarded. After a couple of months of unperturbed evaporation, pale-red columnar crystals pertaining to some of the reported phases were obtained, within a mixture of further untargeted products. The acquisition of one particular phase

could not so far be adequately controlled, its appearance being dependent on the solvent quality/ratio and crystallization conditions.

2.2. Refinement

All three title structures could be solved in a conventional way (*SHELXS97*; Sheldrick, 2008), but refinement (*SHELXL2016*; Sheldrick, 2015) posed some problems derived from the fact that the structures showed large solvent-accessible voids of 29, 46 and 7 vol% and any further improvement in the refinement was jeopardized by the disordered water/DMF solvent molecules delocalized in these regions. A direct consequence of this was the impossibility of refining (even with restraints) the active H atoms in the structures, which had to be treated, as had the rest, in the riding approximation [N—H = 0.86 Å and C—H = 0.93 Å, with $U_{iso}(H) = 1.2U_{eq}(host)$]. In view of these characteristics, the refinements were treated under the 'partial structure factors' algorithm implemented as the SQUEEZE option (Spek, 2015) in the *PLATON* package (Spek, 2009), which allowed for reasonable structural descriptions and reported R factors of 0.074 for (I), 0.078 for (II) and 0.086 for (III). For the non-H atoms, rigid-bond restraints were applied to the anisotropic displacement parameters of bonded (1,2-) and nonbonded (1,3-) atom pairs. In addition, similarity restraints were applied to the geometries of the two independent organic ligands of the cation in each structure.

2.3. Topological analysis

Topological analysis was performed using the *ToposPro* program package (Blatov *et al.*, 2014). The determination of all intermolecular interactions was carried out by means of the recently proposed 'domains method' (Blatov, 2016) that is based on Voronoi partition and implemented in the *AutoCN* program, which is a part of the *ToposPro* code. Among intermolecular interactions, the D—H$\cdots A$ hydrogen bonds in a fragment are identified in accordance with the following additional geometrical criteria: $d(H\cdots A) < 2.5$ Å, $d(D\cdots A) < 3.5$ Å and $\angle D$—H$\cdots A > 120°$ (D = N, O; A = N, O, F, S, Cl). The underlying nets of the investigated structures, which represent the overall connectivity of molecules in hydrogen-bonded networks, were obtained after the simplification procedure performed in the *ADS* program. This includes the representation of a molecule by its centre of mass, keeping the connectivity of molecules with each other by means of hydrogen bonds; all hydrogen bonds between a given pair of molecules transform to the same edge between the molecular centres of mass in the simplified net. The TTD collection of periodic network topologies and the TTO collection containing representatives of different topological types were used to determine the topological type of underlying nets (Blatov *et al.*, 2014). The RCSR three-letter symbols (O'Keeffe *et al.*, 2008) and the Koch & Fischer (1978) nomenclature for 1- or 2-periodic sphere packings are used to designate network topologies. The nets absent in the RCSR database are designated with the *ToposPro* NDn nomen-

Table 1
Crystal and refinement data for (I), (II) and (III) (herein reported), and (IV) (Guo *et al.*, 2011) (included for comparison).

	(I)	(II)	(III)	(IV) (CSD refcode OYAKEF)
Crystal data				
Chemical formula	[Ni(C$_{19}$H$_{13}$N$_5$)$_2$]SO$_4$ + Solv.	[Ni(C$_{19}$H$_{13}$N$_5$)$_2$]SO$_4$ + Solv.	[Ni(C$_{19}$H$_{13}$N$_5$)$_2$]SO$_4$·C$_3$H$_7$NO·4.25H$_2$O + Solv.	[Ni(C$_{19}$H$_{13}$N$_5$)$_2$]SO$_4$
M_r	777.46	777.46	925.10	777.46
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Tetragonal, $I\bar{4}$	Orthorhombic, $Pccn$	Monoclinic, $P2_1/c$
Temperature (K)	294	294	294	296
a, b, c (Å)	9.8015 (6), 20.9572 (15), 21.7012 (17)	28.596 (2), 28.596 (2), 13.5438 (9)	13.406 (5), 24.365 (5), 28.114 (5)	13.735 (8), 13.838 (8), 20.270 (11)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 90, 90	90, 106.133 (10), 90
V (Å^3)	4457.7 (5)	11075.0 (19)	9183 (4)	3701 (4)
Z	4	8	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.53	0.43	0.53	0.64
Crystal size (mm)	0.50 × 0.24 × 0.18	0.38 × 0.14 × 0.12	0.28 × 0.18 × 0.14	0.27 × 0.24 × 0.21
Data collection				
Diffractometer	Oxford Diffraction Gemini CCD S Ultra diffractometer	Oxford Diffraction Gemini CCD S Ultra diffractometer	Oxford Diffraction Gemini CCD S Ultra diffractometer	Bruker APEXII CCD diffractometer
Absorption correction	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.82, 0.92	0.96, 0.98	0.90, 0.94	0.847, 0.878
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19326, 9840, 5651	16294, 11374, 4172	32970, 10959, 4106	17697, 6347, 4602
R_{int}	0.085	0.095	0.166	0.052
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.680	0.679	0.691	0.595
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.074, 0.210, 0.98	0.078 0.220, 0.89	0.086, 0.334, 0.85	0.085, 0.193, 1.08
No. of reflections	9840	11374	10959	6347
No. of parameters	487	488	581	487
No. of restraints	586	586	552	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.47, −0.31	0.55, −0.23	0.67, −0.52	1.83, −1.22
Absolute structure	Flack x determined using 1523 quotients [$(I^+) - (I^-)$]/[$(I^+) + (I^-)$] (Parsons *et al.*, 2013)	Refined as an inversion twin	–	–
Absolute structure parameter	0.006 (19)	0.45 (3)	–	–

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

clature (Alexandrov *et al.*, 2011), where N is a sequence of coordination numbers of all non-equivalent nodes of the net, D is the periodicity of the net (D = M, C, L and T for 0-, 1-, 2- and 3-periodic nets, respectively) and n is the ordinal number of the net in the set of all non-isomorphic nets with the given ND sequence. The local connectivity of the molecules was described by means of the molecular connection type symbol (MCTS) L^{mbtkpghond} proposed in Aman *et al.* (2014) for the description of intermolecular connectivity in hydrogen-bonded networks. Each molecule (L) is designated by superscripts M, B, T, K, P, G, H, O, N and D depending on the number n = 1–10 of its atoms (both hydrogen-bond donors and acceptors) involved in the formation of intermolecular hydrogen bonds. The total number of molecules connected to a given molecule is listed as the upper index in the line mbtkpghond, where each integer m, b, t, k, *etc.*, corresponds to the number of molecules connected by one, two, three, four, *etc.*, hydrogen bonds. Additionally, a recent inclusion in the *ToposPro* package was applied to evaluate the coordination

modes of both the complex cation and the sulfate anion. This algorithm compares the similarity of the coordination figure of an atom or a molecule to some idealized coordination figures on the basis of comparison of angular fingerprints of coordination polyhedra (Shevchenko *et al.*, 2017). In these calculations, parameters δ and σ (as defined in Shevchenko's paper) were given values of 18 and 9°, respectively.

3. Results and discussion

3.1. Crystal structure

Table 1 presents crystal and refinement data for (I), (II) and (III) (reported herein), and (IV) (Guo *et al.*, 2011), included for comparison purposes. As already stated, the structures consist of [Ni(H$_2$L)$_2$]$^{2+}$ cations acting as fourfold hydrogen-bond donors (in the role of nodes) and sulfate counter-anions as hydrogen-bond acceptors (acting as linkers). Figs. 1(*c*), 1(*d*) and 1(*e*) show displacement ellipsoid plots for (I), (II) and
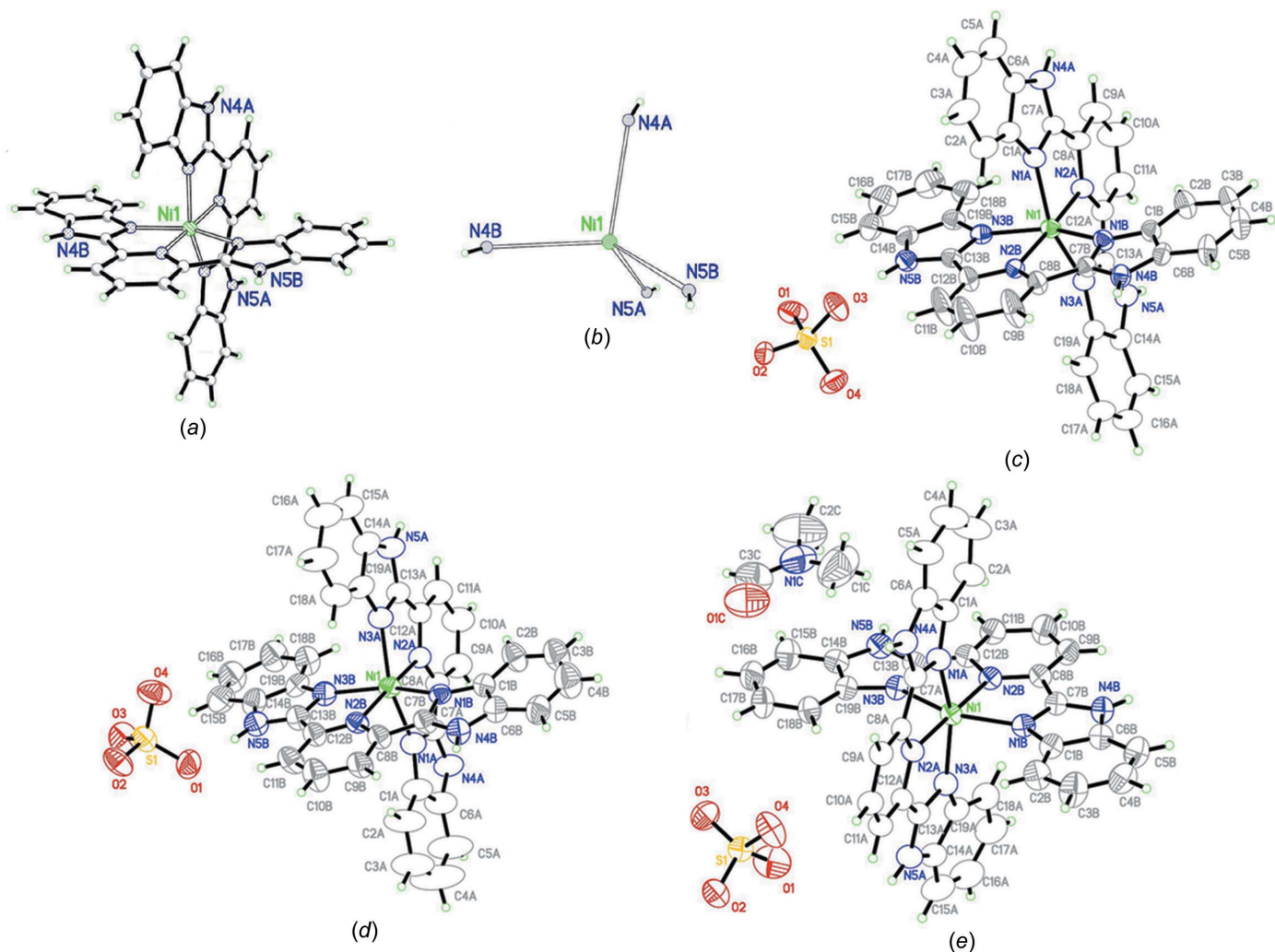
Figure 1
(a). A general ML_2 nucleus. (b) A schematic representation of panel (a) as a fourfold hydrogen-bonding donor node. (c)/(d)/(e) Displacement ellipsoid plots of the asymmetric units in structures (I), (II) and (III), respectively (water molecules not shown), drawn at the 40% probability level. The H_2L ligands, at right angles to each other, have been drawn with different line shading, for clarity.

(III), respectively, showing the (common) numbering scheme used. Both the cation and the anion display the geometries usually reported in the literature and will not be discussed in particular detail since our interest will be concentrated on their hydrogen-bonding behaviour (only a comparative table of similar coordination distances is provided; Table 2). Table 3 presents the hydrogen-bonding interactions for the three structures discussed herein (where all the available N—H groups are involved), as well as for the already reported (IV). Inspection of the table shows that in structures (I) and (II),

each sulfate ion binds to four different $Ni(H_2L)_2$ units through its four O atoms bound to four different N—H groups. In structure (III), instead, the sulfate anion binds to three $Ni(H_2L)_2$ units due to two O atoms (O1 and O3) being involved in a split hydrogen bond to the N5B—H5NB group. This leaves a fourth N—H group unbound to sulfate, but which binds to a solvent water molecule instead (N5A—H5AA···O3W).[1]

In (I) and (II), this connectivity leads to three-dimensional structures having large channels (Fig. 2). In the case of (I), there is only one type (denoted **A**) which runs along [100] and accounts for 30% of the total structure volume (Fig. 2a); in (II), there are two types (**A** and **B**), both running along [001] and accounting for as much as 45% (Fig. 2b). These volumes are in turn occupied by the disordered water/DMF solvent molecules. In (III), the result of $Ni(H_2L)_2···SO_4$ hydrogen bonding is a much simpler one-dimensional supramolecular structure, with interchain linkage diffusely mediated by water/DMF solvent molecules. Fig. 3(a) displays a horizontal view of column **A** in (I), showing the lateral 'mesh' which wraps the

<hr/>

[1] At this stage, it could be argued that the hydrogen-bonding analysis, as performed herein, would be potentially incomplete due to the unresolved water/DMF solvent molecules not being taken into account, in spite of their potential capability for hydrogen bonding. An argument against this position is to be found precisely in the 'unobservance' of defined solvent molecules: hydrogen bonding to the mainframe, when present at all, has a definite 'anchoring effect', whose most immediate result is the concentration of the corresponding electron density in a rather well-defined portion of space, thus rendering the molecule 'crystallographically visible' in a difference map. An example of this is the already discussed N5A—H5AA···O3W hydrogen bond in structure (III), which renders the O3W solvent molecule 'detectable'.

Table 2
Selected coordination distances (Å) for (I), (II), (III) and (IV).

Bond	(I)	(II)	(III)	(IV)
Ni1—N1A	2.108 (5)	2.128 (7)	2.118 (5)	2.117 (6)
Ni1—N2A	2.029 (5)	2.037 (6)	2.017 (4)	2.023 (6)
Ni1—N3A	2.113 (5)	2.115 (7)	2.086 (5)	2.128 (6)
Ni1—N1B	2.112 (6)	2.149 (7)	2.116 (5)	2.101 (6)
Ni1—N2B	2.022 (5)	2.026 (6)	2.021 (4)	1.998 (6)
Ni1—N3B	2.120 (6)	2.109 (7)	2.101 (5)	2.101 (6)

Table 3
Hydrogen-bond geometry (Å, °) for (I), (II), (III) and (IV).

