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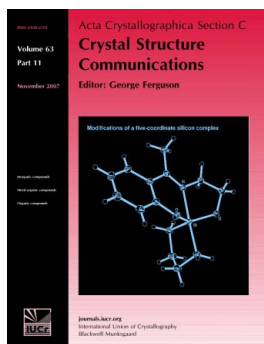
Sebastián Suarez, Fabio Doctorovich, Miguel Angel Harvey and Ricardo Baggio

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Tetraaqua(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')nickel(II) sulfate monohydrate: a simple molecule with an extremely complex hydrogen-bonding scheme

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The title ionic compound, $[\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, is composed of an Ni^{II} cation coordinated by a chelating 4,4'-dimethyl-2,2'-bipyridine ligand *via* its two N atoms [mean $\text{Ni}-\text{N} = 2.056(2) \text{ \AA}$] and by four aqua ligands [mean $\text{Ni}-\text{O} = 2.073(9) \text{ \AA}$], the net charge being balanced by an external sulfate anion. The whole structure is stabilized by a solvent water molecule. Even though the individual constituents are rather featureless, they generate an extremely complex supramolecular structure consisting of a central hydrogen-bonded two-dimensional hydrophilic nucleus made up of complex cations, sulfate anions and coordinated and solvent water molecules, with pendant hydrophobic 4,4'-dimethyl-2,2'-bipyridine ligands which interact laterally with their neighbours *via* $\pi-\pi$ interactions. The structure is compared with closely related analogues in the literature.

Comment

The combination in the same crystal structure of a large number of water molecules (as potentially active hydrogen-bonding donors) in conjunction with highly charged inorganic anions (as eventual acceptors for these hydrogen bonds) has always been an almost certain path to the generation of complex hydrogen-bonding networks. Among these systems, highly hydrated sulfate complexes have shown rich interconnectivity and have thus become extremely appealing systems for those interested in the morphology and architecture of supramolecular structures. The title compound, $[\text{Ni}(\text{dmbpy})(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ (IIa) (where $\text{dmbpy} = 4,4'$ -dimethyl-2,2'-bipyridine = $L3$), is a member of a larger family

having the general formula $[\text{Tr}Lx(\text{H}_2\text{O})_4]\text{SO}_4 \cdot n\text{H}_2\text{O}$, where Tr is a transition metal, Lx is an N,N' -chelating neutral aromatic base and n represents the hydration state. In a search of the Cambridge Structural Database (CSD, Version 5.33; Allen, 2002), we identified several of these closely related analogues, and the results are briefly presented in Fig. 1 and Table 1. It

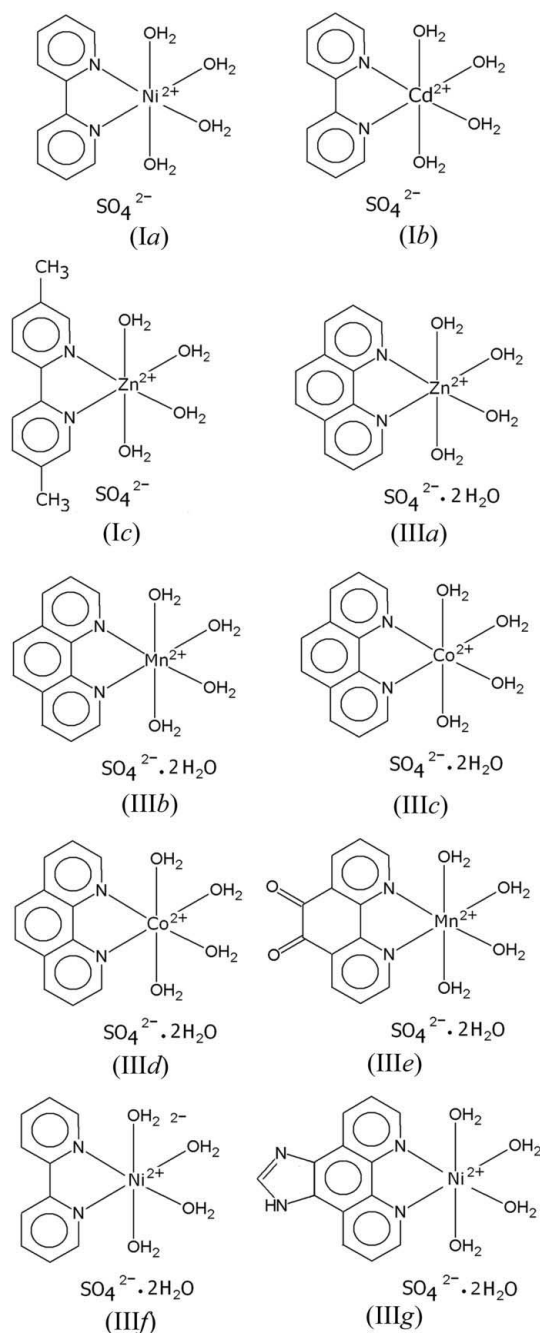
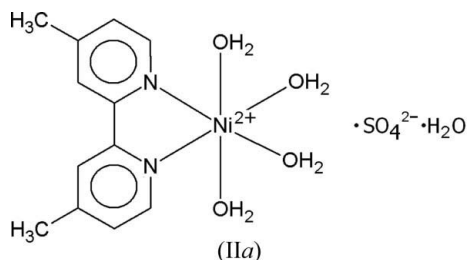


Figure 1

The $[\text{Tr}Lx(\text{H}_2\text{O})_4]\text{SO}_4 \cdot n\text{H}_2\text{O}$ family, as found in the Cambridge Structural Database (CSD, Version 5.33; Allen, 2002). The members shown are: (Ia) (CSD refcode XEQAZ; Boonlue *et al.*, 2012), (Ib) (BEQRUK; Harvey *et al.*, 1999), (Ic) (POWTEB; Zhao & Bai, 2009), (IIa) (BONWAC; Zhang *et al.*, 1999), (IIIb) (AFOLIQ04; Wu *et al.*, 2004), (IIIc) (DURXEU; Zhang *et al.*, 2010), (IIId) (WUQMEA; Zhu *et al.*, 2004), (IIIe) (NERYEP; Wang, Sun *et al.*, 2006), (IIIf) (CUPJEC; Healy *et al.*, 1984) and (IIIg) (VIWYEG; Wang, Liu *et al.*, 2006).

can be seen therein that examples with $n = 0$ [codes (Ia)–(Ic)] and $n = 2$ [codes (IIIa)–(IIIg)] have already been reported, but the present case seems to be the first reported with $n = 1$. These compounds present a wide diversity of crystal structures [there is only one isostructural/isomorphous family present, made up of compounds (IIIa)–(IIId), with Tr = Zn, Mn, Cd and Co, respectively]. On the other hand, in most of the structures in Fig. 1, a rather similar packing trend can be observed, *viz.* a central hydrogen-bonded hydrophilic nucleus made up of the cation, the sulfate anion and the four aqua and solvent water molecules, with pendant hydrophobic *Lx* ligands which interact laterally with their neighbours *via* π – π interactions. However, the similarities end at this point, since comparison of the structures shows that the hydrogen-bonding networks generated at the hydrophilic nuclei are quite different, as are the ways in which the pendant hydrophobic ligands interact with each other in order to link the hydrophilic networks. This fact will be further addressed below during a discussion of the packing of the title Ni^{II} compound, (IIa).



