Tetraaqua(4,4'-dimethyl-2,2'-bipyridine-κ²N,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


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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 \text{Ni}^{II} cation coordinated by a chelating \text{4,4'-dimethyl-2,2'-bipyridine} ligand via its two N atoms [mean \text{Ni}—\text{N} = 2.056 (2) Å] and by four aqua ligands [mean \text{Ni}—\text{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. 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 \text{4,4'-dimethyl-2,2'-bipyridine} ligands which interact laterally with their neighbours via π–π 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, \([\text{Ni}(\text{dmbpy})(\text{H}_2\text{O})_4]\text{SO}_4\cdot\text{H}_2\text{O}, \text{(IIa)}\) (where dmbpy = \text{4,4'-dimethyl-2,2'-bipyridine} = \text{L3}), is a member of a larger family having the general formula \([\text{TrL}_x(\text{H}_2\text{O})_n]\text{SO}_4\cdot\text{nH}_2\text{O}, \text{where Tr is a transition metal, L}_x\text{ is an } N,N'\text{-chelating neutral aromatic base and } n \text{ 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](image-url)
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/isomorphic family present, made up of compounds (IIIa)–(IIIg), with \( \text{Tr} = \text{Zn, Mn, Cd and Co, respectively} \). 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 \( L_x \) ligands which interact laterally with their neighbours via \( \pi-\pi \) 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 \( \text{Ni}^{II} \) 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 \( \text{Ni}^{II} \) cation coordinated by a chelating dmbpy ligand via its two N atoms [mean \( \text{Ni}—\text{N} = 2.056 (2) \ \text{Å} \) and by four aqua ligands [mean \( \text{Ni}—\text{O} = 2.073 (9) \ \text{Å} \), 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 dmbpy chelate angle [\( \text{Ni}1—\text{Ni}1—\text{N}2 = 79.34 (5) \)°]. The anion is very regular as well, with a tight span of \( \text{S}—\text{O} \) bond lengths and \( \text{O}—\text{S}—\text{O} \) angles [1.4717 (11)–1.4928 (10) \ \text{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, \( \pi-\pi \) contacts etc.) in order to define the three-dimensional crystal structure.

The dicationic [\( \text{Ni(dmbpy)H}_2\text{O}_4 \)]\(^{2+} \) subunit is naturally divided into two quite different parts: (i) the planar organic ligand chelating atom \( \text{Ni1} \) 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 \( \{10 \overline{1}\} \) (shown sideways in Fig. 3, in heavy lines). All ten water \( \text{H} \) atoms take part in these fairly strong interactions (Table 3, entries 1 to 10), with \( \text{H}—\text{O} \) distances up to 2 \ \text{Å} \ and \( \text{O}—\text{H}—\text{O} \) 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 \( \text{O1W, O2W} \) and \( \text{O4W} \) fulfil similar roles, bridging opposite sulfates on both sides of the metal atom. In contrast, water molecule \( \text{O3W} \) links the \( \text{O5W} \) solvent molecule through...
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 hydrogen-bonding structure (Fig. 3, heavy lines) is a broad sheet ca 3.5 Å thick, decorated by pendant 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 (101) 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 (IIIf) (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**

\[
\text{[Ni(C14H12N2)(H2O)4]SO4•H2O} \quad V = 1735.24 (17) \text{ Å}^3
\]

\[
M_r = 429.09
\]

Monoclinic, P21/n

\[
\alpha = 11.8007 (3) \text{ Å} \quad \mu = 1.29 \text{ mm}^{-1}
\]

\[
\beta = 11.7095 (3) \text{ Å} \quad T = 150 \text{ K}
\]

\[
\gamma = 13.6967 (3) \text{ Å} \quad \epsilon = 0.48 \times 0.18 \times 0.14 \text{ mm}
\]

\[
\beta = 113.530 (12)^\circ
\]


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**Metal-organic compounds**

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*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 + 1, y, z; (ii) -x + 1, y + 1, z; (iii) -x + 1, -y + 1, -z; (iv) -x + 2, -y + 1, -z + 1.]
metal-organic compounds

Table 1
Comparison of reported compounds with the general formula [Tr(Lx)(H₂O)₅]SO₄·nH₂O (Tr is a transition metal).

