Triaqua(4-hydroxypyridine-2,6-dicarboxylato)nickel(II) sesquihydrate

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The reaction of nickel(II) nitrate hexahydrate with the proton-transfer compound piperazinediium 4-hydroxypyridine-2,6-dicarboxylate, (pipzH$_2$)(hypydc), where pipz is piperazine and hypydcH$_2$ is 4-hydroxypyridine-2,6-dicarboxylic acid, in aqueous solution leads to the formation of the title complex, [Ni(C$_7$H$_3$NO$_5$)(H$_2$O)$_3$]·1.5H$_2$O. Nickel(II) is coordinated by three donor atoms of the tridentate dianionic ligand, and three water molecules, in a slightly distorted octahedral geometry. The range of H···A and D···A distances, and D—H···A angles indicates the presence of strong hydrogen bonding in this complex, which involves the coordinated and uncoordinated water molecules (one of which lies on a twofold rotation axis), giving a three-dimensional network.

Related literature

For related literature see: Aghabozorg, Ghadermazi & Nemati (2006); Aghabozorg *et al.* (2006a,b); Moghimi *et al.* (2005); Sheshmani *et al.* (2006).
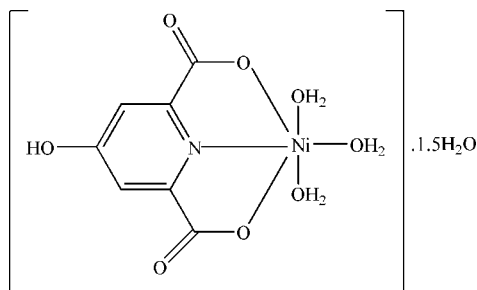
Experimental

Crystal data

[Ni(C$_7$H$_3$NO$_5$)(H$_2$O)$_3$]·1.5H$_2$O
M_r = 320.89
Monoclinic, $C2/c$
a = 14.881 (12) Å
b = 6.878 (6) Å
c = 22.409 (19) Å
β = 90.049 (15)°

V = 2294 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.74 mm^{-1}
T = 150 (2) K
0.43 × 0.34 × 0.07 mm

Data collection

Bruker SMART 1000 diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.522, T_{max} = 0.888

10569 measured reflections
2019 independent reflections
1567 reflections with $I > 2\sigma(I)$
R_{int} = 0.121

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.161
S = 1.06
2019 reflections

169 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.09 e Å^{-3}
$\Delta\rho_{min}$ = −1.02 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···O1^i	0.84	1.82	2.649 (5)	167
O6—H6A···O2^{ii}	0.95	1.85	2.720 (5)	151
O6—H6B···O10^{iii}	0.95	1.97	2.829 (5)	149
O7—H7A···O9^{iv}	0.95	1.99	2.911 (7)	163
O7—H7B···O4^{iii}	0.95	1.89	2.782 (5)	156
O8—H8A···O2^v	0.95	1.96	2.852 (5)	157
O8—H8A···O5^{vi}	0.95	2.58	3.123 (5)	116
O8—H8B···O10^{vii}	0.95	1.92	2.867 (5)	172
O9—H9A···O6	0.95	2.28	3.142 (6)	151
O10—H10A···O6^{iii}	0.95	2.12	2.829 (5)	131
O10—H10B···O3^{vii}	0.95	1.97	2.893 (5)	164

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

References

Aghabozorg, H., Ghadermazi, M. & Nemati, A. (2006). *Anal. Sci. X*, **22**, x233–x234.

Aghabozorg, H., Ghadermazi, M. & Sadr-Khanlou, E. (2006a). *Anal. Sci. X*, **22**, x253–x254.

Aghabozorg, H., Ghadermazi, M. & Sadr-Khanlou, E. (2006b). *Anal. Sci. X*, **22**, x255–x256.