Selected coordination parameters for (IIa) are presented in Table 2, while a view of the very simple asymmetric unit can be seen in Fig. 2. It consists of an Ni^{II} cation coordinated by a

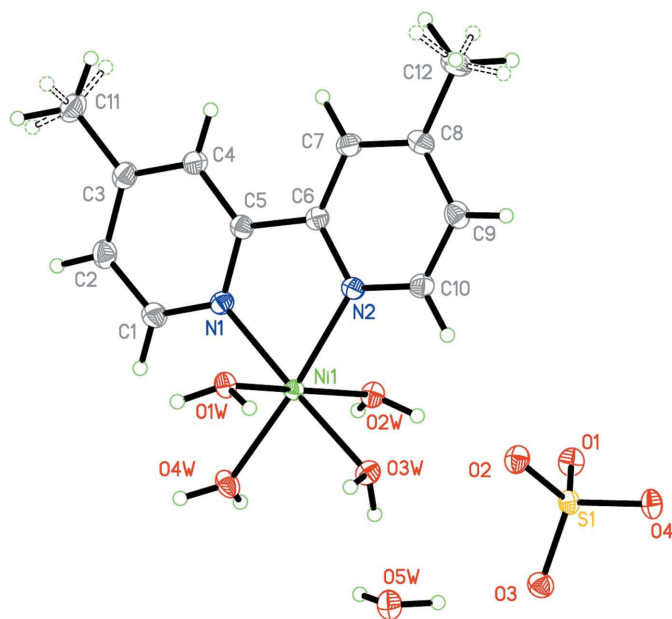


Figure 2
The asymmetric unit of (IIa), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed bonds indicate the alternative orientations of the disordered methyl groups.

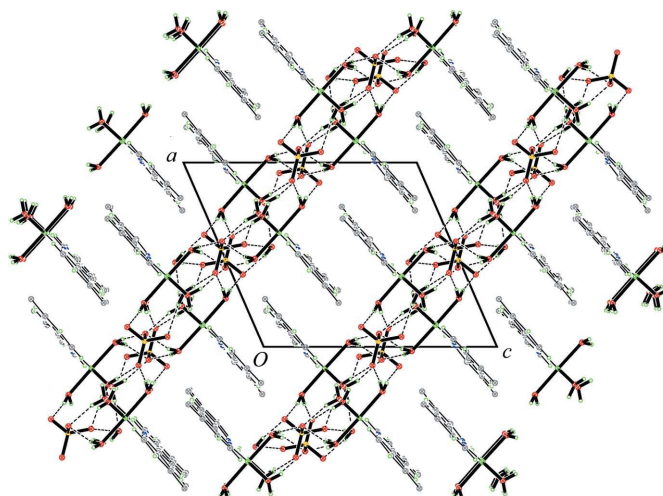


Figure 3
A packing view of (IIa), projected down [010], showing the alternation of hydrophilic (narrow profiles in heavy lines) and hydrophobic (broader profiles in weak lines) planes running parallel to (101). Dashed lines indicate intermolecular O—H...O interactions.

chelating dmby ligand *via* its two N atoms [mean Ni—N = 2.056 (2) Å] and by four aqua ligands [mean Ni—O = 2.073 (9) Å], the net charge being balanced by an external sulfate anion. The whole structure is stabilized by a solvent water molecule.

The only noticeable distortion from octahedral symmetry in the cationic group is seen in the small dmby chelate angle [N1—Ni1—N2 = 79.34 (5)°]. The anion is very regular as well, with a tight span of S—O bond lengths and O—S—O angles [1.4717 (11)–1.4928 (10) Å and 108.38 (6)–111.23 (6)°, respectively], suggesting an almost complete delocalization of the double bonds. This rather predictable geometry of the individual building blocks arising from the strongest forces (covalent and coordination) contrasts with the complex way in which these same units interact with each other *via* much weaker nonbonding interactions (hydrogen bonds, π – π contacts *etc.*) in order to define the three-dimensional crystal structure.

The dicationic $[\text{Ni}(\text{dmby})(\text{H}_2\text{O})_4]^{2+}$ subunit is naturally divided into two quite different parts: (i) the planar organic ligand chelating atom Ni1 on one side, and (ii) the bulky highly hydrophilic counterpart including the cation and the four aqua ligands on the other side. The hydrogen-bonding interactions in which the latter ‘hemipolyhedron’ takes part, in conjunction with the sulfate counter-anion and the additional solvent water molecule, give rise to a formidable two-dimensional hydrogen-bonding network evolving parallel to (101) (shown sideways in Fig. 3, in heavy lines). All ten water H atoms take part in these fairly strong interactions (Table 3, entries 1 to 10), with H...O distances up to 2 Å and O—H...O angles wider than 160°. Fig. 4 shows a very detailed view of this carbon-free structure, where the general behaviour of each water unit can be appreciated. Thus, coordinated water molecules O1W, O2W and O4W fulfil similar roles, bridging opposite sulfates on both sides of the metal atom. In contrast, water molecule O3W links the O5W solvent molecule through

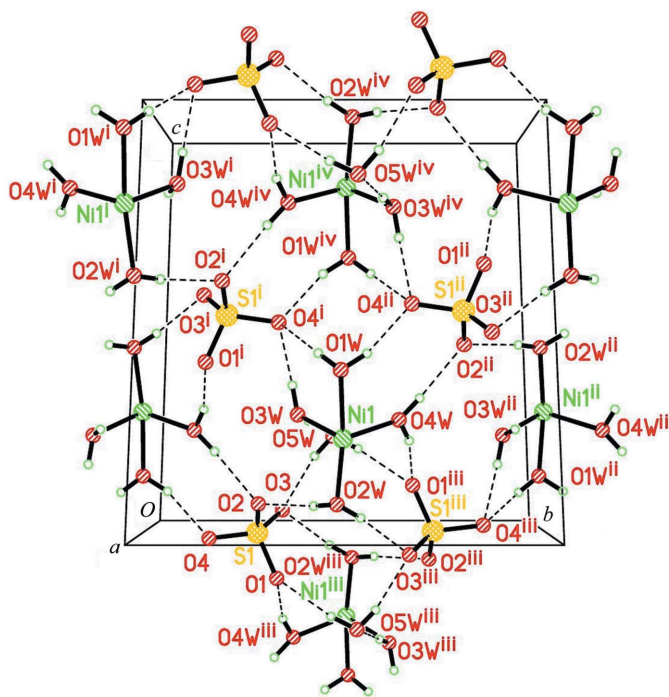


Figure 4

A packing view of the carbon-free hydrophilic structure in (IIa), shown in a slanted projection down [100] in order to minimize overlap, and where all the interactions presented in Table 3 and the loops described in Tables S4 and S5 (see *Supplementary materials*) are clearly visible (dashed lines). [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + 2, -y + 1, -z + 1$.]

