Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Piperazinium tetraaquadi-μ-citrato-dinickelate(II)

Hai-Yan Song,[a] Chang-Cang Huang,[a]* Jian-Hai Luo,[a] Xi-He Huang[a] and Dong-Sheng Liu[a,b]

[a]Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, People's Republic of China, and [b]Department of Chemistry, Jinggangshan University, Ji'an, Jiangxi 343009, People's Republic of China
Correspondence e-mail: cchuang@fzu.edu.cn

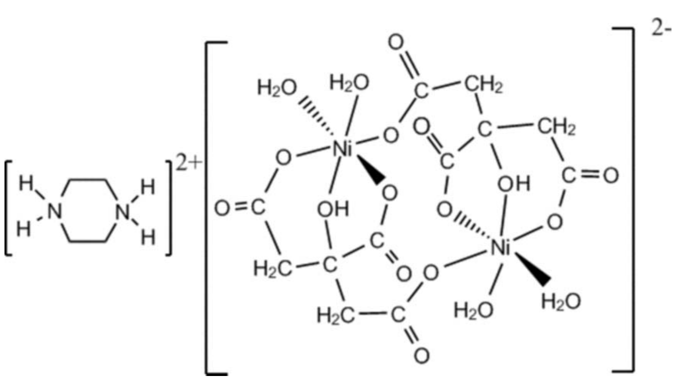
Received 30 March 2007; accepted 24 April 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.073; data-to-parameter ratio = 15.6.

The title complex, $(C_4H_{12}N_2)[Ni_2(C_6H_5O_7)_2(H_2O)_4]$, was synthesized under solvothermal conditions. Both cation and anion possess crystallographically imposed inversion symmetry. The citrate ion acts as a quadridentate ligand, coordinating through the hydroxyl and two carboxylate O atoms to one nickel atom, and bridging the second metal centre through the remaining carboxylate group. The coordination around each Ni^{II} atom is completed to distorted octahedral by the O atoms of two water molecules. The crystal structure is stabilized by intra- and intermolecular O—H···O and N—H···O hydrogen-bonding interactions.

Related literature

For related literature, see: Baggio & Perec (2004); Baker *et al.* (1983); Kaliva *et al.* (2004); Kefalas *et al.* (2005); Kotsakis *et al.* (2003); Wang *et al.* (2005); Xiang *et al.* (2005); Zhang *et al.* (2006); Zhou *et al.* (2005).



Experimental

Crystal data

$(C_4H_{12}N_2)[Ni_2(C_6H_5O_7)_2(H_2O)_4]$
M_r = 655.80
Monoclinic, $P2_1/n$
a = 13.342 (3) Å
b = 6.7054 (13) Å
c = 13.613 (3) Å
β = 106.93 (3)°
V = 1165.1 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.71 mm^{-1}
T = 298 (2) K
0.20 × 0.18 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: none
10894 measured reflections
2677 independent reflections
2462 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.073
S = 1.08
2677 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O2	2.0078 (14)	Ni1—O4	2.0622 (12)
Ni1—O6^i	2.0419 (13)	Ni1—O1W	2.0638 (15)
Ni1—O2W	2.0498 (13)	Ni1—O1	2.0769 (12)
O2—Ni1—O6^i	89.77 (6)	O2W—Ni1—O1W	83.96 (6)
O2—Ni1—O2W	90.44 (5)	O4—Ni1—O1W	90.65 (6)
O6^i—Ni1—O2W	93.06 (6)	O2—Ni1—O1	80.03 (5)
O2—Ni1—O4	90.63 (5)	O6^i—Ni1—O1	90.23 (5)
O6^i—Ni1—O4	175.09 (5)	O2W—Ni1—O1	169.91 (5)
O2W—Ni1—O4	91.84 (5)	O4—Ni1—O1	85.02 (5)
O2—Ni1—O1W	174.29 (5)	O1W—Ni1—O1	105.63 (5)
O6^i—Ni1—O1W	89.43 (6)		

Symmetry code: (i) $-x+1, -y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O6	0.85	1.83	2.5632 (18)	144
O1W—H1WA···O7^i	0.85	1.91	2.645 (2)	143
O2W—H2WB···O5^{ii}	0.85	1.88	2.7163 (19)	167
O2W—H2WA···O5^{iii}	0.85	2.08	2.903 (2)	165
N1—H1A···O5^{ii}	0.90	1.89	2.765 (2)	163
N1—H1B···O3^{iv}	0.90	2.11	2.960 (2)	157

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL97*.