Bruker (1998). *SADABS* (Version 2004/1), *SAINT* (Version 6.01), *SMART* (Version 5.059) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Moghimi, A., Sheshmani, S., Shokrollahi, A., Shamsipour, M., Kickelbick, G. & Aghabozorg, H. (2005). *Z. Anorg. Allg. Chem.* **631**, 160–169.

metal-organic compounds

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheshmani, S., Aghabozorg, H., Mohammad Panah, F., Alizadeh, R., Kickelbick, G., Nakhjavan, B., Moghimi, A., Ramezanipour, F. & Aghabozorg, H. R. (2006). *Z. Anorg. Allg. Chem.* **632**, 469–474.

supplementary materials

Triaqua(4-hydroxypyridine-2,6-dicarboxylato)nickel(II) sesquihydrate

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Comment

The chemical formula and the *ORTEP* diagram indicate that the cationic fragment $(pipzH_2)^{2+}$ has been missed during complexation and only the anionic species of the starting proton transfer compound has contributed to the complex. This is similar to some other complexes containing only the anionic fragments of their starting proton transfer compounds. The N(1)–Ni(1)–O(7) angle revealed an octahedral axis with 3.73° deviation from ideal linearity, therefore, O(1), O(4), O(6) and O(8) are equatorial positions of the distorted octahedral. Both weak and strong hydrogen bonds with D···A distances ranging from 2.649 (5) to 3.142 (6) Å, are observed in the crystal. The presence of OH group of 4-hydroxypyridine-2,6-dicarboxylate, carboxylate and water molecules in the crystal structure causes the hydrogen bonding network of the system to be more extended, as its hydrogen bonds has an important linking role among the crystal lattice fragments. Also, two halves of the units $[Ni(hypydc)(H_2O)_3]$, are kept together through hydrogen bonding between water molecules and oxygen atom of carboxylate group. Figures 1 and 2 are shown the molecular structure and packing diagram of this complex, respectively.

Experimental

To 20 ml of an aqueous solution of $(pipzH_2)(hypydc)$ (584 mg, 2 mmol) was added 10 ml of an aqueous solution of nickel(II) nitrate hexahydrate (290 mg, 1 mmol). Upon standing, crystals were precipitated after 20 days. The pure crystalline complex $[Ni(hypydc)(H_2O)_3]$. $2H_2O$, were decomposed at >400 °C.

Refinement

Hydrogen atoms were positioned geometrically and refined with a riding model (including torsional freedom for methyl groups), with C—H = 0.95–0.98 Å, and with U(H) constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.
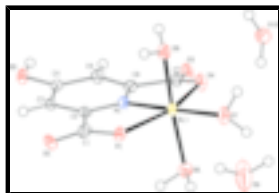
Figures

Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids.

Fig. 2. The packing of (I), showing molecules connected by O–H···O hydrogen bonds (dashed lines).

supplementary materials

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$M_r = 320.89$	$D_x = 1.859$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C2yc	Cell parameters from 4075 reflections
$a = 14.881$ (12) Å	$\theta = 2.7–27.3°$
$b = 6.878$ (6) Å	$\mu = 1.74$ mm^{-1}
$c = 22.409$ (19) Å	$T = 150$ (2) K
$\beta = 90.049$ (15)°	Block, blue
$V = 2294$ (3) Å^3	$0.43 \times 0.34 \times 0.07$ mm
$Z = 8$	