Structure	D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
(I)	N4A—H4N$A\cdots$O2^i	0.86	1.82	2.654 (8)	163
	N5A—H5N$A\cdots$O1^{ii}	0.86	1.85	2.701 (8)	171
	N4B—H4N$B\cdots$O4^{iii}	0.86	1.85	2.685 (9)	164
	N5B—H5N$B\cdots$O3	0.86	1.81	2.663 (9)	173
(II)	N4A—H4N$A\cdots$O3^i	0.86	1.85	2.706 (10)	172
	N5A—H5N$A\cdots$O1^{ii}	0.86	2.51	3.049 (10)	121
	N5A—H5N$A\cdots$O2^{ii}	0.86	2.04	2.883 (11)	165
	N4B—H4N$B\cdots$O4^{iii}	0.86	1.85	2.746 (10)	177
	N5B—H5N$B\cdots$O1	0.86	1.75	2.605 (10)	174
(III)	N4A—H4$AA\cdots$O4^i	0.86	1.89	2.732 (7)	168
	N5A—H5$AA\cdots$O3W	0.86	1.97	2.802 (7)	163
	N4B—H4$BA\cdots$O2^{ii}	0.86	1.79	2.646 (7)	175
	N5B—H5$BA\cdots$O1^{iii}	0.86	2.29	3.024 (8)	143
	N5B—H5$BA\cdots$O3^{iii}	0.86	2.19	2.959 (9)	149
(IV)	N4A—H4N$A\cdots$O2^i	0.86	2.04	2.7418 (16)	138
	N5A—H5N$A\cdots$O3	0.86	1.94	2.7966 (16)	176
	N4B—H4N$B\cdots$O1^{ii}	0.86	1.82	2.6806 (16)	179
	N5B—H5N$B\cdots$O4^{iii}	0.86	2.11	2.8356 (17)	142

Symmetry codes for (I): (i) $-x + \frac{3}{2}, -y, z - \frac{1}{2}$; (ii) $-x + \frac{5}{2}, -y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 2$. Symmetry codes for (II): (i) $y, -x + 1, -z$; (ii) $-x + \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$. Symmetry codes for (III): (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + \frac{3}{2}, y, z - \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z + 1$. Symmetry codes for (IV): (i) $y, -x + 1, -z$; (ii) $-x + \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

column and which is made up of one single type of [Ni(H$_2L$)$_2\cdots$SO$_4$]$_3$ loop [**A1**, $R_6^6(24)$, shaded in the figure]. This loop is topologically identical to that of column **A** in (II) (loop **A1**) represented in Fig. 3(b). The topological similarities are also reflected in the characteristics of the columns generated: as a crude estimator, we have taken the 'diameters' of the columns, as measured by the projected distances between opposite Ni^{2+} cations, which gives roughly ∼15.5–16.0 Å for (I) and ∼14.0 Å for (II). The main difference between both structures comes from the second column, *i.e.* **B**, which is absent in (I) but present in (II) (see Fig. 2), and which shows a more complex mesh structure (Fig. 3c), presenting large [Ni(H$_2L$)$_2\cdots$SO$_4$]$_3$ loops [**B1**, $R_6^6(24)$] similar to **A1** described already, combined with smaller [Ni(H$_2L$)$_2\cdots$SO$_4$]$_2$ loops [**B2**, $R_4^4(16)$]. This allows for a larger diameter in the column, which, with a similar estimator as before, is ∼20.0 Å. A different scenario is seen for structure (III), where the connectivity results in the [100] chains shown in projection in Fig. 4(a) and in turn interconnected by water-mediated hydrogen bonds. These interactions are hard to describe, since water H atoms could not be detected, but there is, however, one significant hydrogen bond fully resolved, having O3W as acceptor and H5NA as donor, and which fulfils an important role in the packing description to follow. Fig. 4(b) presents a rotated view of Fig. 4(a) along the horizontal axis, and shows the way in

which chains align in the (010) plane. Note the fact that only three N—H groups are involved in chain formation (one of them in a bifurcated mode), the fourth being involved in the hydrogen bond to the O3W solvent molecule. In structure (IV) (reported in Guo *et al.*, 2011), the hydrogen-bonded network is defined by [010] chains (viewed as closed loops in Fig. 5a), which are linked along [100] *via* an N—H$\cdots$OSO$_3$ hydrogen bond to form slightly corrugated two-dimensional arrays parallel to (001) and shown in projection as the undulating structures running top to bottom in Fig. 5(a). Fig. 5(b), in turn, presents a rotated view of Fig. 5(a), displaying these two-dimensional substructures in full.
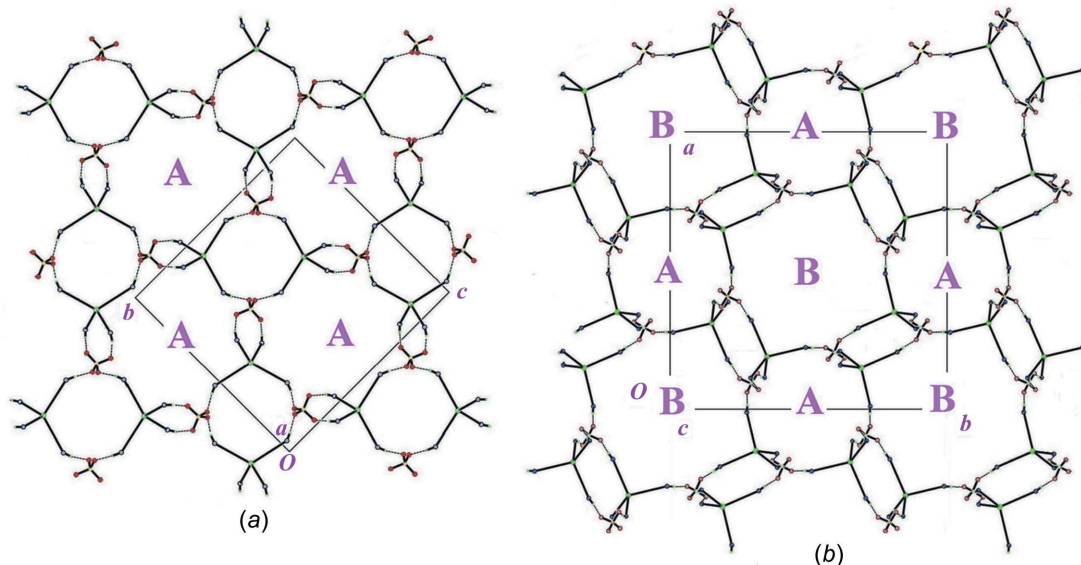

Figure 2
Schematic projections of structures (I) and (II) along the channels, showing (a) structure (I) (only channels of type **A**) and (b) structure (II) (channels of types **A** and **B**).

(a)

(b)

(c)
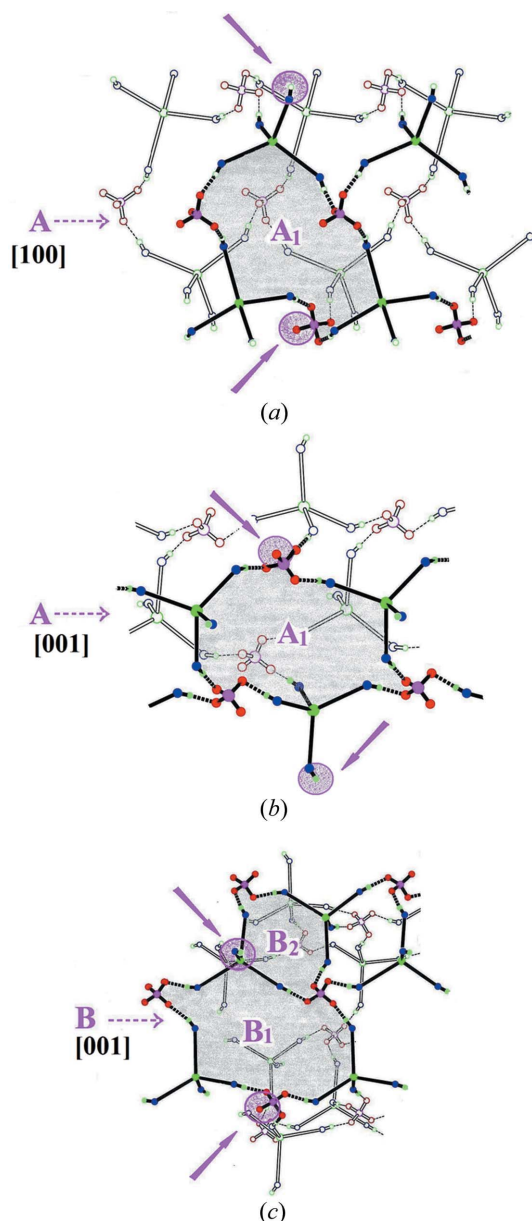
Figure 3
Schematic representation of the meshes wrapping channels (displayed horizontally) in (I) and (II) for (a) channel **A** of structure (I), showing mesh motif **A1**, (b) channel **A** of structure (II), showing mesh motif **A1**, and (c) channel **B** of structure (II), showing mesh motifs **B1** and **B2**. Broken arrows suggest the tube direction. (The full arrows are relevant to the discussion in document SD1 of the supporting information.)

A point common to all three solvatomorphs (I), (II) and (III) is the fact that they are directly related to the structure of this unsolvated 'parent' (IV), and which could be considered as the reference frame from which all three derive. A detailed analysis of the way in which this relationship is achieved is presented in document SD1 of the supporting information.

3.2. Analysis of the topology of the hydrogen-bonded networks

In structures (I), (II) and (IV), both the complex cation and the sulfate anion have four active centres (atoms that parti-

cipate in hydrogen bonding) and form one hydrogen bond with each of the four neighbours; therefore the connection type of both ions is K^4 (see Fig. S1 in the supporting information). On the contrary, in structure (III), the ions have different local connectivities of K^{31} and K^{21} for the cation and anion, respectively. The standard representation of the hydrogen-bonded structures leads to the underlying nets shown in Fig. 6. The **sql** topological type of the underlying net in (IV) is the most abundant among layered hydrogen-bonded structures (Zolotarev et al., 2014), while the **unc** and **atn** topologies found in (I) and (II), respectively, are very uncommon for hydrogen-bond frameworks in molecular crystals, especially the **atn** net. In the TTO collection, there are 11 molecular structures with **unc** topology and only one with **atn** topology (see Table S1 in the supporting information). The hydrogen-bonded ladder in structure (III) possesses $4^4(0,2)$ topology, which is the second most abundant among structures with 1-periodic hydrogen-bonded systems. To explore the bonding preferences of the complex cations with composition

(a)

(b)
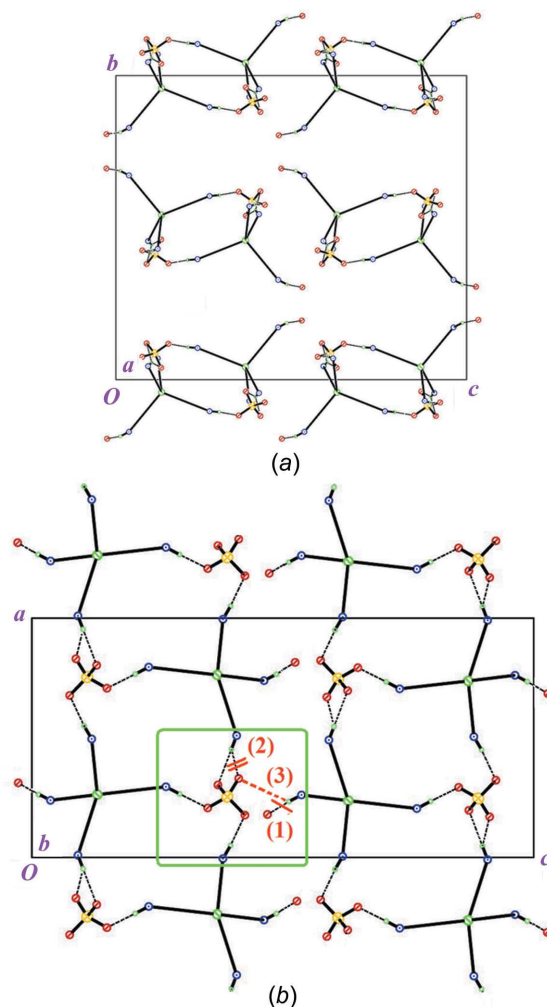
Figure 4
(a) View in projection of the [100] columnar arrays in (III) (closed loops). Note the N—H···OW hydrogen bond, limiting the interconnectivity of the chains. Only the O3W solvent molecule has been considered in the analysis, for clarity. (b) A view of the (010) plane, showing (vertically) the parallel [100] columns. (The square inset is relevant to the discussion in document SD1 of the supporting information.)
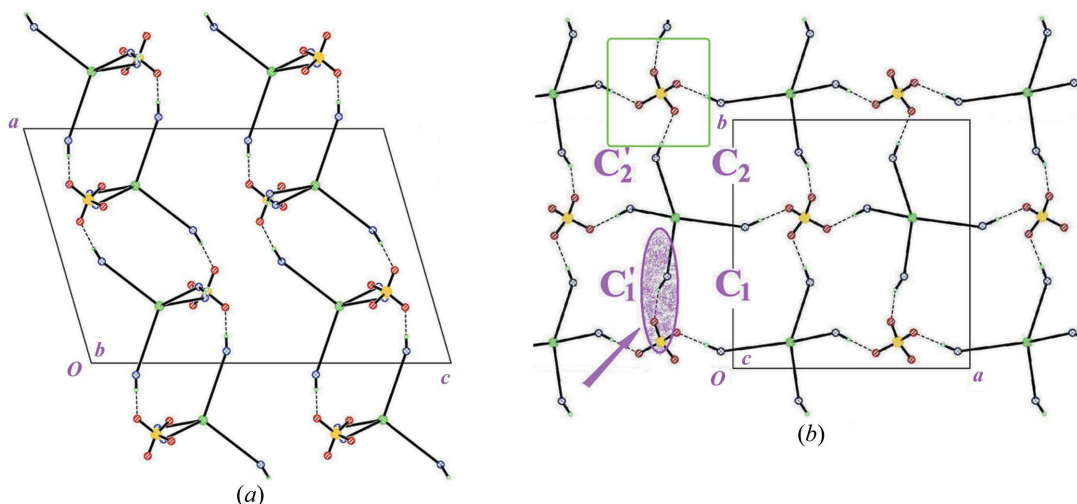
Figure 5
(*a*) A view in projection of the [010] columnar arrays in (IV) (closed loops), linked along [100] to form the slightly undulating (001) planes coming out of the plane of the figure. (*b*) One of these isolated planes, seen in full display. (The square inset, full arrow and C labels are relevant to the discussion in document SD1 of the supporting information.)

$M(H_2L)_2$, we extracted from the CSD 20 crystal structures (see Table S2 in the supporting information) with the same ligand, *i.e.* 2,6-bis(1*H*-benzimidazol-2-yl)pyridine, denoted H_2L. From the analysis of the structures, one can assume that the connection type of such cations is usually of the K type (four active centres), because in all the 20 structures, it engages all N—H groups in bonding, but for the seven rare-earth-containing cations, the connectivity is greater because of the extra ligands engaged in the formation of additional hydrogen bonds. The only structure (CSD refcode EYINAB;

Harvey *et al.*, 2004) with an anion of double negative charge, namely solvated Zn^{II}–$(H_2L)_2$–peroxodisulfate, has the same topology as (III), *i.e.* $4^4(0,2)$, though the coordination type of the cation (MCTS K^4) in this structure is different from that found in (III) (MCTS K^{31}). With the aim of exploring the local connectivity preferences of the sulfate anion, a sample of 843 crystal structures with sulfate anions forming hydrogen bonds was extracted from the CSD by means of the *ConQuest* program (Bruno *et al.*, 2002). Structures comprising both sulfate and hydrogen sulfate anions were eliminated from the
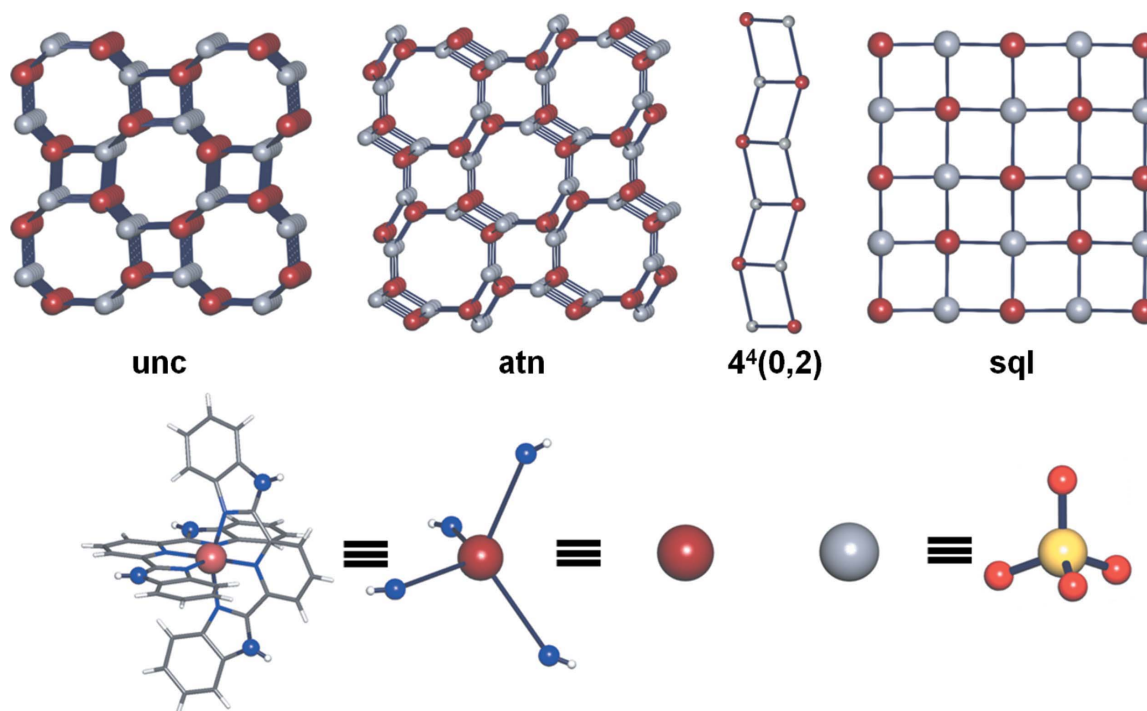
Figure 6
The underlying nets in the crystal structures of (I), (II), (III) and (IV) (left to right), with the corresponding topological type of the net underneath. The underlying net represents the connection pattern of complex cations and sulfate anions (nodes of the net) by means of hydrogen bonds (edges between nodes). The **unc** net is intrinsically chiral.