This work was supported financially by the Education Foundation of Fujian Province (No. JB06049) and Fouzhou University (No. XRC0645).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2135).

References

Baggio, R. & Perec, M. (2004). *Inorg. Chem.* **43**, 6965–6968.
Baker, E. N., Baker, H. M., Anderson, B. F. & Reeves, R. D. (1983). *Inorg. Chim. Acta*, **78**, 281–285.
Kaliva, M., Raptopoulou, C. P., Terzis, A. & Salifoglou, A. (2004). *Inorg. Chem.* **43**, 2895–2950.
Kefalas, E. T., Dakanali, M., Panagiotidis, P., Raptopoulou, C. P., Terzis, A., Mavromoustakos, T., Kyrikou, I., Karligiano, N., Bino, A. & Salifoglou, A. (2005). *Inorg. Chem.* **44**, 4818–4828.
Kotsakis, N., Raptopoulou, C. P., Tangoulis, V., Terzis, A., Giapintzakis, J., Jakusch, T., Kiss, T. & Salifoglou, A. (2003). *Inorg. Chem.* **42**, 22–31.
Rigaku (1998). *RAPID-AUTO*. PC version. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1993). *SHELXTL/PC*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Wang, W. G., Zhang, X. F., Chen, F., Ma, C. B., Chen, C. G., Liu, Q. T., Liao, D. Z. & Li, L. C. (2005). *Polyhedron*, **24**, 1656–1668.
Xiang, S. C., Wu, X. T., Zhang, J. J., Fu, R. B., Hu, S. G. & Zhang, X. D. (2005). *J. Am. Chem. Soc.* **127**, 16352–16353.
Zhang, G. Q., Yang, G. Q. & Ma, J. S. (2006). *Cryst. Growth Des.* **6**, 375–381.
Zhou, Z. H., Deng, Y. F. & Wan, H. L. (2005). *Cryst. Growth Des.* **5**, 1109–1117.

supplementary materials

Acta Cryst. (2007). E**63**, m1552-m1553 [**doi:10.1107/S1600536807020569**]

Piperazinium tetraaquadi-μ-citrato-dinickelate(II)

H.-Y. Song, C.-C. Huang, J.-H. Luo, X.-H. Huang and D.-S. Liu

Comment

Up to now, hundreds of metal citrate complexes with diverse architectures have been synthesized and well documented in the literature (Kaliva *et al.*, 2004; Kefalas *et al.*, 2005; Wang *et al.*, 2005; Xiang *et al.*, 2005; Zhang *et al.*, 2006). Some complexes contain centrosymmetric dimers with 1-D polymeric chain or 2-D layer structure (Zhou *et al.*, 2005; Baggio & Perec, 2004), some are similar to the title complex (Baker *et al.*, 1983; Kotsakis *et al.*, 2003), most of them have monovalent counter ions. In this paper, the complex we report has a divalent organic piperazinium cation. Its structure is shown in Fig. 1. Each citrate ligand is triply deprotonated, and chelates to the Ni atom through the α-hydroxyl, α-carboxyl and one β-carboxyl oxygen atom. The other β-carboxyl oxygen atom spans over to the second Ni atom of the dimer. The distorted octahedral coordination sphere of each nickel atom is completed by the oxygen atoms of two water molecules. Selected geometric parameters of the complex are given in Table 1. The piperazinium cations occupy the space between the nickel-citrate dimers. The anions and the cations are connected by strong N—H···O hydrogen bonds. There are intramolecular hydrogen bonds between the hydroxyl groups and the carboxyl groups. Hydrogen bonding interactions are also observed between the coordinated water molecules and the carboxyl groups of neighbouring anions, forming a three-dimensional network (Table 2, Fig. 2).