atom H3WA, thus disrupting an eventual 'twofold' topological symmetry with the introduction of further interconnection paths. The final result is a tight mesh of hydrogen-bonded structures of different kinds and complexity, starting with the ten elemental *D* hydrogen-bonding motifs, combining into 20 different chain motifs (linking symmetry-equivalent points in the structure) and ending up with 16 independent third-level rings formed through the intricate combination of the first two types. [For an introduction to graph-set analysis and notation, see Etter *et al.* (1990) and Bernstein *et al.* (1995).]

Tables S4 and S5 in the *Supplementary materials* disclose through their graph-set descriptors the chains and rings generated in the hydrogen-bonded structure of (IIa) up to the third level, *viz.* involving up to three different *D* hydrogen-bonding types. The resulting two-dimensional hydrophilic structure (Fig. 3, heavy lines) is a broad sheet *ca* 3.5 Å thick, decorated by pendant hydrophobic dmbpy groups evolving outwards on both sides and which interdigitate neighbouring counterparts at a graphitic distance from each other (see details below). This defines a still thicker hydrophobic region, also in the form of a broad sheet, this time *ca* 7.1 Å wide (Fig. 3, weak lines), leading to a 'sharing' of the (10 $\bar{1}$) space in an approximate 2:1 ratio.

As stated above, this type of packing has analogues in the literature, albeit with differences based mainly on the characteristics of the organic ligand (*Lx*) and the variable hydration state (*nH₂O*). When the *Lx* organic ligand has

conventional hydrogen-bonding active sites present, as in (IIIe) (O atom) and (IIIg) (N atom and N—H group), there is no net separation between the hydrophilic and hydrophobic sections and all centres are involved in hydrogen bonding, rendering the supramolecular organization essentially three-dimensional; the much weaker π – π interactions between aromatic rings simply complement the latter hydrogen-bonding interactions and have little impact on the overall construction. When the *Lx* ligand lacks these active sites (*e.g.* all remaining cases in Fig. 1), the structures adopt instead the already described packing organizations with a central two-dimensional hydrogen-bonded hydrophilic nucleus decorated by pendant *Lx* groups, although the finer details depend on *Lx* and *n*. We shall give a comparative discussion of (IIa) and (IIIf) (*L1* is 2,2'-bipyridine and *n* = 2) as a representative case to show which main differences are usually found. In particular, the two-dimensional hydrophilic core is *ca* 40% thicker in (IIIf) than in (IIa), as a consequence of the higher hydration state. The result is that the hydrophobic zone is *ca* 10% narrower due to the fact that the pendant bipyridine molecules in (IIIf) lack the 'bumping' terminal methyl groups, distinctive of dmbpy in (IIa).

There is an additional consequence derived from this absence in (IIIf) and it is the interactive character of the 'front line' pyridine H atoms [those equivalent to atoms H4 and H7 in (IIa)] which, being free of methyl steric hindrance, take part in rather strong hydrogen bonds to neighbouring sulfate O atoms. This can be seen in the H...O and C—H...O values [2.35 (1) Å and 155 (1)°, and 2.45 (1) Å and 136 (1)°, respectively] for these contacts in (IIIf), compared with the much weaker methyl contacts in (IIa), shown in Table 3 (final two entries), which are not even capable of clamping the (rotationally disordered) methyl ends into a stable structure (see *Refinement*). These nonconventional hydrogen bonds might add some additional interplanar cohesion in (IIIf) to that already provided by the graphitic π – π interactions which are common (and comparable) in both structures. In fact, both (IIa) and (IIIf) present their adjacent pyridine rings at extremely similar intercentroid/interplanar distances, *viz.* 3.685 (1)/3.45 (2) and 3.662 (2)/3.35 (2) Å for (IIa) and (IIIf), respectively.

Experimental

A 0.10 *M* methanol solution (2 ml) of 4,4'-dimethyl-2,2'-bipyridine was added to a similar volume of a 0.10 *M* aqueous solution of NiSO₄·H₂O. The initially colourless solutions immediately turned pale red after mixing. The resulting solution was left to stand at 313 K for a couple of days, after which time well developed light-blue crystals of (IIa) suitable for X-ray data collection were obtained.

Crystal data

[Ni(C ₁₂ H ₁₂ N ₂)(H ₂ O) ₄]SO ₄ ·H ₂ O	<i>V</i> = 1735.24 (17) Å ³
<i>M_r</i> = 429.09	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo K α radiation
<i>a</i> = 11.8007 (3) Å	μ = 1.29 mm ^{−1}
<i>b</i> = 11.7095 (3) Å	<i>T</i> = 150 K
<i>c</i> = 13.6967 (3) Å	0.48 × 0.18 × 0.14 mm
β = 113.530 (12)°	

Table 1

Comparison of reported compounds with the general formula $[\text{Tr}(\text{Lx})(\text{H}_2\text{O})_4]\text{SO}_4 \cdot n\text{H}_2\text{O}$ (Tr is a transition metal).

Ligand codes: L1 is 2,2'-bipyridine; L2 is 5,5'-dimethyl-2,2'-bipyridine; L3 is 4,4'-dimethyl-2,2'-bipyridine; L4 is 1,10-phenanthroline; L5 is 1,10-phenanthroline-5,6-dione; L6 is 1H-imidazo[4,5-f][1,10]phenanthroline.