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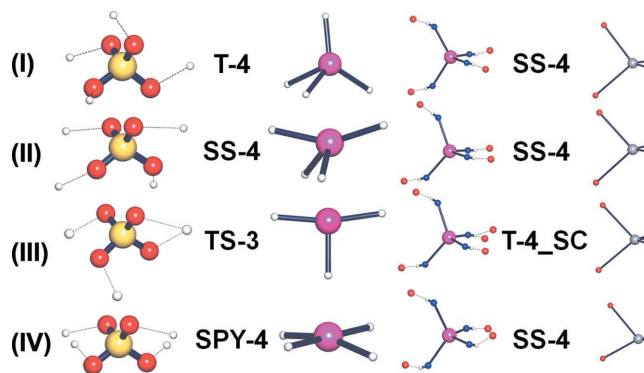
Figure 7
Hydrogen bonds formed by the molecular ions in structures (I)–(IV), along with the resulting coordination modes: T-4 is a tetrahedron, SS-4 is a see-saw, TS-3 is T-shaped, SPY-4 is square-planar and T-4_SC is distorted face-capped tetrahedron (Hartshorn *et al.*, 2007).

set due to unreliable localization of the H-atom position in the hydrogen sulfate anion. The distribution of the sulfate-anion connectivity demonstrates (see Table S3 in the supporting information) that the K^4 connection type found in (I), (II) and (IV) is not common and accounts for only 1.26% (13 examples) among 1034 sulfate anions found in the set of crystal structures without disorder of the sulfate anion. The K^{21} connection type found in (III) is even rarer, with only one example. For sulfate anions that are hydrogen bonded to four neighbouring molecules, the frequency of occurrence of connection types goes down according to $K^{04} > K^{13} > K^{22} > T^4 > K^4 > K^{31}$ (see Fig. S1 in the supporting information), *i.e.* typically, the sulfate anion forms two hydrogen bonds *via* each O atom (K^{04}). The other feature to be examined was the coordination modes of the molecular ions in (I)–(IV). The

data on the coordination figures of the ions are presented in Fig. 7. Additionally, the coordination figure similarities were calculated for complex cations in the set of 20 structures and sulfate anions in the large set of 834 structures described above. Only six structures out of 20 contain the complex cation with MCTS K^4, *i.e.* hydrogen bonded to four sulfate O atoms as in (I) and (II) (see Table S2 in the supporting information). The see-saw coordination SS-4 shown in Fig. 7 (which can be seen as a distorted tetrahedron) is typical for this cation, the same coordination figure that was realized in structures (I) and (II), though there are two examples of the tetrahedral T-4 coordination mode. In structure (III), five O atoms (four from sulfate and one from water) result in the T-4_SC (distorted face-capped tetrahedron) coordination mode found in $[M(H_2L)_2]^{2+}$ picrates. The distribution of the coordination figures determined for 1020 (14 sulfate anions form only one hydrogen bond, *i.e.* the ion is monocoordinated) independent sulfate anions from the large set of sulfate structures (see Table S4 in the supporting information) reveals that for 72 sulfate anions coordinated by four H atoms only: the SPY-4 (noncoplanar, 36 examples) and SS-4 (see-saw, 31 examples) coordination modes prevail, with only five structures featuring tetrahedral T-4 coordination. That means that in (I), (II) and (IV), all the common coordination modes of the sulfate anion were manifested. In structure (III), the TS-3 (T-shaped) coordination mode was found; this appeared in 12 out of 31 structures with a sulfate anion bonded to three H atoms.

3.3. Theoretical hydrogen-bonded networks

In order to explore the probable network topologies of the crystal structures of (I), (II) and (IV) with four-coordinated underlying nets, a set of similar hydrogen-bonded crystal
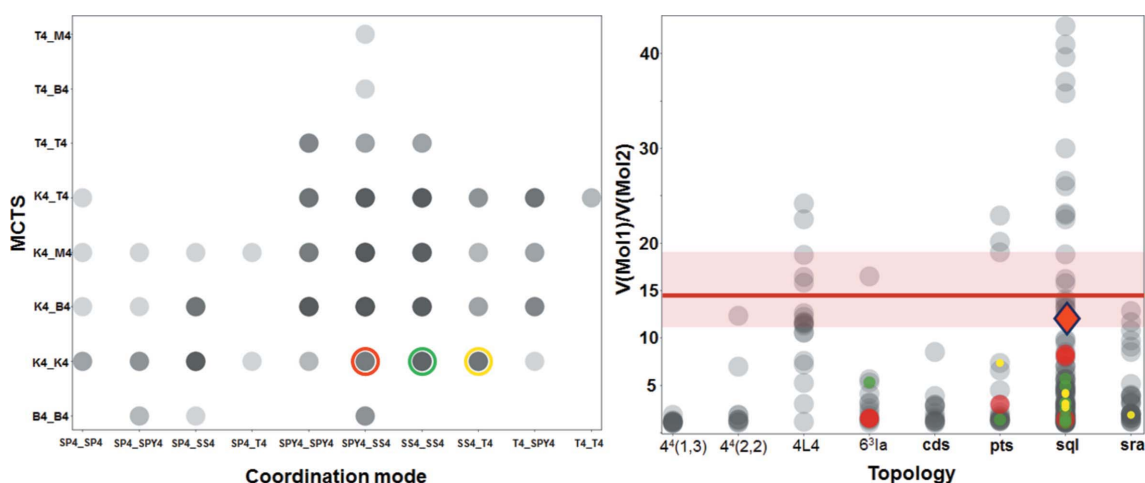
Figure 8
(Left) Two-dimensional frequency plot of MCTS *versus* coordination mode of molecules in the set of 239 structures defined in §3.3. Red, green and yellow circles define the pairs of MCTS–coordination mode found in structures (IV), (II) and (I), respectively. The shade of a point depends on the number of structures with a given combination of MCTS and coordination mode (more transparent points correspond to pairs with smaller numbers of representatives). (Right) Two-dimensional frequency plot of the molecular volume ratio *versus* hydrogen-bond network topology. Coloured points correspond to the structures with pairs of MCTS–coordination mode observed in (I), (II) and (IV). The red line and pale-red rectangle correspond, respectively, to the $V_{mean}[M(H_2L)_2]/V_{mean}(SO_4) = 14.4$ and to the span of the same ratio, taking into account standard deviations of molecular volumes. The red diamond corresponds to the structure of (IV). Data analysis was performed by means of the *Python glue* library (Goodman, 2012).

structures composed of two crystallographically non-equivalent molecules (one molecule comprises only hydrogen-bond donors and the other only hydrogen-bond acceptors) was extracted from the CSD by means of the *ToposPro* program (Blatov *et al.*, 2014). The connection types of molecules were of the L^4 (L = K, T, B and M) type, with four single hydrogen bonds and more than 10 representatives for each topological type. As a result, 239 (see Table S5 in the supporting information) structures were retrieved. To take into account the relative dimensions of the molecules, the ratio of molecular volumes (calculated using molecular Voronoi polyhedra) was added to the list of structural descriptors (MCTS and coordination mode). For structures (I), (II) and (IV), the values are 16.0, 16.1 and 12.0, respectively. The mean molecular volumes and their standard deviations (SD) are $V_{mean}[M(H_2L)_2]$ = 775 Å^3 (SD = 42.8) and $V_{mean}(SO_4)$ = 53.7 Å^3 (SD = 11.3), computed from the volumes of 13 complex cations and 1034 sulfate anions. Now, knowing the typical connectivities and coordination modes of both complex cation and sulfate anion, we can conclude that the **sql** topology observed for unsolvated (IV) (SS-4/SPY-4) was expected to appear because structures with the same molecular connectivity K^4 and a molecular volume ratio closer to $V_{mean}[Me(H_2L)_2]/V_{mean}(SO_4)$ = 775/53.7 = 14.4, also have an **sql** topology [8 (MUSHUD; Plass & Yozgatli, 2003) and 8.3 (WUCKUC; Moon & Choi, 2015)] (Fig. 8). Besides, one can see that other topological types for a given coordination mode were realized with a smaller $V(Mol1)/V(Mol2)$ ratio, *i.e.* where the two molecules have comparable volumes, which is not the case for the sulfate anion and the $[Ni(H_2L)_2]^{2+}$ cation. This, again, emphasizes the significance of the solvent molecules that might direct the crystallization of porous structures (I) and (II) and lead to such unusual topologies.

4. Final remarks

The $[Ni(H_2L)_2]^{2+}(SO_4)^{2-}$ system, despite having simple building blocks with only four active centres each, shows the importance of the solvent, which can unpredictably change the outcome of the crystallization process. The unsolvated structure (IV) was probably to be expected based on the analysis of the set of related structures, but structures (I) and (II), evidently, are the outcome of the structure-directing influence of solvents. Structure (III) can be seen as an intermediate step *en route* to unsolvated polymorph (IV) due to very similar tubular hydrogen-bonded fragments. Even if we are on our way towards the further screening of this promising system through the diversification of solvents, metals and linkers, the challenge posed is extremely difficult to tackle, due to the unpredictability of the synthetic outcomes, a fact supported by the topological and structural analysis of the sets of similar structures. Our present efforts are focused on minimizing these latter drawbacks.

References

Alexandrov, E. V., Blatov, V. A., Kochetkov, A. V. & Proserpio, D. M. (2011). *CrystEngComm*, **11**, 3947–3958.
Aman, F., Asiri, A. M., Siddiqui, W. A., Arshad, M. N., Ashraf, A., Zakharov, N. S. & Blatov, V. A. (2014). *CrystEngComm*, **16**, 1963–1970.
Blatov, V. A. (2016). *Struct. Chem.* **27**, 1605–1611.
Blatov, V. A., Shevchenko, A. P. & Proserpio, D. M. (2014). *Cryst. Growth Des.* **14**, 3576–3586.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Goodman, A. A. (2012). *Astron. Nachr.* **333**, 505–514.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Guo, Y. C., Chen, S. Y., Qiu, D. F., Feng, Y. Q. & Song, W. H. (2011). *Chin. J. Inorg. Chem.* **27**, 1517–1520.
Hartshorn, R. M., Hey-Hawkins, E., Kalio, R. & Leigh, G. J. (2007). *Pure Appl. Chem.* **79**, 1779–1799.
Harvey, M. A., Baggio, S., Ibañez, A. & Baggio, R. (2004). *Acta Cryst.* C**60**, m375–m381.
Harvey, M. A., Baggio, S., Muñoz, J. C. & Baggio, R. (2003). *Acta Cryst.* C**59**, m283–m285.
Harvey, M. A., Suarez, S., Doctorovich, F. & Baggio, R. (2013). *Acta Cryst.* C**69**, 47–51.
Koch, E. & Fischer, W. (1978). *Z. Kristallogr.* **148**, 107–152.
Larsson, K. & Öhrström, L. (2003). *CrystEngComm*, **5**, 222–225.
Moon, D. & Choi, J.-H. (2015). *Acta Cryst.* E**71**, 210–212.
O'Keeffe, M., Peskov, M. A., Ramsden, S. J. & Yaghi, O. M. (2008). *Acc. Chem. Res.* **41**, 1782–1789.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Plass, W. & Yozgatli, H.-P. (2003). *Z. Anorg. Allg. Chem.* **629**, 65–70.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Shevchenko, A. P., Blatov, I. A., Kitaevaand, E. V. & Blatov, V. A. (2017). *Cryst. Growth Des.* **17**, 774–785.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Spek, A. L. (2015). *Acta Cryst.* C**71**, 9–18.
Zolotarev, P. N., Arshad, M. N., Asiri, A. M., Al-Amshany, Z. M. & Blatov, V. A. (2014). *Cryst. Growth Des.* **14**, 1938–1949.

supporting information

Topological study of diverse hydrogen-bonded patterns found in a system of a nickel(II) complex and the sulfate anion

Miguel Angel Harvey, Sebastián Suarez, Pavel N. Zolotarev, Davide M. Proserpio and Ricardo Baggio

Computing details

For all structures, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

Bis[2,6-bis(1*H*-benzimidazol-2-yl-κN^3)pyridine-κN]nickel(II) sulfate (I)

Crystal data

[Ni(C$_{19}$H$_{13}$N$_5$)$_2$]SO$_4$	$D_x = 1.158$ Mg m^{-3}
$M_r = 777.46$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 4887 reflections
$a = 9.8015$ (6) Å	$\theta = 3.8–28.1°$
$b = 20.9572$ (15) Å	$\mu = 0.53$ mm^{-1}
$c = 21.7012$ (17) Å	$T = 294$ K
$V = 4457.7$ (5) Å^3	Needle, light_red
$Z = 4$	$0.50 \times 0.24 \times 0.18$ mm
$F(000) = 1600$	

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer	19326 measured reflections
	9840 independent reflections
Radiation source: fine-focus sealed tube	5651 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.085$
ω scans, thick slices	$\theta_{max} = 28.9°$, $\theta_{min} = 3.6°$
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)	$h = -12 \rightarrow 11$
	$k = -26 \rightarrow 28$
$T_{min} = 0.82$, $T_{max} = 0.92$	$l = -26 \rightarrow 28$

Refinement

Refinement on F^2	586 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.074$	
$wR(F^2) = 0.210$	H-atom parameters constrained
$S = 0.98$	$w = 1/[\sigma^2(F_o^2) + (0.0908P)^2]$
9840 reflections	where $P = (F_o^2 + 2F_c^2)/3$
487 parameters	$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Absolute structure: Flack x determined using 1523 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.006 (19)

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	0.88293 (9)	0.08567 (5)	0.84243 (4)	0.0392 (3)
N1A	0.6872 (5)	0.0444 (3)	0.8476 (3)	0.0448 (15)
N2A	0.8989 (5)	0.0117 (3)	0.7826 (3)	0.0424 (14)
N3A	1.0826 (5)	0.0964 (3)	0.8072 (3)	0.0439 (14)
N4A	0.5513 (6)	−0.0333 (3)	0.8142 (3)	0.0555 (18)
H4NA	0.523803	−0.066115	0.793923	0.067*
N5A	1.2442 (6)	0.0573 (3)	0.7459 (3)	0.0508 (17)
H5NA	1.285383	0.031955	0.720939	0.061*
C1A	0.5640 (7)	0.0489 (4)	0.8785 (4)	0.0469 (18)
C2A	0.5188 (8)	0.0932 (4)	0.9213 (4)	0.061 (2)
H2AA	0.572642	0.126997	0.934752	0.074*
C3A	0.3880 (8)	0.0832 (5)	0.9424 (5)	0.080 (3)
H3AA	0.353593	0.111188	0.971828	0.096*
C4A	0.3063 (9)	0.0350 (5)	0.9228 (5)	0.075 (3)
H4AA	0.219539	0.030882	0.939718	0.090*
C5A	0.3475 (7)	−0.0071 (5)	0.8795 (4)	0.066 (2)
H5AA	0.290457	−0.039530	0.865700	0.079*
C6A	0.4781 (7)	0.0003 (4)	0.8567 (4)	0.0482 (18)
C7A	0.6749 (7)	−0.0053 (3)	0.8099 (3)	0.0461 (19)
C8A	0.7926 (7)	−0.0270 (4)	0.7752 (4)	0.052 (2)
C9A	0.8036 (8)	−0.0816 (5)	0.7394 (5)	0.076 (3)
H9AA	0.728977	−0.108296	0.733392	0.091*
C10A	0.9262 (9)	−0.0949 (5)	0.7132 (5)	0.090 (4)
H10A	0.935425	−0.131541	0.689406	0.108*
C11A	1.0384 (9)	−0.0550 (4)	0.7212 (5)	0.072 (3)
H11A	1.122472	−0.064533	0.703554	0.086*
C12A	1.0199 (6)	−0.0005 (3)	0.7564 (4)	0.0457 (18)
C13A	1.1186 (7)	0.0496 (3)	0.7702 (3)	0.0435 (16)
C14A	1.2933 (7)	0.1143 (3)	0.7692 (4)	0.0482 (18)
C15A	1.4155 (8)	0.1466 (4)	0.7584 (5)	0.067 (3)
H15A	1.483524	0.129796	0.733345	0.081*
C16A	1.4288 (9)	0.2035 (5)	0.7866 (5)	0.076 (3)
H16A	1.508808	0.226567	0.780600	0.092*
C17A	1.3282 (8)	0.2293 (4)	0.8244 (5)	0.071 (3)
H17A	1.342304	0.269074	0.842373	0.086*