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<th>Compound</th>
<th>Tr</th>
<th>L</th>
<th>n</th>
<th>Space Group</th>
<th>Z</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>V (Å³)</th>
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<tr>
<td>(I)</td>
<td>Ni</td>
<td>L₁</td>
<td>0</td>
<td>P2₁/c</td>
<td>4</td>
<td>9.565</td>
<td>9.605</td>
<td>18.477</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>2970.2 (3)</td>
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<tr>
<td>(II)</td>
<td>Cd</td>
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<td>9.858</td>
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<td>90</td>
<td>90</td>
<td>3630.6 (14)</td>
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<td>(III)</td>
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<td>L₁</td>
<td>0</td>
<td>P2₁/c</td>
<td>4</td>
<td>9.966</td>
<td>9.858</td>
<td>18.700</td>
<td>92.47</td>
<td>90</td>
<td>90</td>
<td>3694.3 (11)</td>
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<td>(IV)</td>
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<td>11.8007</td>
<td>11.7095</td>
<td>13.6967</td>
<td>90</td>
<td>90</td>
<td>120</td>
<td>17352.4 (17)</td>
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<td>(V)</td>
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<td>L₅</td>
<td>1</td>
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<td>90</td>
<td>90</td>
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<td>7.793</td>
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<td>90</td>
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<td>L₆</td>
<td>2</td>
<td>P_Ti</td>
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<td>75.676</td>
<td>77.393</td>
<td>71.423</td>
<td>946.4 (15)</td>
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Table 2
Selected bond lengths (Å).

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<th>Ligand codes: Lx</th>
<th>Ni₁–N₁</th>
<th>Ni₁–O₁</th>
<th>Ni₁–O₂</th>
<th>Ni₁–O₃</th>
<th>Ni₁–O₄</th>
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<tr>
<td></td>
<td>2.0545 (12)</td>
<td>2.0864 (11)</td>
<td>2.0587 (12)</td>
<td>2.0719 (11)</td>
<td>2.0673 (11)</td>
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</table>

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

<table>
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<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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<tr>
<td>O1W—H1WA···O4</td>
<td>0.83 (1)</td>
<td>2.00 (1)</td>
<td>2.7959 (15)</td>
<td>160 (2)</td>
</tr>
<tr>
<td>O1W—H1WB···O4$a$</td>
<td>0.84 (1)</td>
<td>1.87 (1)</td>
<td>2.6913 (15)</td>
<td>164 (2)</td>
</tr>
<tr>
<td>O2W—H2WA···O2</td>
<td>0.83 (1)</td>
<td>1.96 (1)</td>
<td>2.7895 (15)</td>
<td>171 (2)</td>
</tr>
<tr>
<td>O2W—H2WB···O3$a$</td>
<td>0.84 (1)</td>
<td>1.86 (1)</td>
<td>2.6985 (15)</td>
<td>172 (2)</td>
</tr>
<tr>
<td>O3W—H3WA···O5</td>
<td>0.84 (1)</td>
<td>1.94 (1)</td>
<td>2.7800 (16)</td>
<td>176 (2)</td>
</tr>
<tr>
<td>O3W—H3WB···O4</td>
<td>0.84 (1)</td>
<td>1.91 (1)</td>
<td>2.7329 (14)</td>
<td>165 (2)</td>
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<tr>
<td>O4W—H4WA···O1</td>
<td>0.83 (1)</td>
<td>2.01 (1)</td>
<td>2.8082 (15)</td>
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<tr>
<td>O4W—H4WB···O2$b$</td>
<td>0.85 (1)</td>
<td>1.98 (1)</td>
<td>2.8253 (15)</td>
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<tr>
<td>O5W—H5WA···O1$b$</td>
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<td>2.00 (1)</td>
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<td>1.96 (1)</td>
<td>2.7963 (15)</td>
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<td>Cl1—H11E···O2$c$</td>
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<td>Cl2—H12A···O3</td>
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Symmetry codes: (i) x+1/2, -y+1, z; (ii) -x+1/2, y+1/2, -z+1/2; (iii) -x+1, -y+1, -z; (iv) -x+2, y, -z; (v) x+1, y, z.