Compound	Tr	Lx	n	Space group	Z	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
(Ia)	Ni	L1	0	Pbca	8	12.3035 (7)	11.6560 (7)	20.7112 (10)	90	90	90	2970.2 (3)
(Ib)	Cd	L1	0	P2 ₁ /c	4	10.262 (2)	12.073 (2)	12.357 (3)	90	92.47 (3)	90	1529.5 (10)
(Ic)	Zn	L2	0	P2 ₁ /c	4	9.565 (2)	9.605 (2)	18.477 (3)	90	102.45 (9)	90	1657.5 (14)
(IIa)	Ni	L3	1	P2 ₁ /n	4	11.8007 (3)	11.7095 (3)	13.6967 (3)	90	113.531 (12)	90	1735.24 (17)
(IIIa)	Zn	L4	2	Pbca	8	8.906 (1)	18.295 (2)	21.855 (3)	90	90	90	3560.9 (15)
(IIIb)	Mn	L4	2	Pbca	8	8.877 (1)	18.508 (3)	22.098 (3)	90	90	90	3630.602 (14)
(IIIc)	Cd	L4	2	Pbca	8	8.8398 (9)	18.700 (2)	22.349 (2)	90	90	90	3694.3 (11)
(IIId)	Co	L4	2	Pbca	8	8.856 (1)	18.318 (3)	21.918 (5)	90	90	90	3555.6 (17)
(IIIe)	Mn	L5	2	C2/m	4	9.6237 (4)	13.9117 (6)	13.8744 (6)	90	97.32 (2)	90	1842.4 (2)
(IIIf)	Ni	L1	2	P1̄	2	7.793 (3)	9.351 (3)	11.476 (4)	87.40 (2)	96.50 (2)	102.37 (2)	811.4 (19)
(IIIg)	Ni	L6	2	P1̄	2	7.266 (2)	11.112 (3)	12.913 (4)	75.676 (4)	77.393 (5)	71.423 (5)	946.4 (15)

Table 2

Selected bond lengths (Å).

Ni1—N1	2.0545 (12)	Ni1—O3W	2.0694 (11)
Ni1—N2	2.0587 (12)	Ni1—O4W	2.0719 (11)
Ni1—O2W	2.0673 (11)	Ni1—O1W	2.0847 (12)

Table 3

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1WA...O4 ⁱ	0.83 (1)	2.00 (1)	2.7959 (15)	160 (2)
O1W—H1WB...O4 ⁱⁱ	0.84 (1)	1.87 (1)	2.6913 (15)	164 (2)
O2W—H2WA...O2	0.83 (1)	1.96 (1)	2.7895 (15)	171 (2)
O2W—H2WB...O3 ⁱⁱⁱ	0.84 (1)	1.86 (1)	2.6985 (15)	172 (2)
O3W—H3WA...O5W	0.84 (1)	1.94 (1)	2.7800 (16)	176 (2)
O3W—H3WB...O4 ⁱ	0.84 (1)	1.91 (1)	2.7329 (14)	165 (2)
O4W—H4WA...O1 ⁱⁱⁱ	0.83 (1)	2.01 (1)	2.8082 (15)	162 (2)
O4W—H4WB...O2 ⁱⁱ	0.85 (1)	1.98 (1)	2.8253 (15)	176 (2)
O5W—H5WA...O1 ⁱⁱⁱ	0.84 (1)	2.00 (1)	2.8397 (16)	172 (2)
O5W—H5WB...O3	0.85 (1)	1.96 (1)	2.7963 (15)	171 (2)
C11—H11E...O2 ^{iv}	0.98	2.58	3.393 (2)	140
C12—H12A...O3 ^v	0.98	2.52	3.453 (2)	158

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + 2, -y + 1, -z$; (v) $x + 1, y, z$.

Data collection

Oxford Gemini CCD S Ultra diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.76$, $T_{\max} = 0.84$
 14064 measured reflections
 3811 independent reflections
 3599 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.075$
 $S = 1.07$
 3811 reflections
 258 parameters
 15 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.54 \text{ e Å}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e Å}^{-3}$

All H atoms were visible in difference maps but were treated differently in the refinement. Those attached to C atoms were placed in geometrically idealized positions and allowed to ride on their

parent atoms, with aromatic C—H = 0.95 Å and methyl C—H = 0.98 Å. These latter groups appear disordered around the C—C bond and they were modelled with six H atoms of half occupancy, at 60° from each other, which were allowed to rotate around their C—C bond, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Water H atoms were refined with restrained O—H and H...H distances of 0.85 (1) and 1.35 (1) Å, respectively. $U_{\text{iso}}(\text{H})$ values were set at $1.5U_{\text{eq}}(\text{C})$ for the methyl groups and at $1.2U_{\text{eq}}(\text{C}, \text{O})$ otherwise.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*, *RPLUTO* (CCDC, 2007) and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3478). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2013). **C69**, 351-355 [doi:10.1107/S0108270113005088]

Tetraaqua(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')nickel(II) sulfate monohydrate: a simple molecule with an extremely complex hydrogen-bonding scheme

Sebastián Suarez, Fabio Doctorovich, Miguel Angel Harvey and Ricardo Baggio

Tetraaqua(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')nickel(II) sulfate monohydrate

Crystal data

[Ni(C₁₂H₁₂N₂)(H₂O)₄]SO₄·H₂O

$M_r = 429.09$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 11.8007(3) \text{ \AA}$

$b = 11.7095(3) \text{ \AA}$

$c = 13.6967(3) \text{ \AA}$

$\beta = 113.530(12)^\circ$

$V = 1735.24(17) \text{ \AA}^3$

$Z = 4$

$F(000) = 896$

$D_x = 1.642 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3870 reflections

$\theta = 2.7\text{--}25.2^\circ$

$\mu = 1.29 \text{ mm}^{-1}$

$T = 150 \text{ K}$

Prism, light blue

$0.48 \times 0.18 \times 0.14 \text{ mm}$

Data collection

Oxford Gemini CCD S Ultra
diffractometer

ω scans, thick slices

Absorption correction: multi-scan
(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.76$, $T_{\max} = 0.84$

14064 measured reflections

3811 independent reflections

3599 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$

$\theta_{\max} = 27.8^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -15 \rightarrow 15$

$k = -15 \rightarrow 14$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.075$

$S = 1.07$

3811 reflections

258 parameters

15 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.8214P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.008$