Experimental

Nickel chloride hexahydrate (0.072 g, 0.3 mmol) and citric acid monohydrate (0.061 g, 0.3 mmol) were dissolved in water/ethanol (1:1 *v*/*v*) solution (5 ml). Piperazine hexahydrate (0.096 g, 0.5 mmol) was then added and the solution stirred for 30 min. The resulting solution was transferred into Teflon-lined autoclave and heated at 130 °C under autogenous pressure for 5 days. Green block crystals suitable for X-ray analysis were collected from the reaction mixture.

Refinement

The structure was solved by Patterson method. All hydrogen atoms were included in the riding model approximation, with C–H = 0.97 Å, N–H = 0.90 Å, O–H = 0.85 Å, and with U_{iso}(H) = 1.2 U_{eq}(C, N, O).

Figures

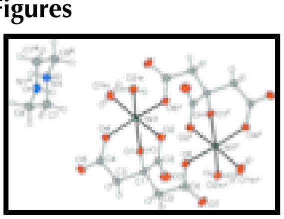


Fig. 1. The crystal structure of the title compound with ellipsoids drawn at the 50% probability level. Symmetry codes: (i) $1 - x, -y, -z$; (ii) $-x, 1 - y, -z$.

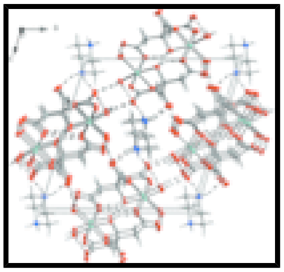


Fig. 2. Packing diagram of the title compound viewed along the *b* axis. Hydrogen bonds are represented by dotted lines.

Piperazinium tetraaquabis(μ_2-citrato)dinickelate(II)

Crystal data

$(C_4H_{12}N_2)[Ni_2(C_6H_5O_7)_2(H_2O)_4]$	F_{000} = 680
M_r = 655.80	D_x = 1.869 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 9899 reflections
a = 13.342 (3) Å	θ = 3.0–27.6º
b = 6.7054 (13) Å	μ = 1.71 mm^{-1}
c = 13.613 (3) Å	*T* = 298 (2) K
β = 106.93 (3)º	Block, green
V = 1165.1 (5) Å^3	0.20 × 0.18 × 0.15 mm
Z = 2	

Data collection

Rigaku R-AXIS RAPID diffractometer	2462 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.046
Monochromator: graphite	θ_{max} = 27.5º
T = 298(2) K	θ_{min} = 3.1º
Oscillation scans	$h = -17 \rightarrow 17$
Absorption correction: none	$k = -8 \rightarrow 8$
10894 measured reflections	$l = -17 \rightarrow 17$
2677 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.029	H-atom parameters constrained
$wR(F^2)$ = 0.073	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.5209P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.08	$(\Delta/\sigma)_{max}$ < 0.001
2677 reflections	$\Delta\rho_{max}$ = 0.36 e Å^{-3}