Data collection
Oxford Gemini CCD S Ultra
diffraclmeter
Absorption correction: multi-scan
3599 reflections with I > 2σ(I)
Tmin = 0.76, Tmax = 0.84

Refinement
R[F² > 2σ(F²)] = 0.027
wR(F²) = 0.075
S = 1.07
3599 reflections
15 restraints

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 Uiso(H) = 1.5Ueq(C). Water H atoms were refined with restrained O—H and H···H distances of 0.85 (1) and 1.35 (1) Å, respectively. Uiso(H) values were set at 1.5Ueq(C) for the methyl groups and at 1.2Ueq(CO) 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).

The authors acknowledge ANPCyT (project No. PME 2006-01113) for the purchase of the Oxford Gemini CCD diffractometer and the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system (Allen, 2002).

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.

References


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supplementary materials


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Tetraaqua(4,4′-dimethyl-2,2′-bipyridine-κ²N,N′)nickel(II) sulfate monohydrate

Crystal data

$[\text{Ni(C}_2\text{H}_7\text{N}_2)(\text{H}_2\text{O})_4]\text{SO}_4\cdot\text{H}_2\text{O}$

$M_r = 429.09$

Monoclinic, $P2_1/n$

Hall symbol: $-P 2yn$

$a = 11.8007$ (3) Å

$b = 11.7095$ (3) Å

$c = 13.6967$ (3) Å

$\beta = 113.530$ (12)°

$V = 1735.24$ (17) Å$^3$

$Z = 4$

$F(000) = 896$

$D_\lambda = 1.642$ Mg m$^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3870 reflections

$\theta = 2.7$–25.2°

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

$T = 150$ K

Prism, light blue

$0.48 \times 0.18 \times 0.14$ mm

Data collection

Oxford Gemini CCD S Ultra diffractometer

$\omega$ scans, thick slices

Absorption correction: multi-scan

(Crystalis PRO; Oxford Diffraction, 2009)

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

14064 measured reflections

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

3811 independent reflections

$\theta_{\text{max}} = 27.8°$, $\theta_{\text{min}} = 1.9°$

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

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

$\theta_{\text{max}} = 27.8°$, $\theta_{\text{min}} = 1.9°$

$R = 0.017$, $wR = 0.051$

$S = 1.07$

15 restraints

Secondary atom site location: difference Fourier map

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

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

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

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

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

Primary atom site location: structure-invariant direct methods
**Special details**

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

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

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<th>Atom</th>
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<th>y</th>
<th>z</th>
<th>U(eq)</th>
<th>Occ. (&lt;1)</th>
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Geometric parameters (Å, º)

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supplementary materials

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C3—C11—H11B 109.5  Ni1—O5W—H5WA 105.3 (13)
H11A—C11—H11B 109.5  Ni1—O5W—H5WB 105.3 (13)
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Hydrogen-bond geometry (Å, °)

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<td>1.91 (1)</td>
<td>2.7329 (14)</td>
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<tr>
<td>O4W···O1</td>
<td>0.83 (1)</td>
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<tr>
<td>O4W···O1</td>
<td>0.85 (1)</td>
<td>1.98 (1)</td>
<td>2.8253 (15)</td>
<td>176 (2)</td>
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<tr>
<td>O5W···O1</td>
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<td>2.00 (1)</td>
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<td>172 (2)</td>
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<td>1.96 (1)</td>
<td>2.7963 (15)</td>
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<tr>
<td>C11···C12</td>
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<tr>
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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.