$\Delta\rho_{\max} = 0.54 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.49 \text{ e \AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ni1	0.881378 (16)	0.496228 (14)	0.221537 (14)	0.01282 (8)	
N1	0.99139 (11)	0.59788 (11)	0.17338 (10)	0.0155 (2)	
N2	0.97379 (11)	0.37435 (11)	0.17329 (9)	0.0143 (2)	
C1	0.99794 (15)	0.71205 (13)	0.17923 (12)	0.0191 (3)	
H1	0.9413	0.7519	0.2003	0.023*	
C2	1.08334 (15)	0.77449 (13)	0.15595 (13)	0.0212 (3)	
H2	1.0854	0.8554	0.1621	0.025*	
C3	1.16645 (14)	0.71816 (13)	0.12344 (12)	0.0197 (3)	
C4	1.15978 (14)	0.59903 (13)	0.11793 (12)	0.0185 (3)	
H4	1.2151	0.5573	0.0966	0.022*	
C5	1.07257 (13)	0.54165 (13)	0.14363 (11)	0.0159 (3)	
C6	1.06101 (13)	0.41472 (13)	0.14155 (11)	0.0151 (3)	
C7	1.13319 (14)	0.34198 (13)	0.10983 (12)	0.0180 (3)	
H7	1.1941	0.3725	0.0882	0.022*	
C8	1.11601 (14)	0.22372 (13)	0.10986 (12)	0.0187 (3)	
C9	1.02545 (15)	0.18412 (13)	0.14215 (12)	0.0200 (3)	
H9	1.0105	0.1045	0.1432	0.024*	
C10	0.95702 (14)	0.26143 (13)	0.17279 (12)	0.0176 (3)	
H10	0.8953	0.2329	0.1945	0.021*	
C11	1.25956 (16)	0.78285 (14)	0.09601 (14)	0.0250 (3)	
H11A	1.3185	0.7291	0.0872	0.037*	0.50
H11B	1.3039	0.8366	0.1534	0.037*	0.50
H11C	1.2171	0.8250	0.0295	0.037*	0.50
H11D	1.2412	0.8647	0.0929	0.037*	0.50
H11E	1.2558	0.7572	0.0267	0.037*	0.50
H11F	1.3426	0.7689	0.1506	0.037*	0.50
C12	1.19356 (16)	0.14301 (14)	0.07717 (14)	0.0260 (3)	
H12A	1.2466	0.1868	0.0511	0.039*	0.50
H12B	1.1396	0.0927	0.0205	0.039*	0.50
H12C	1.2451	0.0969	0.1386	0.039*	0.50
H12D	1.1742	0.0642	0.0890	0.039*	0.50
H12E	1.2813	0.1582	0.1196	0.039*	0.50
H12F	1.1758	0.1540	0.0015	0.039*	0.50
S1	0.46711 (3)	0.28090 (3)	−0.00349 (3)	0.01434 (10)	
O1	0.44429 (10)	0.33060 (9)	−0.10842 (8)	0.0192 (2)	
O2	0.59885 (10)	0.28740 (9)	0.06801 (8)	0.0191 (2)	
O3	0.39200 (10)	0.34164 (9)	0.04476 (8)	0.0193 (2)	
O4	0.42903 (10)	0.15839 (9)	−0.01878 (8)	0.0183 (2)	
O1W	1.02352 (11)	0.49105 (9)	0.37309 (9)	0.0167 (2)	
H1WA	1.0124 (17)	0.4397 (10)	0.4106 (12)	0.020*	

H1WB	1.0407 (17)	0.5513 (9)	0.4098 (12)	0.020*
O2W	0.73828 (10)	0.48140 (9)	0.07310 (9)	0.0165 (2)
H2WA	0.6904 (13)	0.4267 (10)	0.0664 (14)	0.020*
H2WB	0.6956 (14)	0.5380 (10)	0.0415 (14)	0.020*
O3W	0.77982 (9)	0.38622 (9)	0.27347 (8)	0.0163 (2)
H3WA	0.7084 (10)	0.4105 (15)	0.2607 (12)	0.020*
H3WB	0.8139 (13)	0.3730 (15)	0.3392 (8)	0.020*
O4W	0.79553 (10)	0.63138 (9)	0.26225 (9)	0.0197 (2)
H4WA	0.7307 (12)	0.6573 (14)	0.2157 (10)	0.024*
H4WB	0.8260 (15)	0.6806 (13)	0.3111 (10)	0.024*
O5W	0.54228 (11)	0.46991 (10)	0.22121 (9)	0.0217 (2)
H5WA	0.5423 (17)	0.5323 (9)	0.1903 (13)	0.026*
H5WB	0.4957 (15)	0.4261 (11)	0.1729 (11)	0.026*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01226 (12)	0.01313 (12)	0.01317 (12)	0.00039 (6)	0.00518 (9)	−0.00047 (6)
N1	0.0149 (6)	0.0167 (6)	0.0149 (6)	−0.0005 (5)	0.0060 (5)	0.0010 (5)
N2	0.0129 (6)	0.0166 (6)	0.0124 (5)	0.0015 (5)	0.0038 (4)	−0.0006 (5)
C1	0.0204 (7)	0.0171 (7)	0.0209 (7)	0.0007 (6)	0.0093 (6)	−0.0004 (6)
C2	0.0250 (8)	0.0159 (7)	0.0229 (8)	−0.0025 (6)	0.0097 (6)	−0.0002 (6)
C3	0.0200 (7)	0.0233 (8)	0.0148 (7)	−0.0048 (6)	0.0059 (6)	−0.0009 (6)
C4	0.0167 (7)	0.0220 (7)	0.0181 (7)	−0.0016 (6)	0.0083 (6)	−0.0020 (6)
C5	0.0156 (7)	0.0181 (7)	0.0125 (6)	−0.0001 (6)	0.0039 (5)	−0.0014 (5)
C6	0.0137 (6)	0.0175 (7)	0.0129 (6)	0.0001 (5)	0.0041 (5)	0.0006 (5)
C7	0.0161 (7)	0.0205 (7)	0.0183 (7)	−0.0002 (6)	0.0079 (6)	−0.0004 (6)
C8	0.0189 (7)	0.0200 (8)	0.0174 (7)	0.0040 (6)	0.0074 (6)	−0.0007 (6)
C9	0.0240 (8)	0.0151 (7)	0.0212 (7)	0.0009 (6)	0.0094 (6)	0.0009 (6)
C10	0.0185 (7)	0.0186 (7)	0.0167 (7)	−0.0009 (6)	0.0083 (6)	0.0003 (6)
C11	0.0250 (8)	0.0263 (8)	0.0256 (8)	−0.0085 (6)	0.0122 (7)	−0.0008 (6)
C12	0.0275 (8)	0.0225 (8)	0.0332 (9)	0.0055 (7)	0.0177 (7)	−0.0018 (7)
S1	0.01558 (18)	0.01209 (17)	0.01343 (18)	0.00009 (13)	0.00376 (13)	0.00039 (12)
O1	0.0211 (5)	0.0182 (5)	0.0167 (5)	−0.0003 (4)	0.0058 (4)	0.0031 (4)
O2	0.0156 (5)	0.0190 (5)	0.0190 (5)	0.0003 (4)	0.0030 (4)	0.0006 (4)
O3	0.0193 (5)	0.0180 (5)	0.0207 (5)	0.0022 (4)	0.0081 (4)	−0.0003 (4)
O4	0.0227 (5)	0.0128 (5)	0.0166 (5)	−0.0018 (4)	0.0050 (4)	−0.0004 (4)
O1W	0.0182 (6)	0.0157 (5)	0.0148 (5)	−0.0010 (4)	0.0052 (4)	−0.0014 (4)
O2W	0.0146 (5)	0.0160 (5)	0.0165 (5)	0.0009 (4)	0.0037 (4)	0.0015 (4)
O3W	0.0141 (5)	0.0184 (5)	0.0149 (5)	0.0003 (4)	0.0042 (4)	0.0019 (4)
O4W	0.0167 (5)	0.0178 (5)	0.0201 (5)	0.0045 (4)	0.0027 (4)	−0.0048 (4)
O5W	0.0248 (6)	0.0186 (5)	0.0203 (5)	−0.0022 (5)	0.0076 (5)	−0.0011 (4)