Data collection

Bruker SMART 1000 diffractometer	2019 independent reflections
Radiation source: fine-focus sealed tube	1567 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.121$
Detector resolution: 100 pixels mm^{-1}	$\theta_{max} = 25.0°$
$T = 150(2)$ K	$\theta_{min} = 1.8°$
ω scans	$h = -17 \rightarrow 17$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$k = -8 \rightarrow 8$
$T_{min} = 0.522$, $T_{max} = 0.888$	$l = -26 \rightarrow 26$
10569 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.057$	H-atom parameters constrained
$wR(F^2) = 0.161$	$w = 1/[\sigma^2(F_o^2) + (0.1044P)^2 + 2.0879P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2019 reflections	$\Delta\rho_{max} = 2.09$ e Å^{-3}
169 parameters	$\Delta\rho_{min} = -1.02$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Ni1	0.52210 (4)	0.24829 (8)	0.63815 (2)	0.0155 (3)
N1	0.6177 (2)	0.1265 (5)	0.58918 (16)	0.0139 (8)
O1	0.4739 (2)	0.2898 (4)	0.54619 (14)	0.0164 (7)
O2	0.5152 (2)	0.2401 (4)	0.45093 (14)	0.0186 (8)
O3	0.7282 (2)	−0.0631 (5)	0.71543 (14)	0.0266 (8)
O4	0.6134 (2)	0.1517 (5)	0.70553 (13)	0.0201 (7)
O5	0.83039 (19)	−0.0744 (5)	0.48988 (13)	0.0177 (7)
H5	0.8737	−0.1062	0.5119	0.021*
O6	0.4476 (2)	−0.0092 (5)	0.64449 (15)	0.0242 (8)
H6A	0.4428	−0.0682	0.6063	0.029*
H6B	0.3863	0.0217	0.6373	0.029*
O7	0.4278 (2)	0.3656 (5)	0.69271 (14)	0.0238 (8)
H7A	0.4393	0.4831	0.7137	0.029*
H7B	0.3992	0.2843	0.7213	0.029*
O8	0.5778 (2)	0.5276 (5)	0.63456 (14)	0.0214 (7)
H8A	0.5601	0.5938	0.5992	0.026*
H8B	0.6406	0.5324	0.6418	0.026*
O9	0.5000	−0.2882 (9)	0.7500	0.073 (3)
H9A	0.5060	−0.2133	0.7146	0.088*
O10	0.7368 (2)	0.0525 (5)	0.83145 (15)	0.0283 (8)
H10A	0.6805	0.0147	0.8152	0.034*
H10B	0.7587	0.1679	0.8133	0.034*
C1	0.5283 (3)	0.2279 (6)	0.5061 (2)	0.0183 (11)
C2	0.6146 (3)	0.1338 (6)	0.52935 (19)	0.0137 (9)
C3	0.6850 (3)	0.0626 (6)	0.49478 (19)	0.0137 (9)
H3	0.6818	0.0663	0.4524	0.016*
C4	0.7612 (3)	−0.0153 (6)	0.5238 (2)	0.0146 (9)
C5	0.7629 (3)	−0.0255 (6)	0.5870 (2)	0.0172 (10)
H5A	0.8129	−0.0786	0.6077	0.021*
C6	0.6881 (3)	0.0456 (6)	0.6176 (2)	0.0159 (9)
C7	0.6769 (3)	0.0447 (7)	0.6852 (2)	0.0173 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0124 (4)	0.0218 (4)	0.0122 (4)	0.0028 (2)	0.0006 (3)	−0.0001 (2)
N1	0.0115 (17)	0.0175 (19)	0.0128 (19)	0.0013 (14)	−0.0006 (14)	−0.0005 (15)
O1	0.0119 (16)	0.0214 (17)	0.0158 (17)	0.0039 (12)	0.0018 (13)	0.0003 (13)
O2	0.0207 (19)	0.0224 (18)	0.0125 (19)	0.0041 (12)	−0.0068 (14)	−0.0010 (12)
O3	0.0264 (18)	0.040 (2)	0.0137 (17)	0.0100 (15)	−0.0024 (14)	0.0013 (15)
O4	0.0208 (16)	0.0279 (19)	0.0118 (16)	0.0080 (14)	0.0007 (12)	0.0003 (14)
O5	0.0127 (15)	0.0247 (18)	0.0156 (16)	0.0069 (12)	0.0026 (12)	0.0001 (14)
O6	0.0220 (17)	0.0281 (18)	0.0226 (18)	−0.0020 (13)	0.0033 (14)	−0.0038 (15)
O7	0.0232 (17)	0.032 (2)	0.0161 (17)	0.0059 (14)	0.0043 (13)	0.0009 (15)
O8	0.0210 (16)	0.0252 (18)	0.0180 (17)	0.0002 (13)	−0.0010 (13)	0.0020 (14)
O9	0.145 (8)	0.038 (4)	0.036 (4)	0.000	0.035 (5)	0.000
O10	0.0250 (18)	0.037 (2)	0.0226 (19)	−0.0041 (15)	−0.0039 (14)	0.0024 (16)
C1	0.022 (3)	0.013 (2)	0.021 (3)	−0.0016 (17)	0.004 (2)	0.0016 (18)
C2	0.012 (2)	0.016 (2)	0.013 (2)	−0.0011 (17)	−0.0020 (16)	−0.0009 (18)
C3	0.016 (2)	0.015 (2)	0.010 (2)	−0.0022 (16)	−0.0007 (17)	−0.0002 (17)
C4	0.014 (2)	0.015 (2)	0.015 (2)	−0.0005 (16)	0.0013 (17)	0.0010 (18)
C5	0.015 (2)	0.020 (2)	0.016 (2)	0.0035 (17)	0.0000 (18)	−0.0002 (19)
C6	0.013 (2)	0.019 (2)	0.015 (2)	−0.0005 (17)	−0.0027 (17)	0.0020 (18)
C7	0.013 (2)	0.025 (2)	0.014 (2)	0.0018 (18)	0.0008 (18)	0.0001 (19)