C18A	1.2091 (8)	0.1975 (4)	0.8356 (5)	0.061 (2)
H18A	1.141536	0.214640	0.860656	0.073*
C19A	1.1936 (7)	0.1381 (3)	0.8076 (4)	0.0469 (18)
N1B	0.8202 (6)	0.1655 (3)	0.7902 (3)	0.0430 (15)
N2B	0.8719 (6)	0.1553 (2)	0.9068 (2)	0.0371 (13)
N3B	0.9392 (6)	0.0370 (2)	0.9242 (3)	0.0411 (14)
N4B	0.7729 (6)	0.2694 (3)	0.7912 (3)	0.0458 (15)
H4NB	0.760629	0.307484	0.804941	0.055*
N5B	0.9636 (7)	0.0440 (3)	1.0261 (3)	0.0473 (15)
H5NB	0.965944	0.060504	1.062391	0.057*
C1B	0.7895 (7)	0.1843 (3)	0.7306 (3)	0.0454 (17)
C2B	0.7839 (10)	0.1499 (4)	0.6764 (3)	0.065 (2)
H2BA	0.804359	0.106636	0.674822	0.078*
C3B	0.7462 (11)	0.1837 (5)	0.6247 (4)	0.075 (3)
H3BA	0.740590	0.162069	0.587424	0.090*
C4B	0.7168 (11)	0.2469 (5)	0.6253 (4)	0.075 (3)
H4BA	0.690994	0.266911	0.588882	0.090*
C5B	0.7242 (10)	0.2814 (4)	0.6777 (4)	0.067 (3)
H5BA	0.704945	0.324872	0.677771	0.080*
C6B	0.7615 (8)	0.2499 (3)	0.7314 (3)	0.0460 (17)
C7B	0.8070 (8)	0.2178 (3)	0.8246 (3)	0.0411 (16)
C8B	0.8339 (9)	0.2138 (3)	0.8902 (3)	0.0477 (19)
C9B	0.8197 (15)	0.2618 (4)	0.9337 (4)	0.099 (4)
H9BA	0.792888	0.302607	0.922180	0.118*
C10B	0.8460 (17)	0.2477 (5)	0.9936 (4)	0.123 (6)
H10B	0.831651	0.278571	1.023653	0.148*
C11B	0.8940 (15)	0.1877 (4)	1.0108 (4)	0.099 (4)
H11B	0.920952	0.179170	1.051076	0.119*
C12B	0.8998 (9)	0.1412 (3)	0.9654 (3)	0.050 (2)
C13B	0.9343 (7)	0.0740 (3)	0.9728 (3)	0.0408 (15)
C14B	0.9891 (8)	−0.0188 (3)	1.0106 (3)	0.0447 (17)
C15B	1.0240 (9)	−0.0708 (3)	1.0469 (4)	0.064 (2)
H15B	1.034589	−0.067328	1.089340	0.077*
C16B	1.0417 (11)	−0.1266 (4)	1.0173 (5)	0.079 (3)
H16B	1.063909	−0.162706	1.040103	0.095*
C17B	1.0280 (11)	−0.1322 (4)	0.9537 (5)	0.077 (3)
H17B	1.043347	−0.171601	0.935233	0.093*
C18B	0.9925 (9)	−0.0814 (4)	0.9179 (4)	0.062 (2)
H18B	0.980261	−0.085581	0.875547	0.074*
C19B	0.9754 (8)	−0.0230 (3)	0.9475 (3)	0.0464 (18)
S1	1.0813 (2)	0.09127 (10)	1.17397 (10)	0.0506 (5)
O1	1.1035 (7)	0.0222 (3)	1.1762 (3)	0.0732 (19)
O2	1.0534 (7)	0.1175 (3)	1.2361 (3)	0.0677 (18)
O3	0.9641 (6)	0.1041 (3)	1.1343 (3)	0.0707 (19)
O4	1.2034 (6)	0.1228 (3)	1.1497 (3)	0.0699 (18)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0392 (5)	0.0372 (5)	0.0412 (5)	−0.0011 (5)	0.0003 (4)	−0.0053 (5)
N1A	0.043 (3)	0.043 (3)	0.048 (4)	−0.001 (3)	0.002 (3)	−0.009 (3)
N2A	0.041 (3)	0.038 (3)	0.048 (4)	−0.002 (2)	0.005 (2)	−0.010 (3)
N3A	0.042 (3)	0.044 (3)	0.046 (3)	−0.004 (2)	0.004 (2)	−0.006 (3)
N4A	0.053 (3)	0.050 (4)	0.064 (4)	−0.016 (3)	0.005 (3)	−0.012 (4)
N5A	0.046 (3)	0.054 (3)	0.053 (4)	−0.003 (3)	0.014 (3)	−0.006 (3)
C1A	0.039 (3)	0.047 (4)	0.055 (4)	0.003 (3)	0.000 (3)	0.000 (3)
C2A	0.053 (4)	0.053 (4)	0.078 (6)	−0.004 (4)	0.017 (4)	−0.012 (4)
C3A	0.057 (4)	0.073 (5)	0.109 (8)	−0.003 (4)	0.029 (4)	−0.007 (6)
C4A	0.056 (5)	0.076 (5)	0.093 (7)	−0.007 (4)	0.021 (5)	0.005 (5)
C5A	0.045 (4)	0.076 (6)	0.077 (6)	−0.009 (4)	0.002 (4)	0.005 (5)
C6A	0.044 (3)	0.048 (4)	0.053 (5)	−0.001 (3)	−0.002 (3)	0.005 (3)
C7A	0.046 (3)	0.045 (4)	0.048 (4)	−0.009 (3)	0.004 (3)	−0.008 (3)
C8A	0.049 (3)	0.051 (4)	0.056 (5)	−0.013 (3)	0.008 (3)	−0.016 (4)
C9A	0.072 (5)	0.069 (5)	0.088 (7)	−0.021 (5)	0.015 (5)	−0.041 (5)
C10A	0.086 (5)	0.066 (6)	0.118 (9)	−0.016 (4)	0.032 (5)	−0.053 (7)
C11A	0.072 (5)	0.060 (4)	0.083 (7)	−0.006 (4)	0.025 (5)	−0.029 (5)
C12A	0.044 (3)	0.046 (3)	0.047 (5)	−0.001 (3)	0.008 (3)	−0.008 (3)
C13A	0.042 (3)	0.044 (3)	0.044 (4)	−0.001 (3)	0.008 (3)	−0.003 (3)
C14A	0.046 (3)	0.050 (3)	0.049 (5)	−0.003 (3)	−0.001 (3)	0.006 (3)
C15A	0.055 (4)	0.074 (5)	0.073 (6)	−0.017 (4)	0.008 (4)	0.004 (5)
C16A	0.058 (5)	0.083 (5)	0.088 (7)	−0.027 (4)	0.005 (4)	−0.006 (5)
C17A	0.066 (4)	0.069 (6)	0.079 (7)	−0.024 (4)	0.001 (4)	−0.008 (5)
C18A	0.058 (4)	0.056 (4)	0.068 (6)	−0.013 (3)	0.004 (4)	−0.011 (4)
C19A	0.045 (3)	0.048 (3)	0.048 (4)	−0.007 (3)	−0.002 (3)	0.002 (3)
N1B	0.049 (4)	0.039 (3)	0.041 (3)	−0.001 (3)	−0.003 (3)	−0.004 (2)
N2B	0.038 (3)	0.035 (2)	0.038 (3)	0.001 (3)	−0.002 (3)	0.000 (2)
N3B	0.040 (3)	0.035 (2)	0.048 (3)	0.001 (3)	0.000 (3)	−0.004 (2)
N4B	0.048 (4)	0.046 (3)	0.044 (3)	0.006 (3)	−0.003 (3)	0.007 (3)
N5B	0.053 (4)	0.040 (3)	0.049 (3)	−0.001 (3)	−0.006 (3)	0.000 (3)
C1B	0.040 (4)	0.055 (3)	0.041 (3)	−0.001 (3)	−0.001 (3)	0.002 (3)
C2B	0.081 (6)	0.068 (5)	0.045 (3)	0.011 (5)	−0.005 (4)	−0.006 (3)
C3B	0.094 (7)	0.092 (5)	0.039 (4)	0.011 (5)	−0.011 (5)	−0.004 (4)
C4B	0.087 (7)	0.093 (5)	0.045 (4)	0.013 (5)	0.002 (5)	0.010 (4)
C5B	0.080 (6)	0.076 (6)	0.044 (3)	0.018 (5)	0.003 (4)	0.017 (4)
C6B	0.042 (4)	0.056 (3)	0.040 (3)	0.003 (3)	0.005 (3)	0.009 (3)
C7B	0.048 (4)	0.036 (3)	0.039 (3)	0.002 (3)	−0.003 (3)	0.000 (2)
C8B	0.069 (5)	0.034 (3)	0.040 (3)	0.006 (3)	−0.007 (3)	0.000 (3)
C9B	0.198 (13)	0.047 (5)	0.051 (4)	0.037 (7)	−0.033 (6)	−0.012 (4)
C10B	0.261 (17)	0.057 (5)	0.051 (4)	0.051 (8)	−0.040 (7)	−0.017 (5)
C11B	0.198 (12)	0.053 (4)	0.045 (5)	0.032 (6)	−0.033 (7)	−0.012 (4)
C12B	0.072 (5)	0.041 (3)	0.039 (3)	0.008 (4)	−0.008 (3)	−0.002 (3)
C13B	0.040 (4)	0.037 (3)	0.046 (3)	0.000 (3)	−0.004 (3)	−0.004 (2)
C14B	0.042 (4)	0.038 (3)	0.055 (3)	−0.003 (3)	−0.003 (3)	0.004 (3)
C15B	0.076 (6)	0.047 (4)	0.068 (5)	0.007 (4)	−0.001 (5)	0.015 (3)

C16B	0.096 (7)	0.047 (4)	0.096 (5)	0.015 (5)	0.002 (6)	0.010 (5)
C17B	0.095 (7)	0.039 (4)	0.098 (5)	0.009 (5)	0.001 (6)	0.000 (4)
C18B	0.070 (5)	0.040 (3)	0.075 (5)	0.001 (4)	−0.004 (4)	−0.010 (3)
C19B	0.047 (4)	0.036 (3)	0.056 (4)	−0.001 (3)	−0.005 (3)	−0.002 (3)
S1	0.0652 (13)	0.0423 (10)	0.0444 (11)	−0.0060 (11)	−0.0112 (9)	0.0104 (11)
O1	0.086 (4)	0.039 (3)	0.094 (5)	−0.008 (3)	−0.038 (4)	0.012 (3)
O2	0.096 (4)	0.070 (4)	0.037 (3)	−0.033 (4)	0.001 (3)	0.004 (3)
O3	0.072 (4)	0.083 (5)	0.057 (4)	0.014 (4)	−0.025 (3)	0.002 (4)
O4	0.076 (4)	0.055 (3)	0.079 (5)	−0.019 (3)	0.015 (4)	0.003 (4)

Geometric parameters (Å, º)

Ni1—N2B	2.022 (5)	C18A—H18A	0.9300
Ni1—N2A	2.029 (5)	N1B—C7B	1.333 (7)
Ni1—N1A	2.108 (5)	N1B—C1B	1.384 (8)
Ni1—N1B	2.112 (6)	N2B—C8B	1.330 (7)
Ni1—N3A	2.113 (5)	N2B—C12B	1.335 (7)
Ni1—N3B	2.120 (6)	N3B—C13B	1.311 (7)
N1A—C7A	1.328 (7)	N3B—C19B	1.400 (7)
N1A—C1A	1.385 (8)	N4B—C7B	1.345 (7)
N2A—C8A	1.330 (7)	N4B—C6B	1.366 (8)
N2A—C12A	1.339 (7)	N4B—H4NB	0.8600
N3A—C13A	1.315 (7)	N5B—C13B	1.350 (7)
N3A—C19A	1.396 (7)	N5B—C14B	1.381 (7)
N4A—C7A	1.349 (7)	N5B—H5NB	0.8600
N4A—C6A	1.364 (8)	C1B—C2B	1.381 (9)
N4A—H4NA	0.8600	C1B—C6B	1.403 (9)
N5A—C13A	1.349 (7)	C2B—C3B	1.377 (9)
N5A—C14A	1.382 (7)	C2B—H2BA	0.9300
N5A—H5NA	0.8600	C3B—C4B	1.355 (11)
C1A—C2A	1.385 (9)	C3B—H3BA	0.9300
C1A—C6A	1.403 (9)	C4B—C5B	1.348 (11)
C2A—C3A	1.378 (9)	C4B—H4BA	0.9300
C2A—H2AA	0.9300	C5B—C6B	1.389 (9)
C3A—C4A	1.357 (11)	C5B—H5BA	0.9300
C3A—H3AA	0.9300	C7B—C8B	1.450 (9)
C4A—C5A	1.351 (10)	C8B—C9B	1.387 (9)
C4A—H4AA	0.9300	C9B—C10B	1.357 (11)
C5A—C6A	1.382 (9)	C9B—H9BA	0.9300
C5A—H5AA	0.9300	C10B—C11B	1.393 (10)
C7A—C8A	1.451 (9)	C10B—H10B	0.9300
C8A—C9A	1.388 (9)	C11B—C12B	1.387 (9)
C9A—C10A	1.358 (10)	C11B—H11B	0.9300
C9A—H9AA	0.9300	C12B—C13B	1.456 (8)
C10A—C11A	1.393 (10)	C14B—C19B	1.380 (9)
C10A—H10A	0.9300	C14B—C15B	1.387 (8)
C11A—C12A	1.387 (9)	C15B—C16B	1.345 (10)
C11A—H11A	0.9300	C15B—H15B	0.9300