Geometric parameters (\AA , $^\circ$)

Ni1—N1	2.0545 (12)	C11—H11A	0.9800
Ni1—N2	2.0587 (12)	C11—H11B	0.9800
Ni1—O2W	2.0673 (11)	C11—H11C	0.9800
Ni1—O3W	2.0694 (11)	C11—H11D	0.9800
Ni1—O4W	2.0719 (11)	C11—H11E	0.9800

Ni1—O1W	2.0847 (12)	C11—H11F	0.9800
N1—C1	1.3397 (19)	C12—H12A	0.9800
N1—C5	1.3524 (19)	C12—H12B	0.9800
N2—C10	1.3366 (19)	C12—H12C	0.9800
N2—C6	1.3524 (18)	C12—H12D	0.9800
C1—C2	1.381 (2)	C12—H12E	0.9800
C1—H1	0.9500	C12—H12F	0.9800
C2—C3	1.394 (2)	S1—O2	1.4717 (11)
C2—H2	0.9500	S1—O1	1.4724 (11)
C3—C4	1.397 (2)	S1—O3	1.4819 (11)
C3—C11	1.501 (2)	S1—O4	1.4928 (10)
C4—C5	1.387 (2)	O1W—H1WA	0.834 (9)
C4—H4	0.9500	O1W—H1WB	0.842 (9)
C5—C6	1.492 (2)	O2W—H2WA	0.834 (9)
C6—C7	1.391 (2)	O2W—H2WB	0.841 (9)
C7—C8	1.400 (2)	O3W—H3WA	0.839 (9)
C7—H7	0.9500	O3W—H3WB	0.841 (9)
C8—C9	1.389 (2)	O4W—H4WA	0.833 (9)
C8—C12	1.503 (2)	O4W—H4WB	0.847 (9)
C9—C10	1.385 (2)	O5W—H5WA	0.844 (9)
C9—H9	0.9500	O5W—H5WB	0.845 (9)
C10—H10	0.9500		
N1—Ni1—N2	79.34 (5)	H11B—C11—H11C	109.5
N1—Ni1—O2W	96.07 (5)	C3—C11—H11D	109.5
N2—Ni1—O2W	87.45 (5)	H11A—C11—H11D	141.1
N1—Ni1—O3W	176.28 (4)	H11B—C11—H11D	56.3
N2—Ni1—O3W	97.61 (5)	H11C—C11—H11D	56.3
O2W—Ni1—O3W	85.87 (4)	C3—C11—H11E	109.5
N1—Ni1—O4W	94.78 (5)	H11A—C11—H11E	56.3
N2—Ni1—O4W	173.98 (5)	H11B—C11—H11E	141.1
O2W—Ni1—O4W	91.93 (4)	H11C—C11—H11E	56.3
O3W—Ni1—O4W	88.31 (5)	H11D—C11—H11E	109.5
N1—Ni1—O1W	88.63 (5)	C3—C11—H11F	109.5
N2—Ni1—O1W	88.89 (4)	H11A—C11—H11F	56.3
O2W—Ni1—O1W	173.41 (4)	H11B—C11—H11F	56.3
O3W—Ni1—O1W	89.19 (4)	H11C—C11—H11F	141.1
O4W—Ni1—O1W	92.28 (4)	H11D—C11—H11F	109.5
C1—N1—C5	118.22 (13)	H11E—C11—H11F	109.5
C1—N1—Ni1	126.00 (10)	C8—C12—H12A	109.5
C5—N1—Ni1	115.41 (10)	C8—C12—H12B	109.5
C10—N2—C6	118.31 (13)	H12A—C12—H12B	109.5
C10—N2—Ni1	126.23 (10)	C8—C12—H12C	109.5
C6—N2—Ni1	115.44 (10)	H12A—C12—H12C	109.5
N1—C1—C2	122.98 (14)	H12B—C12—H12C	109.5
N1—C1—H1	118.5	C8—C12—H12D	109.5
C2—C1—H1	118.5	H12A—C12—H12D	141.1
C1—C2—C3	119.62 (14)	H12B—C12—H12D	56.3
C1—C2—H2	120.2	H12C—C12—H12D	56.3