Comparisons of reported compounds with the general formula Tr(Lx)(H₂O)₄.nH₂O (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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tr</th>
<th>Lx</th>
<th>Space group</th>
<th>Za (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ia)</td>
<td>Ni</td>
<td>L₁</td>
<td>Pbc</td>
<td>12.3035 (7)</td>
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<td>90</td>
<td>90</td>
<td>2970.2 (3)</td>
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<td>P2₁/c</td>
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<td>(Ic)</td>
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<td>L₂</td>
<td>P2₁/c</td>
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<td>113.531 (12)</td>
<td>90</td>
<td>1735.24 (17)</td>
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<tr>
<td>(IIIa)</td>
<td>Zn</td>
<td>L₄</td>
<td>Pbca</td>
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<td>11.7095 (3)</td>
<td>13.6967 (3)</td>
<td>90</td>
<td>113.531 (12)</td>
<td>90</td>
<td>1735.24 (17)</td>
</tr>
<tr>
<td>(IIIb)</td>
<td>Mn</td>
<td>L₄</td>
<td>Pbca</td>
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<td>90</td>
<td>3560.9 (15)</td>
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<tr>
<td>(IIIc)</td>
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<td>L₄</td>
<td>Pbca</td>
<td>8.877 (1)</td>
<td>18.508 (3)</td>
<td>22.098 (3)</td>
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<td>90</td>
<td>90</td>
<td>3630.602 (14)</td>
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<tr>
<td>(IIId)</td>
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<td>L₄</td>
<td>Pbca</td>
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<td>22.349 (2)</td>
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<td>90</td>
<td>90</td>
<td>3694.3 (11)</td>
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<td>L₅</td>
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<td>Pbca</td>
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<td>18.508 (3)</td>
<td>22.098 (3)</td>
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<td>90</td>
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</table>

Supplementary Table S4. Hydrogen-bonded chains in (IIa), involving up to three different primary hydrogen bonds between groups of atoms Gr₁

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

<table>
<thead>
<tr>
<th>No.</th>
<th>Descriptor*</th>
<th>Gr₁</th>
<th>Gr2</th>
<th>Gr3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C2,2(8)</td>
<td>(H1WA-O1W-Ni1-O2W-H2WA)</td>
<td>(O2-S1-O4)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C2,2(8)</td>
<td>(H1WB-O1W-Ni1-O2W-H2WA)</td>
<td>(O2-S1-O4)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C2,2(8)</td>
<td>(H2WA-O2W-Ni1-O3W-H3WB)</td>
<td>(O4-S1-O2)^i</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C2,2(8)</td>
<td>(H2WB-O2W-Ni1-O3W-H3WB)</td>
<td>(O4-S1-O3)^i</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C1,2(6)</td>
<td>(H2WA-O2W-Ni1-O4W-H4WB)</td>
<td>O2^ii</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C2,2(8)</td>
<td>(H2WB-O2W-Ni1-O4W-H4WB)</td>
<td>(O2-S1-O3)^ii</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>C2,2(8)</td>
<td>(H3WB-O3W-Ni1-O4W-H4WA)</td>
<td>(O1-S1-O4)^iii</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>C2,2(8)</td>
<td>(H1WA-O1W-Ni1-O4W-H4WA)</td>
<td>(O1-S1-O4)^iii</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>C2,2(8)</td>
<td>(H1WB-O1W-Ni1-O4W-H4WA)</td>
<td>(O1-S1-O4)^iii</td>
<td></td>
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<tr>
<td>10</td>
<td>C2,2(8)</td>
<td>(H1WA-O1W-Ni1-O2W-H2WA)</td>
<td>(O3-S1-O4)^iii</td>
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<tr>
<td>11</td>
<td>C2,2(8)</td>
<td>(H1WB-O1W-Ni1-O2W-H2WB)</td>
<td>(O3-S1-O4)^iii</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>C2,2(6)</td>
<td>(H4WB-O4W-H4WA)</td>
<td>(O1-S1-O2)^iii</td>
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</tr>
<tr>
<td>13</td>
<td>C3,3(8)</td>
<td>(H3WB-O3W-H3WA)</td>
<td>(O5W-H5WB)</td>
<td>(O3-S1-O4)</td>
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</tbody>
</table>
### Supplementary Table S5. Hydrogen-bonded rings in (IIa), involving up to three different primary hydrogen bonds between groups of atoms \( \text{Gr}_i \)