C12A—C13A	1.458 (8)	C16B—C17B	1.390 (11)
C14A—C19A	1.378 (9)	C16B—H16B	0.9300
C14A—C15A	1.394 (8)	C17B—C18B	1.364 (9)
C15A—C16A	1.348 (10)	C17B—H17B	0.9300
C15A—H15A	0.9300	C18B—C19B	1.393 (9)
C16A—C17A	1.392 (10)	C18B—H18B	0.9300
C16A—H16A	0.9300	S1—O3	1.461 (6)
C17A—C18A	1.367 (9)	S1—O1	1.464 (6)
C17A—H17A	0.9300	S1—O4	1.465 (6)
C18A—C19A	1.393 (8)	S1—O2	1.481 (6)
N2B—Ni1—N2A	176.0 (2)	C19A—C18A—H18A	121.5
N2B—Ni1—N1A	102.2 (2)	C14A—C19A—C18A	120.6 (6)
N2A—Ni1—N1A	77.9 (2)	C14A—C19A—N3A	108.8 (6)
N2B—Ni1—N1B	77.5 (2)	C18A—C19A—N3A	130.3 (6)
N2A—Ni1—N1B	106.5 (2)	C7B—N1B—C1B	105.6 (5)
N1A—Ni1—N1B	95.1 (3)	C7B—N1B—Ni1	112.2 (4)
N2B—Ni1—N3A	102.9 (2)	C1B—N1B—Ni1	142.2 (5)
N2A—Ni1—N3A	77.2 (2)	C8B—N2B—C12B	121.3 (6)
N1A—Ni1—N3A	154.9 (2)	C8B—N2B—Ni1	119.5 (4)
N1B—Ni1—N3A	89.5 (3)	C12B—N2B—Ni1	119.2 (4)
N2B—Ni1—N3B	77.5 (2)	C13B—N3B—C19B	104.5 (5)
N2A—Ni1—N3B	98.5 (2)	C13B—N3B—Ni1	112.2 (4)
N1A—Ni1—N3B	89.7 (3)	C19B—N3B—Ni1	143.2 (5)
N1B—Ni1—N3B	155.0 (2)	C7B—N4B—C6B	107.0 (5)
N3A—Ni1—N3B	96.5 (2)	C7B—N4B—H4NB	126.5
C7A—N1A—C1A	105.8 (5)	C6B—N4B—H4NB	126.5
C7A—N1A—Ni1	111.8 (4)	C13B—N5B—C14B	105.9 (6)
C1A—N1A—Ni1	142.3 (5)	C13B—N5B—H5NB	127.0
C8A—N2A—C12A	121.8 (5)	C14B—N5B—H5NB	127.0
C8A—N2A—Ni1	118.8 (4)	C2B—C1B—N1B	131.0 (7)
C12A—N2A—Ni1	119.0 (4)	C2B—C1B—C6B	120.9 (6)
C13A—N3A—C19A	105.1 (5)	N1B—C1B—C6B	108.1 (6)
C13A—N3A—Ni1	113.0 (4)	C3B—C2B—C1B	115.9 (7)
C19A—N3A—Ni1	141.8 (4)	C3B—C2B—H2BA	122.0
C7A—N4A—C6A	107.1 (5)	C1B—C2B—H2BA	122.0
C7A—N4A—H4NA	126.5	C4B—C3B—C2B	123.5 (8)
C6A—N4A—H4NA	126.5	C4B—C3B—H3BA	118.2
C13A—N5A—C14A	106.2 (6)	C2B—C3B—H3BA	118.2
C13A—N5A—H5NA	126.9	C5B—C4B—C3B	121.4 (8)
C14A—N5A—H5NA	126.9	C5B—C4B—H4BA	119.3
C2A—C1A—N1A	130.5 (6)	C3B—C4B—H4BA	119.3
C2A—C1A—C6A	121.4 (6)	C4B—C5B—C6B	117.8 (8)
N1A—C1A—C6A	108.0 (6)	C4B—C5B—H5BA	121.1
C3A—C2A—C1A	114.7 (7)	C6B—C5B—H5BA	121.1
C3A—C2A—H2AA	122.6	N4B—C6B—C5B	132.6 (7)
C1A—C2A—H2AA	122.6	N4B—C6B—C1B	106.8 (6)
C4A—C3A—C2A	123.9 (8)	C5B—C6B—C1B	120.5 (7)

C4A—C3A—H3AA	118.0	N1B—C7B—N4B	112.6 (5)
C2A—C3A—H3AA	118.0	N1B—C7B—C8B	119.0 (6)
C5A—C4A—C3A	121.8 (8)	N4B—C7B—C8B	128.4 (6)
C5A—C4A—H4AA	119.1	N2B—C8B—C9B	120.8 (6)
C3A—C4A—H4AA	119.1	N2B—C8B—C7B	111.7 (6)
C4A—C5A—C6A	116.9 (8)	C9B—C8B—C7B	127.5 (6)
C4A—C5A—H5AA	121.5	C10B—C9B—C8B	118.4 (7)
C6A—C5A—H5AA	121.5	C10B—C9B—H9BA	120.8
N4A—C6A—C5A	132.2 (7)	C8B—C9B—H9BA	120.8
N4A—C6A—C1A	106.7 (6)	C9B—C10B—C11B	121.2 (8)
C5A—C6A—C1A	121.1 (7)	C9B—C10B—H10B	119.4
N1A—C7A—N4A	112.3 (5)	C11B—C10B—H10B	119.4
N1A—C7A—C8A	119.5 (6)	C12B—C11B—C10B	117.2 (7)
N4A—C7A—C8A	127.8 (6)	C12B—C11B—H11B	121.4
N2A—C8A—C9A	120.6 (6)	C10B—C11B—H11B	121.4
N2A—C8A—C7A	111.7 (6)	N2B—C12B—C11B	120.9 (6)
C9A—C8A—C7A	127.7 (6)	N2B—C12B—C13B	111.5 (5)
C10A—C9A—C8A	118.2 (7)	C11B—C12B—C13B	127.6 (6)
C10A—C9A—H9AA	120.9	N3B—C13B—N5B	114.0 (5)
C8A—C9A—H9AA	120.9	N3B—C13B—C12B	119.5 (6)
C9A—C10A—C11A	121.6 (7)	N5B—C13B—C12B	126.5 (6)
C9A—C10A—H10A	119.2	C19B—C14B—N5B	106.5 (6)
C11A—C10A—H10A	119.2	C19B—C14B—C15B	122.5 (7)
C12A—C11A—C10A	117.4 (7)	N5B—C14B—C15B	130.9 (7)
C12A—C11A—H11A	121.3	C16B—C15B—C14B	116.3 (8)
C10A—C11A—H11A	121.3	C16B—C15B—H15B	121.8
N2A—C12A—C11A	120.4 (6)	C14B—C15B—H15B	121.8
N2A—C12A—C13A	111.3 (5)	C15B—C16B—C17B	122.3 (8)
C11A—C12A—C13A	128.3 (6)	C15B—C16B—H16B	118.8
N3A—C13A—N5A	113.2 (5)	C17B—C16B—H16B	118.8
N3A—C13A—C12A	118.9 (5)	C18B—C17B—C16B	121.6 (8)
N5A—C13A—C12A	127.7 (6)	C18B—C17B—H17B	119.2
C19A—C14A—N5A	106.6 (6)	C16B—C17B—H17B	119.2
C19A—C14A—C15A	122.3 (7)	C17B—C18B—C19B	117.0 (7)
N5A—C14A—C15A	131.1 (7)	C17B—C18B—H18B	121.5
C16A—C15A—C14A	115.9 (8)	C19B—C18B—H18B	121.5
C16A—C15A—H15A	122.0	C14B—C19B—C18B	120.1 (7)
C14A—C15A—H15A	122.0	C14B—C19B—N3B	109.1 (6)
C15A—C16A—C17A	122.9 (8)	C18B—C19B—N3B	130.7 (7)
C15A—C16A—H16A	118.6	O3—S1—O1	108.6 (4)
C17A—C16A—H16A	118.6	O3—S1—O4	110.3 (4)
C18A—C17A—C16A	121.3 (8)	O1—S1—O4	109.7 (4)
C18A—C17A—H17A	119.3	O3—S1—O2	108.8 (4)
C16A—C17A—H17A	119.3	O1—S1—O2	111.4 (4)
C17A—C18A—C19A	116.9 (7)	O4—S1—O2	108.1 (4)
C17A—C18A—H18A	121.5		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N4A—H4NA⋯O2ⁱ	0.86	1.82	2.654 (8)	163
N5A—H5NA⋯O1ⁱⁱ	0.86	1.85	2.701 (8)	171
N4B—H4NB⋯O4ⁱⁱⁱ	0.86	1.85	2.685 (9)	164
N5B—H5NB⋯O3	0.86	1.81	2.663 (9)	173

Symmetry codes: (i) $-x+3/2, -y, z-1/2$; (ii) $-x+5/2, -y, z-1/2$; (iii) $x-1/2, -y+1/2, -z+2$.

Bis[2,6-bis(1*H*-benzimidazol-2-yl-κN^3)pyridine-κN]nickel(II) sulfate (II)

Crystal data

[Ni(C₁₉H₁₃N₅)₂]SO₄	$D_x = 0.933$ Mg m⁻³
$M_r = 777.46$ _	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Tetragonal, $I\bar{4}$	Cell parameters from 3126 reflections
$a = 28.596$ (2) Å	$\theta = 4.0–24.9°$
$c = 13.5438$ (9) Å	$\mu = 0.43$ mm⁻¹
$V = 11075.0$ (17) Å³	$T = 294$ K
$Z = 8$	Needles, light_red
$F(000) = 3200$	$0.38 \times 0.14 \times 0.12$ mm

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer	16294 measured reflections
Radiation source: fine-focus sealed tube	11374 independent reflections
Graphite monochromator	4172 reflections with $I > 2\sigma(I)$
ω scans, thick slices	$R_{int} = 0.095$
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)	$\theta_{max} = 28.9°$, $\theta_{min} = 3.6°$
	$h = -31 \rightarrow 33$
	$k = -38 \rightarrow 37$
$T_{min} = 0.96$, $T_{max} = 0.98$	$l = -18 \rightarrow 9$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.078$	$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2]$
$wR(F^2) = 0.220$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.89$	$(\Delta/\sigma)_{max} < 0.001$
11374 reflections	$\Delta\rho_{max} = 0.55$ e Å⁻³
488 parameters	$\Delta\rho_{min} = -0.23$ e Å⁻³
586 restraints	Absolute structure: Refined as an inversion twin
	Absolute structure parameter: 0.45 (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. Refined as a 2-component inversion twin

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Ni1	0.64892 (5)	0.18669 (5)	0.10607 (8)	0.0538 (4)
N1A	0.5815 (2)	0.2131 (3)	0.1423 (5)	0.062 (2)
N2A	0.6099 (2)	0.1636 (3)	−0.0099 (5)	0.0531 (19)
N3A	0.6974 (2)	0.1497 (3)	0.0178 (5)	0.061 (2)
N4A	0.5075 (3)	0.2189 (3)	0.0920 (5)	0.075 (2)
H4NA	0.483254	0.217136	0.054487	0.089*
N5A	0.7103 (3)	0.1091 (3)	−0.1203 (5)	0.068 (2)
H5NA	0.704557	0.094781	−0.174876	0.082*
C1A	0.5558 (3)	0.2366 (4)	0.2124 (6)	0.078 (3)
C2A	0.5689 (4)	0.2539 (5)	0.3048 (7)	0.116 (5)
H2AA	0.599239	0.250325	0.328178	0.139*
C3A	0.5360 (4)	0.2759 (6)	0.3593 (8)	0.126 (5)
H3AA	0.544595	0.290804	0.417519	0.151*
C4A	0.4893 (5)	0.2765 (8)	0.3294 (10)	0.190 (9)
H4AA	0.467164	0.287917	0.373500	0.228*
C5A	0.4733 (4)	0.2606 (6)	0.2344 (9)	0.138 (6)
H5AA	0.442980	0.264417	0.211100	0.165*
C6A	0.5091 (3)	0.2388 (5)	0.1817 (7)	0.084 (3)
C7A	0.5506 (3)	0.2021 (4)	0.0710 (6)	0.056 (2)
C8A	0.5646 (3)	0.1756 (3)	−0.0156 (6)	0.056 (2)
C9A	0.5358 (3)	0.1621 (4)	−0.0931 (6)	0.079 (3)
H9AA	0.504281	0.170180	−0.095187	0.094*
C10A	0.5563 (4)	0.1363 (5)	−0.1659 (7)	0.091 (4)
H10A	0.538173	0.125808	−0.218326	0.109*
C11A	0.6050 (3)	0.1251 (4)	−0.1639 (7)	0.079 (3)
H11A	0.619238	0.109115	−0.215507	0.095*
C12A	0.6297 (3)	0.1391 (3)	−0.0818 (6)	0.055 (2)
C13A	0.6780 (3)	0.1318 (3)	−0.0631 (6)	0.057 (2)
C14A	0.7533 (3)	0.1129 (4)	−0.0763 (6)	0.070 (3)
C15A	0.7965 (3)	0.1010 (5)	−0.1081 (8)	0.094 (4)
H15A	0.801520	0.086460	−0.168601	0.112*
C16A	0.8319 (4)	0.1116 (5)	−0.0462 (9)	0.114 (5)
H16A	0.862131	0.102871	−0.063832	0.137*
C17A	0.8253 (4)	0.1354 (6)	0.0443 (8)	0.116 (5)
H17A	0.850964	0.142010	0.084021	0.139*
C18A	0.7822 (3)	0.1485 (4)	0.0737 (7)	0.080 (3)
H18A	0.777337	0.164500	0.132678	0.096*
C19A	0.7450 (3)	0.1369 (4)	0.0108 (6)	0.065 (3)
N1B	0.6459 (3)	0.1332 (2)	0.2173 (5)	0.0525 (18)
N2B	0.6829 (3)	0.2170 (2)	0.2206 (5)	0.0533 (19)
N3B	0.6708 (3)	0.2514 (3)	0.0476 (5)	0.063 (2)
N4B	0.6554 (3)	0.1188 (3)	0.3777 (5)	0.068 (2)
H4NB	0.663031	0.122576	0.438651	0.081*
N5B	0.7053 (3)	0.3203 (3)	0.0782 (5)	0.067 (2)
H5NB	0.719367	0.341965	0.110748	0.080*

C1B	0.6283 (3)	0.0894 (3)	0.2377 (6)	0.058 (2)
C2B	0.6095 (4)	0.0554 (3)	0.1762 (7)	0.082 (3)
H2BA	0.607350	0.060309	0.108477	0.098*
C3B	0.5944 (5)	0.0151 (4)	0.2172 (9)	0.104 (4)
H3BA	0.581404	−0.007986	0.177407	0.125*
C4B	0.5983 (5)	0.0078 (4)	0.3186 (9)	0.120 (5)
H4BA	0.587447	−0.020378	0.344123	0.144*
C5B	0.6179 (4)	0.0410 (3)	0.3860 (8)	0.086 (3)
H5BA	0.619811	0.036275	0.453831	0.103*
C6B	0.6339 (4)	0.0811 (3)	0.3389 (6)	0.070 (3)
C7B	0.6630 (4)	0.1495 (3)	0.3036 (6)	0.064 (3)
C8B	0.6850 (4)	0.1950 (3)	0.3084 (6)	0.063 (3)
C9B	0.7042 (4)	0.2157 (3)	0.3924 (7)	0.076 (3)
H9BA	0.703975	0.200865	0.453502	0.091*
C10B	0.7233 (4)	0.2590 (4)	0.3793 (7)	0.094 (4)
H10B	0.737897	0.273297	0.432737	0.113*
C11B	0.7220 (4)	0.2832 (3)	0.2871 (7)	0.077 (3)
H11B	0.734631	0.312904	0.279180	0.093*
C12B	0.7006 (4)	0.2597 (3)	0.2109 (6)	0.061 (3)
C13B	0.6930 (4)	0.2774 (3)	0.1145 (6)	0.064 (3)
C14B	0.6915 (4)	0.3231 (3)	−0.0184 (7)	0.074 (3)
C15B	0.6943 (4)	0.3587 (4)	−0.0847 (7)	0.090 (3)
H15B	0.708964	0.386891	−0.070613	0.108*
C16B	0.6739 (5)	0.3497 (4)	−0.1730 (8)	0.100 (4)
H16B	0.673751	0.373328	−0.220207	0.120*
C17B	0.6529 (5)	0.3064 (4)	−0.1973 (7)	0.094 (4)
H17B	0.641722	0.301502	−0.260922	0.113*
C18B	0.6489 (4)	0.2721 (3)	−0.1290 (6)	0.076 (3)
H18B	0.634138	0.243910	−0.143115	0.092*
C19B	0.6683 (3)	0.2813 (3)	−0.0361 (6)	0.060 (2)
S1	0.79506 (12)	0.40472 (10)	0.1171 (2)	0.0672 (8)
O1	0.7526 (3)	0.3852 (3)	0.1690 (5)	0.099 (3)
O2	0.8230 (3)	0.4275 (3)	0.1943 (5)	0.086 (2)
O3	0.7816 (3)	0.4362 (3)	0.0395 (5)	0.095 (3)
O4	0.8206 (4)	0.3659 (3)	0.0714 (5)	0.110 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0611 (9)	0.0644 (9)	0.0361 (6)	−0.0025 (7)	−0.0033 (7)	−0.0036 (7)
N1A	0.068 (3)	0.079 (5)	0.040 (3)	−0.001 (2)	−0.0065 (16)	−0.008 (3)
N2A	0.062 (2)	0.062 (4)	0.036 (2)	−0.004 (2)	−0.001 (2)	−0.001 (3)
N3A	0.069 (3)	0.073 (4)	0.042 (3)	0.000 (3)	−0.0023 (18)	−0.007 (3)
N4A	0.067 (3)	0.105 (6)	0.052 (4)	0.009 (3)	−0.003 (2)	−0.017 (4)
N5A	0.076 (3)	0.086 (6)	0.042 (3)	0.011 (3)	0.002 (2)	−0.004 (3)
C1A	0.085 (4)	0.103 (7)	0.046 (3)	0.015 (4)	−0.005 (2)	−0.014 (4)
C2A	0.106 (6)	0.176 (11)	0.066 (4)	0.048 (7)	−0.024 (4)	−0.052 (5)
C3A	0.117 (5)	0.182 (13)	0.078 (7)	0.053 (7)	−0.014 (4)	−0.051 (7)