C3—C2—H2	120.2	C8—C12—H12E	109.5
C2—C3—C4	117.25 (14)	H12A—C12—H12E	56.3
C2—C3—C11	121.33 (14)	H12B—C12—H12E	141.1
C4—C3—C11	121.43 (14)	H12C—C12—H12E	56.3
C5—C4—C3	120.09 (14)	H12D—C12—H12E	109.5
C5—C4—H4	120.0	C8—C12—H12F	109.5
C3—C4—H4	120.0	H12A—C12—H12F	56.3
N1—C5—C4	121.82 (14)	H12B—C12—H12F	56.3
N1—C5—C6	114.86 (12)	H12C—C12—H12F	141.1
C4—C5—C6	123.32 (13)	H12D—C12—H12F	109.5
N2—C6—C7	121.72 (13)	H12E—C12—H12F	109.5
N2—C6—C5	114.69 (12)	O2—S1—O1	111.23 (6)
C7—C6—C5	123.59 (13)	O2—S1—O3	109.84 (6)
C6—C7—C8	119.92 (14)	O1—S1—O3	109.68 (6)
C6—C7—H7	120.0	O2—S1—O4	108.78 (6)
C8—C7—H7	120.0	O1—S1—O4	108.38 (6)
C9—C8—C7	117.41 (13)	O3—S1—O4	108.88 (6)
C9—C8—C12	121.48 (14)	Ni1—O1W—H1WA	111.9 (12)
C7—C8—C12	121.11 (14)	Ni1—O1W—H1WB	118.4 (12)
C10—C9—C8	119.60 (14)	H1WA—O1W—H1WB	107.1 (13)
C10—C9—H9	120.2	Ni1—O2W—H2WA	115.1 (12)
C8—C9—H9	120.2	Ni1—O2W—H2WB	121.8 (12)
N2—C10—C9	123.03 (14)	H2WA—O2W—H2WB	107.9 (13)
N2—C10—H10	118.5	Ni1—O3W—H3WA	112.9 (12)
C9—C10—H10	118.5	Ni1—O3W—H3WB	112.8 (12)
C3—C11—H11A	109.5	H3WA—O3W—H3WB	107.3 (12)
C3—C11—H11B	109.5	Ni1—O4W—H4WA	118.1 (12)
H11A—C11—H11B	109.5	Ni1—O4W—H4WB	129.3 (12)
C3—C11—H11C	109.5	H4WA—O4W—H4WB	109.1 (13)
H11A—C11—H11C	109.5	H5WA—O5W—H5WB	105.3 (13)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1 <i>W</i> —H1 <i>WA</i> ...O4 ⁱ	0.83 (1)	2.00 (1)	2.7959 (15)	160 (2)
O1 <i>W</i> —H1 <i>WB</i> ...O4 ⁱⁱ	0.84 (1)	1.87 (1)	2.6913 (15)	164 (2)
O2 <i>W</i> —H2 <i>WA</i> ...O2	0.83 (1)	1.96 (1)	2.7895 (15)	171 (2)
O2 <i>W</i> —H2 <i>WB</i> ...O3 ⁱⁱⁱ	0.84 (1)	1.86 (1)	2.6985 (15)	172 (2)
O3 <i>W</i> —H3 <i>WA</i> ...O5 <i>W</i>	0.84 (1)	1.94 (1)	2.7800 (16)	176 (2)
O3 <i>W</i> —H3 <i>WB</i> ...O4 ⁱ	0.84 (1)	1.91 (1)	2.7329 (14)	165 (2)
O4 <i>W</i> —H4 <i>WA</i> ...O1 ⁱⁱⁱ	0.83 (1)	2.01 (1)	2.8082 (15)	162 (2)
O4 <i>W</i> —H4 <i>WB</i> ...O2 ⁱⁱ	0.85 (1)	1.98 (1)	2.8253 (15)	176 (2)
O5 <i>W</i> —H5 <i>WA</i> ...O1 ⁱⁱⁱ	0.84 (1)	2.00 (1)	2.8397 (16)	172 (2)
O5 <i>W</i> —H5 <i>WB</i> ...O3	0.85 (1)	1.96 (1)	2.7963 (15)	171 (2)
C11—H11 <i>E</i> ...O2 ^{iv}	0.98	2.58	3.393 (2)	140
C12—H12 <i>A</i> ...O3 ^v	0.98	2.52	3.453 (2)	158

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

Compararison of reported compounds with the general formula $Tr(Lx)(H_2O)_4.nH_2O$ (Tr is a transition metal)

Ligand codes: $L1$ is 2,2'-bipyridine; $L2$ is 5,5'-dimethyl-2,2'-bipyridine; $L3$ is 4,4'-dimethyl-2,2'-bipyridine; $L4$ is 1,10-phenanthroline; $L5$ is 1,10-phenanthroline-5,6-dione; $L6$ is 1*H*-imidazo[4,5-*f*][1,10]phenanthroline.

Compound	Tr	Lx	n	Space group	Z	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
(Ia)	Ni	$L1$	0	$Pbca$	8	12.3035 (7)	11.6560 (7)	20.7112 (10)	90	90	90	2970.2 (3)
(Ib)	Cd	$L1$	0	$P21/c$	4	10.262 (2)	12.073 (2)	12.357 (3)	90	92.47 (3)	90	1529.5 (10)
(Ic)	Zn	$L2$	0	$P21/c$	4	9.565 (2)	9.605 (2)	18.477 (3)	90	102.45 (9)	90	1657.5 (14)
(IIa)	Ni	$L3$	1	$P21/n$	4	11.8007 (3)	11.7095 (3)	13.6967 (3)	90	113.531 (12)	90	1735.24 (17)
(IIIa)	Zn	$L4$	2	$Pbca$	8	8.906 (1)	18.295 (2)	21.855 (3)	90	90	90	3560.9 (15)
(IIIb)	Mn	$L4$	2	$Pbca$	8	8.877 (1)	18.508 (3)	22.098 (3)	90	90	90	3630.602 (14)
(IIIc)	Cd	$L4$	2	$Pbca$	8	8.8398 (9)	18.700 (2)	22.349 (2)	90	90	90	3694.3 (11)
(IIId)	Co	$L4$	2	$Pbca$	8	8.856 (1)	18.318 (3)	21.918 (5)	90	90	90	3555.6 (17)
(IIIe)	Mn	$L5$	2	$C2/m$	4	9.6237 (4)	13.9117 (6)	13.8744 (6)	90	97.32 (2)	90	1842.4 (2)
(IIIf)	Ni	$L1$	2	$P\bar{1}$	2	7.793 (3)	9.351 (3)	11.476 (4)	87.40 (2)	96.50 (2)	102.37 (2)	811.4 (19)
(IIIg)	Ni	$L6$	2	$P\bar{1}$	2	7.266 (2)	11.112 (3)	12.913 (4)	75.676 (4)	77.393 (5)	71.423 (5)	946.4 (15)

Supplementary Table S4. Hydrogen-bonded chains in (IIa), involving up to three different primary hydrogen bonds between groups of atoms Gri

The interactions have the form of $Gr1 \cdots Gr2 \cdots Gr3 \cdots Gr1^*$ open chains, with $Gr1^*$ some symmetry equivalent of $Gr1$ and where ' \cdots ' denotes hydrogen bonding.

No.	Descriptor*	Gr1	Gr2	Gr3
1	C2,2(8)	(H1WA-O1W-Ni1-O2W-H2WA)	(O2-S1-O4)	
2	C2,2(8)	(H1WB-O1W-Ni1-O2W-H2WA)	(O2-S1-O4)	
3	C2,2(8)	(H2WA-O2W-Ni1-O3W-H3WB)	(O4-S1-O2) ⁱ	
4	C2,2(8)	(H2WB-O2W-Ni1-O3W-H3WB)	(O4-S1-O3) ⁱ	
5	C1,2(6)	(H2WA-O2W-Ni1-O4W-H4WB)	O2 ⁱⁱ	
6	C2,2(8)	(H2WB-O2W-Ni1-O4W-H4WB)	(O2-S1-O3) ⁱⁱ	
7	C2,2(8)	(H3WB-O3W-Ni1-O4W-H4WA)	(O1-S1-O4) ⁱⁱⁱ	
8	C2,2(8)	(H1WA-O1W-Ni1-O4W-H4WA)	(O1-S1-O4) ⁱⁱⁱ	
9	C2,2(8)	(H1WB-O1W-Ni1-O4W-H4WA)	(O1-S1-O4) ⁱⁱⁱ	
10	C2,2(8)	(H1WA-O1W-Ni1-O2W-H2WB)	(O3-S1-O4) ⁱⁱⁱ	
11	C2,2(8)	(H1WB-O1W-Ni1-O2W-H2WB)	(O3-S1-O4) ⁱⁱⁱ	
12	C2,2(6)	(H4WB-O4W-H4WA)	(O1-S1-O2) ⁱⁱⁱ	
13	C3,3(8)	(H3WB-O3W-H3WA)	(O5W-H5WB)	(O3-S1-O4)