172 parameters	$\Delta\rho_{min} = -0.58$ e Å^{-3}
Primary atom site location: patt	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 $F^2 > \sigma(F^2)$ 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	0.356449 (16)	0.10184 (3)	0.089492 (15)	0.01502 (9)
O1	0.46895 (9)	0.27879 (17)	0.05413 (8)	0.0168 (2)
H1	0.4979	0.2121	0.0167	0.020*
O1W	0.21588 (10)	0.1791 (2)	−0.01518 (10)	0.0267 (3)
H1WA	0.2010	0.0965	−0.0647	0.032*
H1WB	0.2207	0.2945	−0.0392	0.032*
O2	0.48547 (10)	0.00460 (18)	0.19579 (9)	0.0210 (3)
O2W	0.26483 (10)	−0.07943 (18)	0.14890 (10)	0.0215 (3)
H2WB	0.2269	−0.0091	0.1760	0.026*
H2WA	0.3034	−0.1542	0.1951	0.026*
O3	0.62422 (12)	0.1371 (2)	0.30710 (10)	0.0308 (3)
O4	0.34262 (10)	0.33467 (19)	0.18366 (10)	0.0225 (3)
O5	0.38093 (11)	0.60449 (18)	0.27900 (11)	0.0247 (3)
O6	0.62307 (10)	0.11233 (19)	0.00955 (10)	0.0239 (3)
O7	0.78853 (11)	0.1785 (2)	0.09831 (11)	0.0329 (3)
N1	0.00054 (13)	0.3898 (2)	0.09153 (11)	0.0207 (3)
H1A	0.0278	0.2936	0.1377	0.025*
H1B	−0.0523	0.4481	0.1095	0.025*
C1	0.54617 (13)	0.3207 (2)	0.15133 (12)	0.0155 (3)
C2	0.55405 (13)	0.1389 (2)	0.22351 (12)	0.0165 (3)
C3	0.50727 (14)	0.5019 (2)	0.19770 (13)	0.0191 (3)
H3A	0.5601	0.5372	0.2610	0.023*
H3B	0.5008	0.6132	0.1507	0.023*
C4	0.40335 (14)	0.4756 (2)	0.22078 (13)	0.0172 (3)
C5	0.65218 (14)	0.3690 (3)	0.13446 (14)	0.0200 (3)
H5A	0.6457	0.4922	0.0958	0.024*
H5B	0.7032	0.3910	0.2007	0.024*
C6	0.69299 (14)	0.2077 (3)	0.07807 (12)	0.0193 (3)
C7	0.08284 (14)	0.5411 (3)	0.09266 (13)	0.0226 (4)
H7A	0.1424	0.4760	0.0792	0.027*

H7B	0.1065	0.6024	0.1600	0.027*
C8	0.04050 (15)	0.7003 (3)	0.01229 (13)	0.0227 (4)
H8A	−0.0152	0.7730	0.0291	0.027*
H8B	0.0959	0.7941	0.0123	0.027*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01363 (13)	0.01736 (13)	0.01496 (13)	−0.00038 (8)	0.00552 (9)	−0.00189 (8)
O1	0.0153 (5)	0.0214 (6)	0.0144 (5)	0.0000 (5)	0.0054 (4)	−0.0003 (5)
O1W	0.0247 (7)	0.0296 (7)	0.0237 (6)	0.0077 (6)	0.0039 (5)	0.0015 (6)
O2	0.0214 (6)	0.0190 (6)	0.0206 (6)	−0.0021 (5)	0.0029 (5)	0.0026 (5)
O2W	0.0207 (6)	0.0231 (6)	0.0238 (6)	0.0001 (5)	0.0112 (5)	0.0014 (5)
O3	0.0296 (7)	0.0320 (7)	0.0225 (6)	−0.0021 (6)	−0.0056 (6)	0.0017 (6)
O4	0.0202 (6)	0.0222 (6)	0.0286 (6)	−0.0044 (5)	0.0123 (5)	−0.0088 (6)
O5	0.0268 (7)	0.0219 (6)	0.0306 (7)	−0.0042 (5)	0.0168 (6)	−0.0100 (5)
O6	0.0162 (6)	0.0321 (7)	0.0240 (6)	−0.0009 (5)	0.0067 (5)	−0.0123 (5)
O7	0.0160 (6)	0.0441 (8)	0.0376 (7)	0.0008 (6)	0.0062 (6)	−0.0163 (7)
N1	0.0228 (8)	0.0223 (7)	0.0181 (7)	0.0029 (6)	0.0078 (6)	0.0051 (6)
C1	0.0142 (7)	0.0168 (7)	0.0163 (7)	−0.0022 (6)	0.0056 (6)	−0.0041 (6)
C2	0.0158 (8)	0.0181 (7)	0.0158 (7)	0.0020 (7)	0.0051 (6)	−0.0027 (6)
C3	0.0194 (8)	0.0158 (7)	0.0244 (8)	−0.0016 (7)	0.0101 (7)	−0.0048 (7)
C4	0.0188 (8)	0.0158 (7)	0.0183 (7)	0.0021 (7)	0.0075 (6)	0.0011 (6)
C5	0.0181 (8)	0.0207 (8)	0.0232 (8)	−0.0043 (7)	0.0092 (7)	−0.0058 (7)
C6	0.0175 (8)	0.0237 (8)	0.0185 (7)	−0.0018 (7)	0.0080 (7)	−0.0019 (7)
C7	0.0211 (8)	0.0272 (9)	0.0181 (8)	−0.0022 (8)	0.0032 (7)	−0.0014 (7)
C8	0.0258 (9)	0.0197 (8)	0.0235 (8)	−0.0034 (7)	0.0085 (7)	−0.0018 (7)