C4A	0.120 (5)	0.34 (2)	0.107 (7)	0.074 (8)	−0.023 (5)	−0.112 (10)
C5A	0.106 (5)	0.221 (14)	0.085 (6)	0.055 (7)	−0.011 (4)	−0.063 (7)
C6A	0.086 (4)	0.113 (8)	0.054 (4)	0.018 (4)	−0.008 (3)	−0.021 (4)
C7A	0.063 (3)	0.071 (5)	0.035 (3)	−0.001 (3)	−0.002 (2)	−0.005 (3)
C8A	0.062 (2)	0.069 (5)	0.035 (3)	−0.002 (3)	−0.002 (2)	−0.004 (3)
C9A	0.078 (4)	0.110 (8)	0.048 (3)	−0.005 (4)	−0.013 (3)	−0.017 (4)
C10A	0.086 (4)	0.131 (9)	0.055 (5)	0.003 (5)	−0.014 (3)	−0.028 (5)
C11A	0.084 (4)	0.103 (9)	0.050 (3)	−0.003 (4)	−0.011 (3)	−0.015 (4)
C12A	0.066 (2)	0.062 (5)	0.037 (3)	−0.003 (3)	0.0007 (19)	−0.001 (3)
C13A	0.066 (2)	0.067 (6)	0.039 (3)	−0.002 (3)	0.000 (2)	−0.004 (3)
C14A	0.077 (3)	0.092 (7)	0.041 (3)	0.006 (3)	0.001 (2)	0.004 (4)
C15A	0.079 (3)	0.140 (11)	0.062 (5)	0.012 (4)	0.002 (3)	−0.018 (6)
C16A	0.083 (4)	0.178 (12)	0.081 (5)	0.020 (6)	−0.006 (4)	−0.041 (6)
C17A	0.081 (3)	0.187 (12)	0.080 (5)	0.039 (6)	−0.017 (4)	−0.043 (6)
C18A	0.076 (3)	0.097 (9)	0.067 (5)	0.020 (4)	−0.013 (3)	−0.016 (5)
C19A	0.070 (3)	0.086 (6)	0.040 (3)	0.005 (2)	0.0014 (18)	0.007 (4)
N1B	0.056 (5)	0.060 (3)	0.042 (2)	0.001 (2)	0.002 (2)	−0.004 (2)
N2B	0.063 (4)	0.056 (3)	0.041 (2)	0.002 (3)	−0.005 (3)	−0.0037 (16)
N3B	0.072 (5)	0.072 (3)	0.045 (2)	−0.006 (3)	−0.006 (3)	0.001 (2)
N4B	0.076 (6)	0.073 (3)	0.054 (3)	−0.007 (3)	−0.011 (4)	0.009 (2)
N5B	0.078 (6)	0.069 (3)	0.053 (3)	−0.004 (3)	−0.005 (3)	0.004 (2)
C1B	0.053 (5)	0.061 (3)	0.059 (3)	0.000 (3)	−0.005 (3)	0.002 (2)
C2B	0.103 (8)	0.068 (4)	0.073 (4)	−0.010 (4)	−0.025 (5)	0.001 (3)
C3B	0.131 (11)	0.074 (5)	0.107 (4)	−0.013 (6)	−0.009 (6)	0.011 (4)
C4B	0.154 (13)	0.098 (7)	0.108 (4)	−0.029 (7)	−0.013 (6)	0.016 (4)
C5B	0.084 (7)	0.081 (4)	0.094 (5)	−0.004 (4)	0.004 (6)	0.019 (3)
C6B	0.075 (7)	0.075 (4)	0.060 (3)	−0.008 (4)	−0.009 (3)	0.005 (2)
C7B	0.086 (6)	0.060 (3)	0.045 (3)	−0.006 (4)	−0.008 (3)	−0.002 (2)
C8B	0.087 (7)	0.061 (3)	0.043 (2)	−0.006 (3)	−0.010 (3)	−0.001 (2)
C9B	0.099 (7)	0.080 (4)	0.048 (3)	−0.011 (5)	−0.013 (4)	−0.008 (3)
C10B	0.128 (10)	0.089 (5)	0.065 (4)	−0.028 (5)	−0.037 (5)	0.005 (4)
C11B	0.105 (8)	0.069 (5)	0.058 (3)	−0.006 (5)	−0.025 (4)	−0.007 (3)
C12B	0.079 (6)	0.059 (3)	0.045 (2)	−0.006 (3)	−0.010 (3)	−0.001 (2)
C13B	0.078 (6)	0.069 (3)	0.046 (2)	−0.006 (3)	−0.010 (3)	0.0026 (19)
C14B	0.077 (7)	0.091 (4)	0.054 (3)	−0.015 (4)	−0.005 (4)	0.010 (2)
C15B	0.114 (9)	0.095 (4)	0.062 (4)	−0.004 (5)	0.011 (4)	0.015 (3)
C16B	0.141 (10)	0.093 (5)	0.066 (4)	−0.014 (6)	0.000 (6)	0.020 (4)
C17B	0.126 (10)	0.088 (5)	0.069 (4)	−0.004 (5)	−0.010 (6)	0.024 (4)
C18B	0.095 (8)	0.078 (5)	0.057 (3)	−0.009 (5)	−0.019 (4)	0.013 (3)
C19B	0.048 (5)	0.083 (4)	0.050 (2)	0.000 (3)	0.000 (3)	0.008 (2)
S1	0.102 (2)	0.0547 (18)	0.0452 (15)	−0.0061 (17)	−0.0069 (17)	0.0074 (15)
O1	0.124 (4)	0.104 (7)	0.070 (4)	−0.041 (5)	0.020 (4)	−0.007 (4)
O2	0.121 (5)	0.067 (5)	0.070 (4)	0.002 (4)	−0.032 (5)	−0.011 (4)
O3	0.137 (7)	0.082 (4)	0.065 (4)	0.002 (5)	−0.015 (4)	0.033 (5)
O4	0.181 (7)	0.071 (4)	0.077 (5)	0.032 (5)	0.028 (5)	0.007 (4)

Geometric parameters (Å, º)

Ni1—N2B	2.026 (6)	C18A—H18A	0.9300
Ni1—N2A	2.037 (6)	N1B—C7B	1.350 (8)
Ni1—N3B	2.109 (7)	N1B—C1B	1.378 (9)
Ni1—N3A	2.115 (7)	N2B—C12B	1.327 (9)
Ni1—N1A	2.128 (7)	N2B—C8B	1.346 (8)
Ni1—N1B	2.149 (7)	N3B—C13B	1.332 (8)
N1A—C7A	1.346 (8)	N3B—C19B	1.421 (9)
N1A—C1A	1.375 (9)	N4B—C7B	1.351 (9)
N2A—C12A	1.326 (8)	N4B—C6B	1.349 (9)
N2A—C8A	1.343 (9)	N4B—H4NB	0.8600
N3A—C13A	1.330 (8)	N5B—C13B	1.369 (9)
N3A—C19A	1.413 (9)	N5B—C14B	1.369 (9)
N4A—C6A	1.342 (9)	N5B—H5NB	0.8600
N4A—C7A	1.354 (9)	C1B—C2B	1.387 (10)
N4A—H4NA	0.8600	C1B—C6B	1.399 (10)
N5A—C13A	1.370 (9)	C2B—C3B	1.350 (11)
N5A—C14A	1.372 (9)	C2B—H2BA	0.9300
N5A—H5NA	0.8600	C3B—C4B	1.394 (12)
C1A—C6A	1.400 (10)	C3B—H3BA	0.9300
C1A—C2A	1.397 (11)	C4B—C5B	1.432 (13)
C2A—C3A	1.350 (11)	C4B—H4BA	0.9300
C2A—H2AA	0.9300	C5B—C6B	1.389 (11)
C3A—C4A	1.395 (12)	C5B—H5BA	0.9300
C3A—H3AA	0.9300	C7B—C8B	1.449 (10)
C4A—C5A	1.438 (13)	C8B—C9B	1.394 (10)
C4A—H4AA	0.9300	C9B—C10B	1.365 (11)
C5A—C6A	1.395 (11)	C9B—H9BA	0.9300
C5A—H5AA	0.9300	C10B—C11B	1.429 (11)
C7A—C8A	1.453 (10)	C10B—H10B	0.9300
C8A—C9A	1.390 (10)	C11B—C12B	1.375 (10)
C9A—C10A	1.365 (11)	C11B—H11B	0.9300
C9A—H9AA	0.9300	C12B—C13B	1.417 (9)
C10A—C11A	1.427 (11)	C14B—C15B	1.359 (10)
C10A—H10A	0.9300	C14B—C19B	1.388 (10)
C11A—C12A	1.377 (9)	C15B—C16B	1.354 (11)
C11A—H11A	0.9300	C15B—H15B	0.9300
C12A—C13A	1.419 (9)	C16B—C17B	1.415 (12)
C14A—C15A	1.352 (10)	C16B—H16B	0.9300
C14A—C19A	1.385 (10)	C17B—C18B	1.353 (11)
C15A—C16A	1.349 (11)	C17B—H17B	0.9300
C15A—H15A	0.9300	C18B—C19B	1.401 (10)
C16A—C17A	1.414 (12)	C18B—H18B	0.9300
C16A—H16A	0.9300	S1—O3	1.436 (7)
C17A—C18A	1.350 (11)	S1—O4	1.464 (9)
C17A—H17A	0.9300	S1—O2	1.469 (8)
C18A—C19A	1.403 (10)	S1—O1	1.509 (8)

N2B—Ni1—N2A	172.9 (3)	C19A—C18A—H18A	121.7
N2B—Ni1—N3B	76.7 (3)	C14A—C19A—C18A	120.3 (8)
N2A—Ni1—N3B	99.1 (3)	C14A—C19A—N3A	110.6 (7)
N2B—Ni1—N3A	109.4 (3)	C18A—C19A—N3A	128.9 (8)
N2A—Ni1—N3A	76.1 (3)	C7B—N1B—C1B	105.8 (7)
N3B—Ni1—N3A	91.8 (3)	C7B—N1B—Ni1	110.2 (5)
N2B—Ni1—N1A	96.1 (3)	C1B—N1B—Ni1	143.4 (5)
N2A—Ni1—N1A	78.3 (3)	C12B—N2B—C8B	120.0 (7)
N3B—Ni1—N1A	92.5 (3)	C12B—N2B—Ni1	120.0 (5)
N3A—Ni1—N1A	154.4 (3)	C8B—N2B—Ni1	119.9 (5)
N2B—Ni1—N1B	77.7 (2)	C13B—N3B—C19B	103.4 (6)
N2A—Ni1—N1B	106.7 (3)	C13B—N3B—Ni1	112.0 (5)
N3B—Ni1—N1B	154.2 (3)	C19B—N3B—Ni1	144.3 (5)
N3A—Ni1—N1B	93.8 (3)	C7B—N4B—C6B	107.6 (7)
N1A—Ni1—N1B	93.2 (3)	C7B—N4B—H4NB	126.2
C7A—N1A—C1A	105.0 (7)	C6B—N4B—H4NB	126.2
C7A—N1A—Ni1	110.3 (5)	C13B—N5B—C14B	108.7 (7)
C1A—N1A—Ni1	144.7 (6)	C13B—N5B—H5NB	125.6
C12A—N2A—C8A	120.4 (7)	C14B—N5B—H5NB	125.6
C12A—N2A—Ni1	120.2 (5)	N1B—C1B—C2B	131.1 (8)
C8A—N2A—Ni1	119.2 (5)	N1B—C1B—C6B	108.0 (7)
C13A—N3A—C19A	104.3 (6)	C2B—C1B—C6B	120.9 (8)
C13A—N3A—Ni1	112.6 (5)	C3B—C2B—C1B	118.3 (9)
C19A—N3A—Ni1	143.1 (5)	C3B—C2B—H2BA	120.8
C6A—N4A—C7A	107.9 (7)	C1B—C2B—H2BA	120.8
C6A—N4A—H4NA	126.0	C2B—C3B—C4B	120.5 (10)
C7A—N4A—H4NA	126.0	C2B—C3B—H3BA	119.7
C13A—N5A—C14A	108.7 (7)	C4B—C3B—H3BA	119.7
C13A—N5A—H5NA	125.6	C3B—C4B—C5B	124.1 (10)
C14A—N5A—H5NA	125.6	C3B—C4B—H4BA	118.0
N1A—C1A—C6A	109.1 (7)	C5B—C4B—H4BA	118.0
N1A—C1A—C2A	130.5 (8)	C6B—C5B—C4B	112.5 (9)
C6A—C1A—C2A	120.3 (8)	C6B—C5B—H5BA	123.7
C3A—C2A—C1A	118.0 (9)	C4B—C5B—H5BA	123.7
C3A—C2A—H2AA	121.0	N4B—C6B—C5B	129.0 (8)
C1A—C2A—H2AA	121.0	N4B—C6B—C1B	107.4 (8)
C2A—C3A—C4A	120.9 (10)	C5B—C6B—C1B	123.5 (9)
C2A—C3A—H3AA	119.6	N4B—C7B—N1B	111.2 (7)
C4A—C3A—H3AA	119.6	N4B—C7B—C8B	128.4 (7)
C3A—C4A—C5A	124.0 (10)	N1B—C7B—C8B	120.5 (7)
C3A—C4A—H4AA	118.0	N2B—C8B—C9B	122.8 (8)
C5A—C4A—H4AA	118.0	N2B—C8B—C7B	111.1 (7)
C6A—C5A—C4A	111.5 (9)	C9B—C8B—C7B	126.0 (8)
C6A—C5A—H5AA	124.3	C10B—C9B—C8B	115.8 (9)
C4A—C5A—H5AA	124.3	C10B—C9B—H9BA	122.1
N4A—C6A—C1A	106.5 (8)	C8B—C9B—H9BA	122.1
N4A—C6A—C5A	128.8 (9)	C9B—C10B—C11B	122.8 (9)