Geometric parameters (Å, °)

Ni1—N1	1.983 (4)	O7—H7A	0.9501
Ni1—O7	2.029 (3)	O7—H7B	0.9501
Ni1—O8	2.094 (4)	O8—H8A	0.9500
Ni1—O6	2.094 (4)	O8—H8B	0.9501
Ni1—O4	2.136 (3)	O9—H9A	0.9500
Ni1—O1	2.200 (4)	O10—H10A	0.9500
N1—C2	1.342 (6)	O10—H10B	0.9499
N1—C6	1.346 (6)	C1—C2	1.529 (6)
O1—C1	1.283 (6)	C2—C3	1.393 (6)
O2—C1	1.254 (6)	C3—C4	1.412 (6)
O3—C7	1.261 (5)	C3—H3	0.9500
O4—C7	1.282 (5)	C4—C5	1.418 (7)
O5—C4	1.344 (5)	C5—C6	1.395 (6)
O5—H5	0.8400	C5—H5A	0.9500
O6—H6A	0.9499	C6—C7	1.525 (6)
O6—H6B	0.9500		
N1—Ni1—O7	176.51 (13)	H7A—O7—H7B	104.3
N1—Ni1—O8	94.73 (14)	Ni1—O8—H8A	111.2
O7—Ni1—O8	86.10 (14)	Ni1—O8—H8B	114.5
N1—Ni1—O6	93.45 (14)	H8A—O8—H8B	113.5
O7—Ni1—O6	85.93 (14)	H10A—O10—H10B	111.5
O8—Ni1—O6	171.13 (13)	O2—C1—O1	124.8 (4)