14	C3,3(10)	(H1WA-O1W-Ni1-O3W-H3WA)	(O5W-H5WB)	(O3-S1-O4)
15	C3,3(10)	(H1WB-O1W-Ni1-O3W-H3WA)	(O5W-H5WB)	(O3-S1-O4)
16	C3,3(10)	(H4WB-O4W-Ni1-O3W-H3WA)	(O5W-H5WB)	(O3-S1-O2)
17	C3,3(10)	(H4WB-O4W-Ni1-O3W-H3WA)	(O5W-H5WA)	(O1-S1-O2) ⁱⁱⁱ
18	C3,3(8)	(H3WB-O3W-H3WA)	(O5W-H5WA)	(O1-S1-O4) ⁱⁱⁱ
19	C3,3(10)	(H1WA-O1W-Ni1-O3W-H3WA)	(O5W-H5WA)	(O1-S1-O4) ⁱⁱⁱ
20	C3,3(10)	(H1WB-O1W-Ni1-O3W-H3WA)	(O5W-H5WA)	(O1-S1-O4) ⁱⁱⁱ

Notes: (*) for an introduction to graph-set analysis and notation, see Bernstein *et al.* (1995) and Etter *et al.* (1990). For a graph-set code $X_a^d(n)$, X is the structure code (C = chain and R = ring), a is the total number of acceptors involved, d is the total number of donors involved and n is the total number of bonds involved. Symmetry codes: (i) $x + 1/2, -y + 1/2, z + 1/2$; (ii) $-x + 3/2, y + 1/2, -z + 1/2$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + 2, -y + 1, -z + 1$.

Supplementary Table S5. Hydrogen-bonded rings in (IIa), involving up to three different primary hydrogen bonds between groups of atoms Gri

The interactions have the form of Gr1...Gr2...Gr3...Gr1 closed loops, where '...' denotes hydrogen bonding.

No.	Descriptor*	Gr1	Gr2	Gr3	Gr4	Gr5	Gr6
1	R1,2(6)	(H1WA-O1W-Ni1-O3W-H3WB)	(O4) ⁱ				
2	R2,2(8)	(H1WB-O1W-Ni1-O4W-H4WB)	(O2-S1-O4) ⁱⁱ				
3	R2,2(8)	(H2WB-O2W-Ni1-O4W-H4WA)	(O1-S1-O3) ⁱⁱⁱ				
4	R3,3(8)	(H4WA-O4W-Ni1-O3W-H3WA)	(O5W-H5WA)	(O1) ⁱⁱⁱ			
5	R3,3(10)	(H2WB-O2W-Ni1-O3W-H3WA)	(O5W-H5WA)	(O1-S1-O3) ⁱⁱⁱ			
6	R3,3(10)	(H2WA-O2W-Ni1-O3W-H3WA)	(O5W-H5WB)	(O3-S1-O2)			
7	R2,4(8)	(H1WB-O1W-H1WA)	(O4) ⁱ	(H1WB-O1W-H1WA) ^{iv}	(O4) ⁱⁱ		
8	R2,4(12)	(H1WB-O1W-Ni1-O3W-H3WB)	(O4) ⁱ	(H1WB-O1W-Ni1-O3W-H3WB) ^{iv}	(O4) ⁱⁱ		
9	R4,4(12)	(H2WB-O2W-H2WA)	(O2-S1-O3)	(H2WB-O2W-H2WA) ⁱⁱⁱ	(O2-S1-O3) ⁱⁱⁱ		
10	R4,4(12)	(H5WB-O5W-H5WA)	(O1-S1-O3) ⁱⁱⁱ	(H5WB-O5W-H5WA) ⁱⁱⁱ	(O1-S1-O3)		

11	R4,4(16)	(H2WA- O2W-Ni1- O4W-H4WA)	(O1-S1-O2) ⁱⁱⁱ	(H2WA- O2W-Ni1- O4W- H4WA) ⁱⁱⁱ	(O1-S1-O2)		
12	R4,4(16)	(H3WB- O3W-Ni1- O4W-H4WB)	(O2-S1-O4) ⁱⁱ	(H3WB- O3W-Ni1- O4W- H4WB) ^{iv}	(O2-S1-O4) ⁱ		
13	R4,4(16)	(H1WA- O1W-Ni1- O4W-H4WB)	(O2-S1-O4) ⁱⁱ	(H1WA- O1W-Ni1- O4W- H4WB) ^{iv}	(O2-S1-O4) ⁱ		
14	R4,6(16)	(H2WB- O2W-Ni1- O3W-H3WA)	(O5W- H5WB)	(O3)	(H2WB- O2W-Ni1- O3W- H3WA) ⁱⁱⁱ	(O5W- H5WB) ⁱⁱⁱ	(O3) ⁱⁱⁱ
15	R6,6(20)	(H2WA- O2W-Ni1- O3W-H3WA)	(O5W- H5WA)	(O1-S1-O2) ⁱⁱⁱ	(H2WA- O2W-Ni1- O3W- H3WA) ⁱⁱⁱ	(O5W- H5WA) ⁱⁱⁱ	(O1-S1-O2)
16	R6,6(20)	(H4WA- O4W-Ni1- O3W-H3WA)	(O5W- H5WB)	(O3-S1-O1)	(H4WA- O4W-Ni1- O3W- H3WA) ⁱⁱⁱ	(O5W- H5WB) ⁱⁱⁱ	(O3-S1-O1) ⁱⁱⁱ

Notes: (*) for an introduction to graph-set analysis and notation, see Bernstein *et al.* (1995) and Etter *et al.* (1990). For a graph-set code $X_a^d(n)$, X is the structure code (C = chain and R = ring), a is the total number of acceptors involved, d is the total number of donors involved and n is the total number of bonds involved. Symmetry codes: (i) $x + 1/2, -y + 1/2, z + 1/2$; (ii) $-x + 3/2, y + 1/2, -z + 1/2$; (iii) $-x + 1, -y + 1, -z$.