C1A—C6A—C5A	124.6 (9)	C9B—C10B—H10B	118.6
N1A—C7A—N4A	111.4 (7)	C11B—C10B—H10B	118.6
N1A—C7A—C8A	121.3 (7)	C12B—C11B—C10B	115.5 (8)
N4A—C7A—C8A	127.3 (7)	C12B—C11B—H11B	122.2
N2A—C8A—C9A	123.0 (8)	C10B—C11B—H11B	122.2
N2A—C8A—C7A	110.7 (7)	N2B—C12B—C11B	123.0 (8)
C9A—C8A—C7A	126.2 (8)	N2B—C12B—C13B	111.2 (7)
C10A—C9A—C8A	116.1 (8)	C11B—C12B—C13B	125.8 (8)
C10A—C9A—H9AA	121.9	N3B—C13B—N5B	112.2 (7)
C8A—C9A—H9AA	121.9	N3B—C13B—C12B	120.1 (7)
C9A—C10A—C11A	121.8 (9)	N5B—C13B—C12B	127.7 (7)
C9A—C10A—H10A	119.1	C15B—C14B—N5B	131.2 (9)
C11A—C10A—H10A	119.1	C15B—C14B—C19B	123.9 (8)
C12A—C11A—C10A	116.8 (8)	N5B—C14B—C19B	104.6 (7)
C12A—C11A—H11A	121.6	C16B—C15B—C14B	114.7 (9)
C10A—C11A—H11A	121.6	C16B—C15B—H15B	122.7
N2A—C12A—C11A	121.7 (8)	C14B—C15B—H15B	122.7
N2A—C12A—C13A	111.2 (7)	C15B—C16B—C17B	123.6 (10)
C11A—C12A—C13A	127.0 (8)	C15B—C16B—H16B	118.2
N3A—C13A—N5A	111.5 (7)	C17B—C16B—H16B	118.2
N3A—C13A—C12A	119.8 (7)	C18B—C17B—C16B	120.8 (9)
N5A—C13A—C12A	128.6 (7)	C18B—C17B—H17B	119.6
C15A—C14A—N5A	131.4 (8)	C16B—C17B—H17B	119.6
C15A—C14A—C19A	123.6 (9)	C17B—C18B—C19B	116.4 (9)
N5A—C14A—C19A	104.8 (7)	C17B—C18B—H18B	121.8
C14A—C15A—C16A	115.5 (9)	C19B—C18B—H18B	121.8
C14A—C15A—H15A	122.2	C14B—C19B—C18B	120.4 (8)
C16A—C15A—H15A	122.2	C14B—C19B—N3B	110.8 (7)
C15A—C16A—C17A	123.1 (10)	C18B—C19B—N3B	128.6 (8)
C15A—C16A—H16A	118.5	O3—S1—O4	107.4 (5)
C17A—C16A—H16A	118.5	O3—S1—O2	112.8 (5)
C18A—C17A—C16A	120.9 (9)	O4—S1—O2	111.5 (5)
C18A—C17A—H17A	119.6	O3—S1—O1	111.0 (6)
C16A—C17A—H17A	119.6	O4—S1—O1	108.4 (5)
C17A—C18A—C19A	116.5 (9)	O2—S1—O1	105.7 (5)
C17A—C18A—H18A	121.7		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N4*A*—H4*NA*···O3[i]	0.86	1.85	2.706 (10)	172
N5*A*—H5*NA*···O2[ii]	0.86	2.04	2.883 (11)	165
N4*B*—H4*NB*···O4[iii]	0.86	1.89	2.746 (10)	177
N5*B*—H5*NB*···O1	0.86	1.75	2.605 (10)	174

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

Bis[2,6-bis(1*H*-benzimidazol-2-yl-κ*N*³)pyridine-κ*N*]nickel(II) sulfate–dimethylformamide–water (1/1/4.25) (III)

Crystal data

[Ni(C$_{19}$H$_{13}$N$_5$)$_2$]SO$_4$·C$_3$H$_7$NO·4.25H$_2$O
M_r = 925.10
Orthorhombic, *Pccn*
a = 13.406 (5) Å
b = 24.365 (5) Å
c = 28.114 (5) Å
V = 9183 (4) Å^3
Z = 8
$F(000)$ = 3844

D_x = 1.338 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 5212 reflections
θ = 3.6–28.0°
μ = 0.53 mm^{-1}
T = 294 K
Fragment, light_red
0.28 × 0.18 × 0.14 mm

Data collection

Oxford Diffraction Gemini CCD S Ultra
    diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans, thick slices
Absorption correction: multi-scan
    (CrysAlis PRO; Oxford Diffraction, 2009)
T_{min} = 0.90, T_{max} = 0.94

32970 measured reflections
10959 independent reflections
4106 reflections with $I > 2\sigma(I)$
R_{int} = 0.166
θ_{max} = 29.4°, θ_{min} = 3.7°
h = −16→18
k = −33→30
l = −37→35

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.086
$wR(F^2)$ = 0.334
S = 0.85
10959 reflections
581 parameters
552 restraints

Hydrogen site location: inferred from
    neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1868P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.76257 (5)	0.45859 (3)	0.36949 (3)	0.0429 (3)	
N1A	0.8559 (3)	0.5276 (2)	0.35855 (18)	0.0468 (11)	
N2A	0.8718 (3)	0.4458 (2)	0.41757 (17)	0.0435 (10)	
N3A	0.7174 (3)	0.3858 (2)	0.40197 (18)	0.0497 (12)	
N4A	0.9952 (4)	0.5700 (2)	0.38078 (18)	0.0505 (12)	
H4AA	1.049741	0.576304	0.395923	0.061*	
N5A	0.7388 (3)	0.3281 (2)	0.46274 (19)	0.0553 (13)	
H5AA	0.765735	0.313306	0.487346	0.066*	
C1A	0.8650 (4)	0.5757 (3)	0.3333 (2)	0.0511 (14)	
C2A	0.8038 (5)	0.5982 (3)	0.2980 (3)	0.0691 (19)	

H2A	0.746253	0.580038	0.288211	0.083*
C3A	0.8301 (6)	0.6472 (4)	0.2781 (3)	0.093 (3)
H3A	0.789639	0.663026	0.255010	0.111*
C4A	0.9189 (6)	0.6741 (3)	0.2926 (3)	0.088 (2)
H4A	0.936407	0.707106	0.278141	0.106*
C5A	0.9805 (5)	0.6528 (3)	0.3277 (3)	0.080 (2)
H5A	1.037865	0.670817	0.337802	0.096*
C6A	0.9515 (4)	0.6033 (3)	0.3466 (2)	0.0551 (14)
C7A	0.9359 (4)	0.5258 (3)	0.3857 (2)	0.0434 (12)
C8A	0.9517 (4)	0.4791 (2)	0.41858 (19)	0.0392 (11)
C9A	1.0338 (4)	0.4684 (3)	0.4457 (2)	0.0495 (14)
H9A	1.089451	0.491149	0.444945	0.059*
C10A	1.0310 (5)	0.4218 (3)	0.4746 (2)	0.0566 (15)
H10A	1.085433	0.413438	0.493752	0.068*
C11A	0.9491 (4)	0.3883 (3)	0.4751 (2)	0.0534 (15)
H11A	0.947521	0.357633	0.494835	0.064*
C12A	0.8689 (4)	0.4002 (2)	0.4461 (2)	0.0461 (12)
C13A	0.7750 (4)	0.3711 (3)	0.4375 (2)	0.0468 (12)
C14A	0.6507 (4)	0.3128 (3)	0.4415 (2)	0.0568 (15)
C15A	0.5796 (5)	0.2716 (3)	0.4507 (3)	0.079 (2)
H15A	0.586130	0.248240	0.476645	0.095*
C16A	0.5005 (6)	0.2671 (4)	0.4201 (3)	0.086 (2)
H16A	0.453090	0.239953	0.425587	0.103*
C17A	0.4883 (6)	0.3022 (3)	0.3808 (3)	0.081 (2)
H17A	0.434175	0.297596	0.360529	0.097*
C18A	0.5560 (5)	0.3431 (3)	0.3724 (3)	0.0628 (17)
H18A	0.547589	0.366991	0.346841	0.075*
C19A	0.6383 (4)	0.3485 (3)	0.4028 (2)	0.0521 (14)
N1B	0.8208 (3)	0.4178 (2)	0.30917 (18)	0.0481 (11)
N2B	0.6529 (3)	0.4703 (2)	0.32124 (17)	0.0445 (11)
N3B	0.6567 (3)	0.5035 (2)	0.40849 (17)	0.0464 (11)
N4B	0.7954 (4)	0.3962 (2)	0.23290 (18)	0.0540 (12)
H4BA	0.765711	0.393393	0.205878	0.065*
N5B	0.5092 (4)	0.5443 (2)	0.40806 (19)	0.0553 (13)
H5BA	0.452919	0.556436	0.397816	0.066*
C1B	0.9025 (4)	0.3893 (3)	0.2918 (2)	0.0520 (14)
C2B	0.9899 (5)	0.3719 (3)	0.3153 (3)	0.071 (2)
H2B	0.999623	0.378303	0.347550	0.085*
C3B	1.0604 (5)	0.3450 (4)	0.2882 (3)	0.089 (3)
H3B	1.119765	0.334159	0.302469	0.107*
C4B	1.0455 (5)	0.3334 (3)	0.2398 (3)	0.075 (2)
H4B	1.095094	0.315615	0.222607	0.090*
C5B	0.9590 (5)	0.3481 (3)	0.2179 (3)	0.0712 (19)
H5B	0.948269	0.339847	0.185998	0.085*
C6B	0.8871 (4)	0.3757 (3)	0.2442 (2)	0.0535 (14)
C7B	0.7601 (4)	0.4215 (3)	0.2716 (2)	0.0469 (13)
C8B	0.6649 (4)	0.4508 (3)	0.2758 (2)	0.0472 (13)
C9B	0.5934 (5)	0.4584 (3)	0.2424 (2)	0.0616 (17)

H9B	0.602302	0.445324	0.211601	0.074*
C10B	0.5063 (5)	0.4861 (3)	0.2549 (3)	0.075 (2)
H10B	0.455736	0.490905	0.232645	0.090*
C11B	0.4953 (5)	0.5068 (3)	0.3016 (2)	0.0596 (16)
H11B	0.438064	0.525831	0.310438	0.072*
C12B	0.5709 (4)	0.4982 (2)	0.3337 (2)	0.0464 (13)
C13B	0.5761 (4)	0.5152 (3)	0.3831 (2)	0.0463 (13)
C14B	0.5470 (4)	0.5508 (3)	0.4526 (2)	0.0507 (13)
C15B	0.5101 (5)	0.5775 (3)	0.4933 (3)	0.0720 (19)
H15B	0.449117	0.595702	0.493034	0.086*
C16B	0.5678 (5)	0.5756 (3)	0.5333 (3)	0.0718 (19)
H16B	0.544805	0.592263	0.561015	0.086*
C17B	0.6605 (5)	0.5494 (3)	0.5338 (3)	0.073 (2)
H17B	0.698427	0.550032	0.561528	0.087*
C18B	0.6966 (5)	0.5229 (3)	0.4948 (2)	0.0582 (16)
H18B	0.756945	0.504184	0.495799	0.070*
C19B	0.6401 (4)	0.5250 (3)	0.4536 (2)	0.0463 (13)
O1C	0.7965 (6)	0.6719 (3)	0.5069 (3)	0.141 (3)
N1C	0.6856 (6)	0.6834 (3)	0.4458 (3)	0.108 (2)
C1C	0.7529 (10)	0.6622 (6)	0.4125 (5)	0.187 (6)
H1C1	0.804412	0.642226	0.428683	0.280*
H1C2	0.782140	0.691813	0.394775	0.280*
H1C3	0.718286	0.638075	0.391136	0.280*
C2C	0.5885 (9)	0.7037 (6)	0.4343 (6)	0.186 (6)
H2C1	0.559437	0.720396	0.461972	0.279*
H2C2	0.547135	0.673844	0.423929	0.279*
H2C3	0.593710	0.730421	0.409372	0.279*
C3C	0.7163 (9)	0.6863 (5)	0.4926 (4)	0.117 (3)
H3C	0.671491	0.700508	0.514672	0.140*
S1	0.74643 (10)	0.41339 (7)	0.61042 (6)	0.0524 (5)
O1	0.6698 (4)	0.3806 (3)	0.5878 (2)	0.103 (2)
O2	0.7929 (3)	0.3821 (2)	0.64958 (16)	0.0685 (13)
O3	0.6975 (6)	0.4610 (2)	0.6293 (2)	0.100 (2)
O4	0.8231 (3)	0.4251 (3)	0.57542 (17)	0.0831 (16)
O1W	0.8030 (7)	0.6612 (3)	0.6051 (3)	0.154 (3)
O2WA	0.7889 (11)	0.5565 (6)	0.6535 (5)	0.107 (5)	0.5
O2WB	0.714 (2)	0.5724 (12)	0.6580 (11)	0.107 (5)	0.25
O3W	0.8399 (4)	0.3018 (2)	0.54695 (17)	0.0882 (17)
O4W	0.6274 (5)	0.2747 (3)	0.6159 (2)	0.1013 (19)
O5W	0.750000	0.750000	0.6651 (5)	0.146 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0302 (4)	0.0524 (5)	0.0462 (5)	0.0020 (3)	−0.0044 (3)	0.0016 (4)
N1A	0.0295 (19)	0.055 (2)	0.056 (3)	0.0014 (19)	−0.0023 (18)	0.005 (2)
N2A	0.0279 (18)	0.055 (2)	0.048 (2)	0.0039 (17)	−0.003 (2)	0.0034 (19)
N3A	0.039 (2)	0.055 (3)	0.054 (3)	−0.0014 (19)	−0.003 (2)	0.001 (2)

N4A	0.034 (2)	0.056 (3)	0.061 (3)	−0.0064 (19)	−0.001 (2)	−0.002 (2)
N5A	0.045 (2)	0.057 (3)	0.064 (3)	−0.001 (2)	0.002 (2)	0.008 (2)
C1A	0.038 (2)	0.056 (3)	0.059 (3)	0.003 (2)	0.000 (2)	0.008 (2)
C2A	0.052 (3)	0.072 (4)	0.083 (4)	0.003 (3)	−0.013 (3)	0.023 (3)
C3A	0.058 (4)	0.090 (4)	0.130 (7)	0.005 (3)	−0.008 (4)	0.053 (5)
C4A	0.060 (4)	0.082 (5)	0.123 (6)	0.003 (3)	0.004 (4)	0.044 (5)
C5A	0.054 (4)	0.073 (4)	0.113 (5)	−0.005 (3)	0.001 (4)	0.029 (4)
C6A	0.041 (3)	0.057 (3)	0.067 (4)	0.000 (2)	0.001 (2)	0.003 (2)
C7A	0.029 (2)	0.050 (2)	0.051 (3)	0.0007 (19)	−0.0006 (19)	0.000 (2)
C8A	0.0256 (18)	0.050 (3)	0.042 (3)	0.0070 (17)	0.0031 (18)	−0.005 (2)
C9A	0.034 (2)	0.057 (3)	0.057 (3)	0.001 (2)	−0.011 (2)	−0.003 (2)
C10A	0.046 (3)	0.057 (3)	0.067 (4)	0.004 (2)	−0.018 (3)	0.000 (3)
C11A	0.051 (2)	0.052 (3)	0.057 (3)	0.003 (2)	−0.013 (3)	0.004 (3)
C12A	0.042 (2)	0.051 (3)	0.045 (3)	0.003 (2)	−0.003 (2)	0.000 (2)
C13A	0.041 (2)	0.049 (3)	0.051 (3)	0.003 (2)	0.001 (2)	−0.001 (2)
C14A	0.044 (3)	0.055 (3)	0.071 (3)	0.003 (2)	0.001 (2)	0.003 (3)
C15A	0.056 (3)	0.061 (4)	0.120 (6)	−0.004 (3)	0.011 (3)	0.005 (4)
C16A	0.059 (4)	0.074 (5)	0.124 (6)	−0.013 (4)	0.009 (4)	0.002 (4)
C17A	0.052 (4)	0.076 (4)	0.115 (5)	−0.009 (3)	0.004 (4)	−0.004 (4)
C18A	0.045 (3)	0.070 (4)	0.074 (4)	−0.003 (3)	−0.004 (3)	−0.003 (3)
C19A	0.039 (2)	0.052 (3)	0.066 (3)	0.001 (2)	0.002 (2)	−0.002 (2)
N1B	0.037 (2)	0.053 (3)	0.055 (2)	0.004 (2)	−0.0016 (17)	0.001 (2)
N2B	0.0304 (19)	0.051 (3)	0.052 (2)	0.0024 (18)	−0.0052 (19)	0.000 (2)
N3B	0.0297 (19)	0.057 (3)	0.053 (2)	0.003 (2)	−0.0032 (18)	−0.005 (2)
N4B	0.043 (2)	0.065 (3)	0.054 (2)	0.000 (2)	0.001 (2)	−0.008 (2)
N5B	0.035 (2)	0.067 (3)	0.063 (2)	0.010 (2)	−0.0027 (19)	0.004 (2)
C1B	0.037 (2)	0.059 (3)	0.061 (3)	0.001 (2)	0.002 (2)	−0.003 (3)
C2B	0.045 (3)	0.094 (5)	0.074 (4)	0.018 (3)	−0.002 (3)	−0.004 (4)
C3B	0.050 (4)	0.119 (6)	0.099 (4)	0.024 (4)	0.000 (3)	−0.023 (5)
C4B	0.048 (3)	0.084 (5)	0.093 (4)	0.008 (3)	0.013 (3)	−0.013 (4)
C5B	0.051 (3)	0.083 (5)	0.079 (4)	0.000 (3)	0.008 (3)	−0.019 (4)
C6B	0.040 (2)	0.062 (4)	0.059 (3)	−0.005 (2)	0.001 (2)	−0.003 (3)
C7B	0.039 (2)	0.052 (3)	0.050 (2)	−0.001 (2)	0.0001 (18)	−0.001 (2)
C8B	0.038 (2)	0.054 (3)	0.050 (2)	−0.001 (2)	−0.0026 (19)	0.002 (2)
C9B	0.060 (3)	0.066 (4)	0.059 (3)	0.008 (3)	−0.020 (3)	−0.009 (3)
C10B	0.064 (4)	0.091 (5)	0.071 (3)	0.020 (3)	−0.024 (3)	−0.014 (4)
C11B	0.043 (3)	0.068 (4)	0.067 (3)	0.013 (3)	−0.016 (3)	−0.003 (3)
C12B	0.028 (2)	0.055 (3)	0.056 (2)	0.003 (2)	−0.0050 (18)	0.005 (2)
C13B	0.030 (2)	0.054 (3)	0.054 (2)	−0.002 (2)	−0.0022 (17)	0.007 (2)
C14B	0.034 (2)	0.059 (4)	0.059 (2)	−0.006 (2)	0.005 (2)	0.006 (2)
C15B	0.053 (4)	0.091 (5)	0.072 (3)	−0.003 (4)	0.014 (3)	−0.010 (3)
C16B	0.071 (3)	0.078 (5)	0.066 (3)	−0.002 (3)	0.011 (3)	−0.011 (4)
C17B	0.068 (3)	0.091 (5)	0.059 (3)	−0.003 (3)	−0.004 (3)	−0.017 (3)
C18B	0.049 (3)	0.070 (4)	0.056 (3)	−0.006 (3)	−0.006 (2)	−0.005 (3)
C19B	0.034 (2)	0.053 (3)	0.052 (2)	−0.006 (2)	0.0035 (19)	−0.003 (2)
O1C	0.110 (5)	0.125 (6)	0.187 (7)	0.006 (5)	−0.010 (5)	0.031 (6)
N1C	0.110 (5)	0.080 (5)	0.133 (5)	0.012 (4)	0.010 (4)	0.013 (5)
C1C	0.209 (13)	0.138 (11)	0.212 (12)	0.006 (9)	0.087 (10)	−0.030 (10)