Geometric parameters (Å, °)

Ni1—O2	2.0078 (14)	N1—C8^{ii}	1.487 (2)
Ni1—O6^{i}	2.0419 (13)	N1—C7	1.492 (2)
Ni1—O2W	2.0498 (13)	N1—H1A	0.9000
Ni1—O4	2.0622 (12)	N1—H1B	0.9000
Ni1—O1W	2.0638 (15)	C1—C3	1.528 (2)
Ni1—O1	2.0769 (12)	C1—C5	1.532 (2)
O1—C1	1.448 (2)	C1—C2	1.550 (2)
O1—H1	0.8499	C3—C4	1.519 (2)
O1W—H1WA	0.8501	C3—H3A	0.9700
O1W—H1WB	0.8500	C3—H3B	0.9700
O2—C2	1.261 (2)	C5—C6	1.516 (2)
O2W—H2WB	0.8501	C5—H5A	0.9700
O2W—H2WA	0.8499	C5—H5B	0.9700
O3—C2	1.245 (2)	C7—C8	1.515 (3)
O4—C4	1.252 (2)	C7—H7A	0.9700
O5—C4	1.266 (2)	C7—H7B	0.9700
O6—C6	1.281 (2)	C8—N1^{ii}	1.487 (2)
O6—Ni1^{i}	2.0419 (12)	C8—H8A	0.9700

O7—C6	1.239 (2)	C8—H8B	0.9700
O2—Ni1—O6^{i}	89.77 (6)	O1—C1—C2	108.98 (13)
O2—Ni1—O2W	90.44 (5)	C3—C1—C2	109.40 (13)
O6^{i}—Ni1—O2W	93.06 (6)	C5—C1—C2	111.48 (14)
O2—Ni1—O4	90.63 (5)	O3—C2—O2	123.64 (16)
O6^{i}—Ni1—O4	175.09 (5)	O3—C2—C1	118.72 (15)
O2W—Ni1—O4	91.84 (5)	O2—C2—C1	117.56 (14)
O2—Ni1—O1W	174.29 (5)	C4—C3—C1	115.69 (14)
O6^{i}—Ni1—O1W	89.43 (6)	C4—C3—H3A	108.4
O2W—Ni1—O1W	83.96 (6)	C1—C3—H3A	108.4
O4—Ni1—O1W	90.65 (6)	C4—C3—H3B	108.4
O2—Ni1—O1	80.03 (5)	C1—C3—H3B	108.4
O6^{i}—Ni1—O1	90.23 (5)	H3A—C3—H3B	107.4
O2W—Ni1—O1	169.91 (5)	O4—C4—O5	121.66 (16)
O4—Ni1—O1	85.02 (5)	O4—C4—C3	121.80 (15)
O1W—Ni1—O1	105.63 (5)	O5—C4—C3	116.54 (15)
C1—O1—Ni1	105.60 (9)	C6—C5—C1	114.11 (14)
C1—O1—H1	108.9	C6—C5—H5A	108.7
Ni1—O1—H1	108.8	C1—C5—H5A	108.7
Ni1—O1W—H1WA	109.8	C6—C5—H5B	108.7
Ni1—O1W—H1WB	109.8	C1—C5—H5B	108.7
H1WA—O1W—H1WB	108.3	H5A—C5—H5B	107.6
C2—O2—Ni1	112.28 (11)	O7—C6—O6	124.52 (16)
Ni1—O2W—H2WB	109.9	O7—C6—C5	119.87 (16)
Ni1—O2W—H2WA	109.8	O6—C6—C5	115.59 (15)
H2WB—O2W—H2WA	108.4	N1—C7—C8	110.69 (15)
C4—O4—Ni1	131.14 (11)	N1—C7—H7A	109.5
C6—O6—Ni1^{i}	128.50 (12)	C8—C7—H7A	109.5
C8^{ii}—N1—C7	110.63 (14)	N1—C7—H7B	109.5
C8^{ii}—N1—H1A	109.5	C8—C7—H7B	109.5
C7—N1—H1A	109.5	H7A—C7—H7B	108.1
C8^{ii}—N1—H1B	109.5	N1^{ii}—C8—C7	110.87 (14)
C7—N1—H1B	109.5	N1^{ii}—C8—H8A	109.5
H1A—N1—H1B	108.1	C7—C8—H8A	109.5
O1—C1—C3	107.15 (13)	N1^{ii}—C8—H8B	109.5
O1—C1—C5	110.25 (13)	C7—C8—H8B	109.5
C3—C1—C5	109.47 (14)	H8A—C8—H8B	108.1