N1—Ni1—O4	78.67 (14)	O2—C1—C2	119.6 (4)
O7—Ni1—O4	97.90 (14)	O1—C1—C2	115.6 (4)
O8—Ni1—O4	93.50 (13)	N1—C2—C3	121.1 (4)
O6—Ni1—O4	91.46 (14)	N1—C2—C1	112.6 (4)
N1—Ni1—O1	76.72 (14)	C3—C2—C1	126.2 (4)
O7—Ni1—O1	106.71 (13)	C2—C3—C4	118.8 (4)
O8—Ni1—O1	88.48 (12)	C2—C3—H3	120.6
O6—Ni1—O1	90.07 (13)	C4—C3—H3	120.6
O4—Ni1—O1	155.39 (12)	O5—C4—C3	118.0 (4)
C2—N1—C6	120.9 (4)	O5—C4—C5	122.5 (4)
C2—N1—Ni1	120.8 (3)	C3—C4—C5	119.5 (4)
C6—N1—Ni1	118.2 (3)	C6—C5—C4	117.3 (4)
C1—O1—Ni1	114.0 (3)	C6—C5—H5A	121.3
C7—O4—Ni1	113.3 (3)	C4—C5—H5A	121.3
C4—O5—H5	109.5	N1—C6—C5	122.3 (4)
Ni1—O6—H6A	109.8	N1—C6—C7	112.7 (4)
Ni1—O6—H6B	107.9	C5—C6—C7	125.1 (4)
H6A—O6—H6B	82.7	O3—C7—O4	126.3 (4)
Ni1—O7—H7A	120.8	O3—C7—C6	118.0 (4)
Ni1—O7—H7B	118.8	O4—C7—C6	115.6 (4)
O8—Ni1—N1—C2	−83.2 (3)	Ni1—N1—C2—C1	−4.7 (5)
O6—Ni1—N1—C2	93.4 (3)	O2—C1—C2—N1	−178.2 (4)
O4—Ni1—N1—C2	−175.8 (3)	O1—C1—C2—N1	1.9 (5)
O1—Ni1—N1—C2	4.1 (3)	O2—C1—C2—C3	2.4 (7)
O8—Ni1—N1—C6	93.3 (3)	O1—C1—C2—C3	−177.5 (4)
O6—Ni1—N1—C6	−90.1 (3)	N1—C2—C3—C4	−1.1 (6)
O4—Ni1—N1—C6	0.7 (3)	C1—C2—C3—C4	178.3 (4)
O1—Ni1—N1—C6	−179.4 (3)	C2—C3—C4—O5	−176.7 (4)
N1—Ni1—O1—C1	−2.8 (3)	C2—C3—C4—C5	2.2 (6)
O7—Ni1—O1—C1	177.9 (3)	O5—C4—C5—C6	178.1 (4)
O8—Ni1—O1—C1	92.4 (3)	C3—C4—C5—C6	−0.8 (6)
O6—Ni1—O1—C1	−96.3 (3)	C2—N1—C6—C5	3.2 (6)
O4—Ni1—O1—C1	−2.7 (5)	Ni1—N1—C6—C5	−173.3 (3)
N1—Ni1—O4—C7	−8.3 (3)	C2—N1—C6—C7	−177.7 (4)
O7—Ni1—O4—C7	171.0 (3)	Ni1—N1—C6—C7	5.8 (5)
O8—Ni1—O4—C7	−102.4 (3)	C4—C5—C6—N1	−1.9 (7)
O6—Ni1—O4—C7	84.9 (3)	C4—C5—C6—C7	179.1 (4)
O1—Ni1—O4—C7	−8.4 (5)	Ni1—O4—C7—O3	−164.3 (4)
Ni1—O1—C1—O2	−178.6 (3)	Ni1—O4—C7—C6	13.6 (5)
Ni1—O1—C1—C2	1.3 (4)	N1—C6—C7—O3	164.9 (4)
C6—N1—C2—C3	−1.6 (6)	C5—C6—C7—O3	−16.0 (7)
Ni1—N1—C2—C3	174.7 (3)	N1—C6—C7—O4	−13.2 (6)
C6—N1—C2—C1	179.0 (4)	C5—C6—C7—O4	165.8 (4)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
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O10—H10A···O6^{iii}	0.95	2.12	2.829 (5)	131
O10—H10B···O3^{vii}	0.95	1.97	2.893 (5)	164

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

Fig. 1

Fig. 2