C2C	0.119 (6)	0.173 (12)	0.266 (16)	0.019 (8)	−0.025 (8)	0.058 (12)
C3C	0.103 (5)	0.114 (8)	0.133 (6)	0.008 (6)	0.011 (5)	0.020 (6)
S1	0.0344 (8)	0.0605 (11)	0.0623 (10)	0.0042 (8)	0.0034 (7)	0.0013 (8)
O1	0.068 (3)	0.110 (4)	0.131 (5)	−0.035 (3)	−0.039 (3)	0.013 (4)
O2	0.051 (2)	0.094 (4)	0.061 (3)	0.022 (3)	0.008 (2)	0.008 (3)
O3	0.130 (5)	0.083 (4)	0.089 (4)	0.051 (4)	0.016 (4)	−0.009 (3)
O4	0.041 (2)	0.146 (5)	0.063 (3)	−0.012 (3)	0.002 (2)	0.012 (3)
O1W	0.184 (7)	0.103 (5)	0.177 (7)	−0.026 (6)	−0.060 (7)	−0.012 (5)
O2WA	0.138 (12)	0.085 (8)	0.099 (7)	−0.043 (10)	−0.044 (11)	0.010 (7)
O2WB	0.138 (12)	0.085 (8)	0.099 (7)	−0.043 (10)	−0.044 (11)	0.010 (7)
O3W	0.131 (5)	0.075 (3)	0.059 (3)	0.017 (3)	0.017 (3)	0.002 (3)
O4W	0.104 (4)	0.087 (4)	0.113 (4)	−0.012 (4)	0.033 (4)	−0.021 (4)
O5W	0.107 (7)	0.161 (10)	0.170 (11)	0.013 (7)	0.000	0.000

Geometric parameters (Å, º)

Ni1—N2A	2.017 (4)	N3B—C19B	1.389 (7)
Ni1—N2B	2.021 (4)	N4B—C7B	1.337 (7)
Ni1—N3A	2.086 (5)	N4B—C6B	1.365 (7)
Ni1—N3B	2.101 (5)	N4B—H4BA	0.8600
Ni1—N1B	2.116 (5)	N5B—C13B	1.341 (7)
Ni1—N1A	2.118 (5)	N5B—C14B	1.360 (8)
N1A—C7A	1.316 (7)	N5B—H5BA	0.8600
N1A—C1A	1.376 (8)	C1B—C6B	1.395 (9)
N2A—C8A	1.344 (7)	C1B—C2B	1.410 (8)
N2A—C12A	1.372 (7)	C2B—C3B	1.379 (9)
N3A—C13A	1.311 (7)	C2B—H2B	0.9300
N3A—C19A	1.396 (7)	C3B—C4B	1.403 (11)
N4A—C7A	1.345 (7)	C3B—H3B	0.9300
N4A—C6A	1.388 (8)	C4B—C5B	1.361 (10)
N4A—H4AA	0.8600	C4B—H4B	0.9300
N5A—C13A	1.356 (8)	C5B—C6B	1.388 (9)
N5A—C14A	1.375 (7)	C5B—H5B	0.9300
N5A—H5AA	0.8600	C7B—C8B	1.468 (8)
C1A—C6A	1.392 (8)	C8B—C9B	1.355 (8)
C1A—C2A	1.400 (9)	C9B—C10B	1.393 (10)
C2A—C3A	1.365 (10)	C9B—H9B	0.9300
C2A—H2A	0.9300	C10B—C11B	1.416 (9)
C3A—C4A	1.420 (11)	C10B—H10B	0.9300
C3A—H3A	0.9300	C11B—C12B	1.372 (8)
C4A—C5A	1.388 (10)	C11B—H11B	0.9300
C4A—H4A	0.9300	C12B—C13B	1.453 (8)
C5A—C6A	1.373 (9)	C14B—C19B	1.399 (8)
C5A—H5A	0.9300	C14B—C15B	1.407 (9)
C7A—C8A	1.482 (8)	C15B—C16B	1.366 (9)
C8A—C9A	1.364 (7)	C15B—H15B	0.9300
C9A—C10A	1.396 (9)	C16B—C17B	1.397 (10)
C9A—H9A	0.9300	C16B—H16B	0.9300

C10A—C11A	1.368 (8)	C17B—C18B	1.362 (9)
C10A—H10A	0.9300	C17B—H17B	0.9300
C11A—C12A	1.379 (8)	C18B—C19B	1.385 (8)
C11A—H11A	0.9300	C18B—H18B	0.9300
C12A—C13A	1.466 (8)	O1C—C3C	1.201 (12)
C14A—C19A	1.404 (9)	N1C—C3C	1.379 (13)
C14A—C15A	1.407 (9)	N1C—C1C	1.399 (13)
C15A—C16A	1.369 (10)	N1C—C2C	1.429 (13)
C15A—H15A	0.9300	C1C—H1C1	0.9600
C16A—C17A	1.407 (11)	C1C—H1C2	0.9600
C16A—H16A	0.9300	C1C—H1C3	0.9600
C17A—C18A	1.370 (10)	C2C—H2C1	0.9600
C17A—H17A	0.9300	C2C—H2C2	0.9600
C18A—C19A	1.402 (8)	C2C—H2C3	0.9600
C18A—H18A	0.9300	C3C—H3C	0.9300
N1B—C7B	1.336 (7)	S1—O3	1.434 (5)
N1B—C1B	1.385 (7)	S1—O1	1.448 (5)
N2B—C12B	1.339 (7)	S1—O4	1.451 (5)
N2B—C8B	1.372 (7)	S1—O2	1.476 (5)
N3B—C13B	1.324 (7)		
N2A—Ni1—N2B	179.2 (2)	C8B—N2B—Ni1	119.4 (4)
N2A—Ni1—N3A	77.65 (19)	C13B—N3B—C19B	106.3 (5)
N2B—Ni1—N3A	101.70 (19)	C13B—N3B—Ni1	112.5 (4)
N2A—Ni1—N3B	102.78 (19)	C19B—N3B—Ni1	141.3 (4)
N2B—Ni1—N3B	77.59 (19)	C7B—N4B—C6B	107.3 (5)
N3A—Ni1—N3B	91.07 (19)	C7B—N4B—H4BA	126.3
N2A—Ni1—N1B	101.35 (19)	C6B—N4B—H4BA	126.3
N2B—Ni1—N1B	78.27 (19)	C13B—N5B—C14B	107.1 (5)
N3A—Ni1—N1B	93.32 (19)	C13B—N5B—H5BA	126.5
N3B—Ni1—N1B	155.86 (18)	C14B—N5B—H5BA	126.5
N2A—Ni1—N1A	77.93 (19)	N1B—C1B—C6B	109.9 (5)
N2B—Ni1—N1A	102.73 (19)	N1B—C1B—C2B	130.0 (6)
N3A—Ni1—N1A	155.57 (19)	C6B—C1B—C2B	120.0 (6)
N3B—Ni1—N1A	93.53 (19)	C3B—C2B—C1B	117.0 (7)
N1B—Ni1—N1A	92.23 (19)	C3B—C2B—H2B	121.5
C7A—N1A—C1A	104.8 (5)	C1B—C2B—H2B	121.5
C7A—N1A—Ni1	111.8 (4)	C2B—C3B—C4B	122.2 (7)
C1A—N1A—Ni1	143.4 (4)	C2B—C3B—H3B	118.9
C8A—N2A—C12A	119.9 (5)	C4B—C3B—H3B	118.9
C8A—N2A—Ni1	120.0 (4)	C5B—C4B—C3B	120.5 (7)
C12A—N2A—Ni1	119.8 (4)	C5B—C4B—H4B	119.8
C13A—N3A—C19A	105.0 (5)	C3B—C4B—H4B	119.8
C13A—N3A—Ni1	113.2 (4)	C4B—C5B—C6B	118.5 (7)
C19A—N3A—Ni1	141.4 (4)	C4B—C5B—H5B	120.7
C7A—N4A—C6A	106.9 (5)	C6B—C5B—H5B	120.7
C7A—N4A—H4AA	126.6	N4B—C6B—C5B	132.8 (6)
C6A—N4A—H4AA	126.6	N4B—C6B—C1B	105.6 (5)

C13A—N5A—C14A	106.9 (5)	C5B—C6B—C1B	121.6 (6)
C13A—N5A—H5AA	126.6	N1B—C7B—N4B	113.4 (5)
C14A—N5A—H5AA	126.6	N1B—C7B—C8B	120.0 (5)
N1A—C1A—C6A	110.3 (5)	N4B—C7B—C8B	126.7 (6)
N1A—C1A—C2A	130.4 (6)	C9B—C8B—N2B	121.1 (5)
C6A—C1A—C2A	119.4 (6)	C9B—C8B—C7B	128.7 (6)
C3A—C2A—C1A	118.7 (7)	N2B—C8B—C7B	110.2 (5)
C3A—C2A—H2A	120.6	C8B—C9B—C10B	118.9 (6)
C1A—C2A—H2A	120.6	C8B—C9B—H9B	120.5
C2A—C3A—C4A	120.3 (7)	C10B—C9B—H9B	120.5
C2A—C3A—H3A	119.9	C9B—C10B—C11B	119.6 (6)
C4A—C3A—H3A	119.9	C9B—C10B—H10B	120.2
C5A—C4A—C3A	122.0 (7)	C11B—C10B—H10B	120.2
C5A—C4A—H4A	119.0	C12B—C11B—C10B	118.6 (6)
C3A—C4A—H4A	119.0	C12B—C11B—H11B	120.7
C6A—C5A—C4A	115.9 (7)	C10B—C11B—H11B	120.7
C6A—C5A—H5A	122.1	N2B—C12B—C11B	120.8 (6)
C4A—C5A—H5A	122.1	N2B—C12B—C13B	110.8 (5)
C5A—C6A—N4A	131.5 (6)	C11B—C12B—C13B	128.4 (6)
C5A—C6A—C1A	123.8 (7)	N3B—C13B—N5B	112.2 (5)
N4A—C6A—C1A	104.7 (5)	N3B—C13B—C12B	119.6 (5)
N1A—C7A—N4A	113.3 (5)	N5B—C13B—C12B	128.2 (5)
N1A—C7A—C8A	120.2 (5)	N5B—C14B—C19B	107.3 (5)
N4A—C7A—C8A	126.4 (5)	N5B—C14B—C15B	132.3 (6)
N2A—C8A—C9A	122.7 (5)	C19B—C14B—C15B	120.4 (6)
N2A—C8A—C7A	109.7 (5)	C16B—C15B—C14B	117.1 (7)
C9A—C8A—C7A	127.7 (5)	C16B—C15B—H15B	121.4
C8A—C9A—C10A	117.3 (6)	C14B—C15B—H15B	121.4
C8A—C9A—H9A	121.4	C15B—C16B—C17B	121.8 (7)
C10A—C9A—H9A	121.4	C15B—C16B—H16B	119.1
C11A—C10A—C9A	120.9 (6)	C17B—C16B—H16B	119.1
C11A—C10A—H10A	119.6	C18B—C17B—C16B	121.6 (7)
C9A—C10A—H10A	119.6	C18B—C17B—H17B	119.2
C10A—C11A—C12A	119.5 (6)	C16B—C17B—H17B	119.2
C10A—C11A—H11A	120.2	C17B—C18B—C19B	117.6 (6)
C12A—C11A—H11A	120.2	C17B—C18B—H18B	121.2
N2A—C12A—C11A	119.7 (5)	C19B—C18B—H18B	121.2
N2A—C12A—C13A	108.5 (5)	C18B—C19B—N3B	131.5 (6)
C11A—C12A—C13A	131.8 (6)	C18B—C19B—C14B	121.3 (6)
N3A—C13A—N5A	113.5 (5)	N3B—C19B—C14B	107.1 (5)
N3A—C13A—C12A	120.1 (6)	C3C—N1C—C1C	117.7 (11)
N5A—C13A—C12A	126.4 (5)	C3C—N1C—C2C	118.0 (11)
N5A—C14A—C19A	105.6 (5)	C1C—N1C—C2C	124.3 (12)
N5A—C14A—C15A	134.1 (7)	N1C—C1C—H1C1	109.5
C19A—C14A—C15A	120.2 (6)	N1C—C1C—H1C2	109.5
C16A—C15A—C14A	117.8 (8)	H1C1—C1C—H1C2	109.5
C16A—C15A—H15A	121.1	N1C—C1C—H1C3	109.5
C14A—C15A—H15A	121.1	H1C1—C1C—H1C3	109.5

C15A—C16A—C17A	122.3 (8)	H1C2—C1C—H1C3	109.5
C15A—C16A—H16A	118.9	N1C—C2C—H2C1	109.5
C17A—C16A—H16A	118.9	N1C—C2C—H2C2	109.5
C18A—C17A—C16A	120.2 (8)	H2C1—C2C—H2C2	109.5
C18A—C17A—H17A	119.9	N1C—C2C—H2C3	109.5
C16A—C17A—H17A	119.9	H2C1—C2C—H2C3	109.5
C17A—C18A—C19A	118.9 (7)	H2C2—C2C—H2C3	109.5
C17A—C18A—H18A	120.5	O1C—C3C—N1C	124.8 (12)
C19A—C18A—H18A	120.5	O1C—C3C—H3C	117.6
N3A—C19A—C18A	130.4 (6)	N1C—C3C—H3C	117.6
N3A—C19A—C14A	109.0 (5)	O3—S1—O1	106.5 (4)
C18A—C19A—C14A	120.6 (6)	O3—S1—O4	114.6 (4)
C7B—N1B—C1B	103.7 (5)	O1—S1—O4	108.3 (4)
C7B—N1B—Ni1	112.1 (4)	O3—S1—O2	109.6 (3)
C1B—N1B—Ni1	144.1 (4)	O1—S1—O2	110.0 (3)
C12B—N2B—C8B	121.0 (5)	O4—S1—O2	107.9 (3)
C12B—N2B—Ni1	119.6 (4)		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N4*A*—H4*AA*⋯O4[i]	0.86	1.89	2.732 (7)	168
N4*B*—H4*BA*⋯S1[ii]	0.86	2.73	3.514 (5)	152
N4*B*—H4*BA*⋯O2[ii]	0.86	1.79	2.646 (7)	176

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