The interactions have the form of \( \text{Gr}_1 \cdots \text{Gr}_2 \cdots \text{Gr}_3 \cdots \text{Gr}_1 \) closed loops, where `···` denotes hydrogen bonding.

<table>
<thead>
<tr>
<th>No.</th>
<th>Descriptor*</th>
<th>Gr1</th>
<th>Gr2</th>
<th>Gr3</th>
<th>Gr4</th>
<th>Gr5</th>
<th>Gr6</th>
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<tbody>
<tr>
<td>1</td>
<td>R1,2(6)</td>
<td>(H1WA-O1W-Ni1-O3W-H3WA)</td>
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<td></td>
<td>(O5W-H5WB)</td>
<td>(O3-S1-O4)</td>
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<tr>
<td>2</td>
<td>R2,2(8)</td>
<td>(H1WB-O1W-Ni1-O3W-H3WA)</td>
<td>(O2-S1-O4)i</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>R2,2(8)</td>
<td>(H2WB-O2W-Ni1-O3W-H3WA)</td>
<td>(O1-S1-O3)iii</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>R3,3(8)</td>
<td>(H4WA-O4W-Ni1-O3W-H3WA)</td>
<td>(O5W-H5WA)</td>
<td></td>
<td>(O1)iii</td>
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<tr>
<td>5</td>
<td>R3,3(10)</td>
<td>(H2WB-O2W-Ni1-O3W-H3WA)</td>
<td>(O5W-H5WA)</td>
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<td>(O1-S1-O3)iii</td>
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<tr>
<td>6</td>
<td>R3,3(10)</td>
<td>(H2WA-O2W-Ni1-O3W-H3WA)</td>
<td>(O5W-H5WB)</td>
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<td>(O3-S1-O2)</td>
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<tr>
<td>7</td>
<td>R2,4(8)</td>
<td>(H1WB-O1W-H1WA)</td>
<td>(O4)i</td>
<td>(H1WB-O1W-H1WA)iv</td>
<td>(O4)i</td>
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<td></td>
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<tr>
<td>8</td>
<td>R2,4(12)</td>
<td>(H1WB-O1W-Ni1-O3W-H3WB)</td>
<td>(O4)i</td>
<td>(H1WB-O1W-Ni1-O3W-H3WB)iv</td>
<td>(O4)i</td>
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<tr>
<td>9</td>
<td>R4,4(12)</td>
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<tr>
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<td>(O1-S1-O3)iii</td>
<td>(H5WB-O5W-H5WA)iii</td>
<td>(O1-S1-O3)</td>
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</tbody>
</table>

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 \( X_d^a(n) \), \( X \) 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) \( -x + 2, -y + 1, -z + 1 \).
<table>
<thead>
<tr>
<th></th>
<th>Structure Code</th>
<th>Symmetry Codes</th>
<th>Details</th>
</tr>
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</tr>
<tr>
<td>12</td>
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<td>(H3WB-O3W-Ni1-O4W-H4WB)</td>
<td>(H3WB-O3W-Ni1-O4W-H4WB)iv (O2-S1-O4)ii (O2-S1-O4)i (O2-S1-O4)i</td>
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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 $X_a^b(n)$, $X$ 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) $x+1$, $y+1$, $z$. 

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