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O6	0.85	1.83	2.5632 (18)	144
O1W—H1WA···O7^{i}	0.85	1.91	2.645 (2)	143
O2W—H2WB···O5^{iii}	0.85	1.88	2.7163 (19)	167
O2W—H2WA···O5^{iv}	0.85	2.08	2.903 (2)	165

N1—H1A···O5^{iii}	0.90	1.89	2.765 (2)	163
N1—H1B···O3^{v}	0.90	2.11	2.960 (2)	157

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

Fig. 1

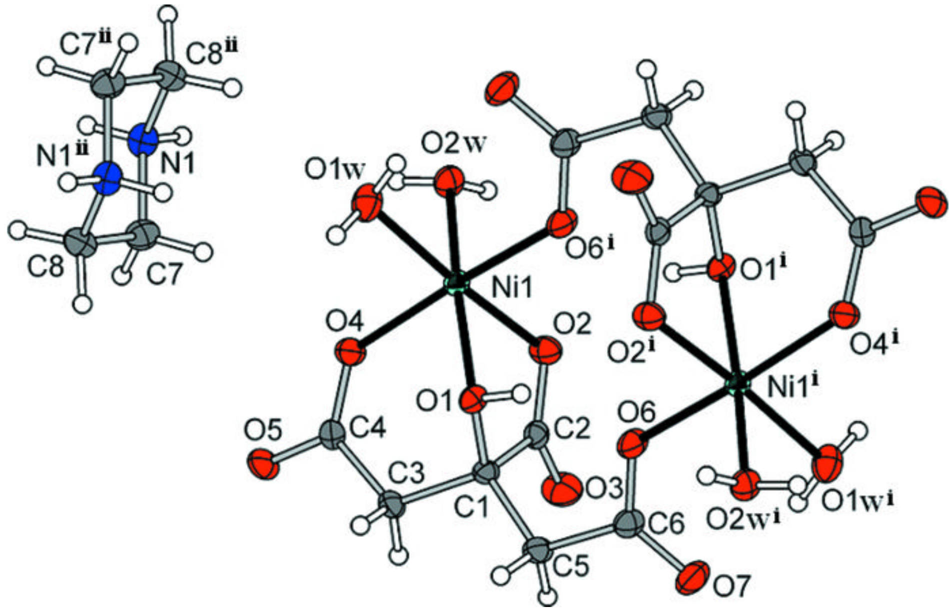

C7ii
C8ii
N1ii
N1
C8
C7
O1w
O2w
O6i
Ni1
O4
O2
O1
O1i
O2i
O4i
Ni1i
O5
C4
C2
O6
C3
C1
O3
C6
O2wi
O1wi
C5
O7

Fig. 2