

Redetermination of nickel(II) formate dihydrate

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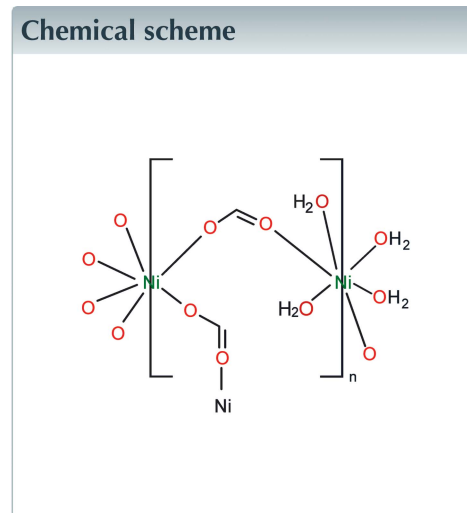
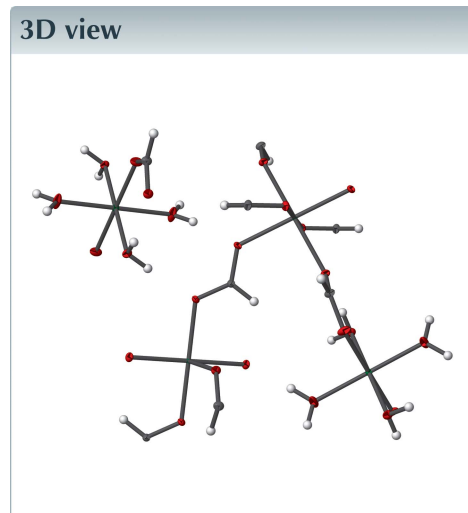
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In comparison with the previous structure determination of poly[di-aqua-di- μ -formate-nickel(II)], $[\text{Ni}(\text{HCOO})_2(\text{H}_2\text{O})_2]_n$, based on Weissenberg film data [Krogmann & Mattes (1963). *Z. Kristallogr.* **118**, 291–302], the current redetermination from modern CCD data revealed the positions of the H atoms, thus making a detailed description of the hydrogen-bonding pattern possible. Both Ni^{2+} cations in the crystal structure are located on inversion centres and are octahedrally coordinated. One Ni^{2+} cation is bound to six O atoms of six formate anions whereas the other Ni^{2+} cation is bound to four O atoms of water molecules and to two formate O atoms. In this way, the formate anions bridge the two types of Ni^{2+} cations into a three-dimensional framework. $\text{O}—\text{H}\cdots\text{O}$ hydrogen bonds of medium strength between water molecules and formate O atoms consolidate the packing.



Structure description

Recycling of tungsten carbide from WC–Ni hard metals or composites thereof can be achieved by debinding WC–Ni with formic acid to selectively dissolve nickel. Nickel formate then can either be crystallized as the dihydrate from the obtained solution, or formic acid can be regenerated through cation exchange with sulfuric acid. In the latter case, nickel can be precipitated as $\text{Ni}(\text{OH})_2$ from the intermediate nickel sulfate solution by adding caustic soda (Weissensteiner, 2012). In the course of these studies it became apparent that a redetermination of the crystal structure of nickel formate dihydrate, $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, (Krogmann & Mattes, 1963) was desirable in terms of higher precision and accuracy and for an unambiguous assignment of the hydrogen-bonding scheme. Although a profile refinement using the Rietveld method has been performed on this material, leading to precise room-temperature lattice parameters (Kellerman *et al.*, 2016), improved structural data are still missing.

Table 1
Comparison of bond lengths (Å) in the current and the previous refinement of Ni(HCOO)₂·2H₂O^(a,b).

	current refinement	previous refinement ^a
Ni1—O1 ⁱ	2.0302 (6)	2.026 (8)
Ni1—O2	2.0503 (6)	2.061 (8)
Ni1—O3	2.0942 (6)	2.097 (8)
Ni2—O5	2.0256 (7)	2.042 (8)
Ni2—O6	2.0663 (6)	2.059 (8)
Ni2—O4	2.1006 (7)	2.090 (8)
O1—C1	1.2593 (10)	1.256 (8)
O2—C1	1.2546 (10)	1.222 (8)
O3—C2 ⁱⁱ	1.2618 (10)	1.278 (8)
O4—C2	1.2607 (10)	1.247 (8)

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$. Notes: (a) Krogmann & Mattes (1963); lattice parameters $a = 8.60$ (1), $b = 7.06$ (1), $c = 9.21$ (2) Å, $\beta = 96.50$ (10)° from single-crystal data at room temperature; (b) lattice parameters $a = 8.5951$ (1), $b = 7.0688$ (5), $c = 9.2152$ (2) Å, $\beta = 97.41$ (1)° from Rietveld profile refinement at room temperature (Kellerman *et al.*, 2016).

The crystal structure of Ni(HCOO)₂·2H₂O comprises two Ni²⁺ cations on inversion centres, one on Wyckoff position 2b (Ni1), one on 2a (Ni2), and two formate anions and two water molecules in general positions. The Ni²⁺ cations are stacked in rows parallel to [101]. Both cations have a distorted octahedral coordination environment by oxygen atoms, but with different types of ligands. Ni1 is bound to six O atoms of six formate

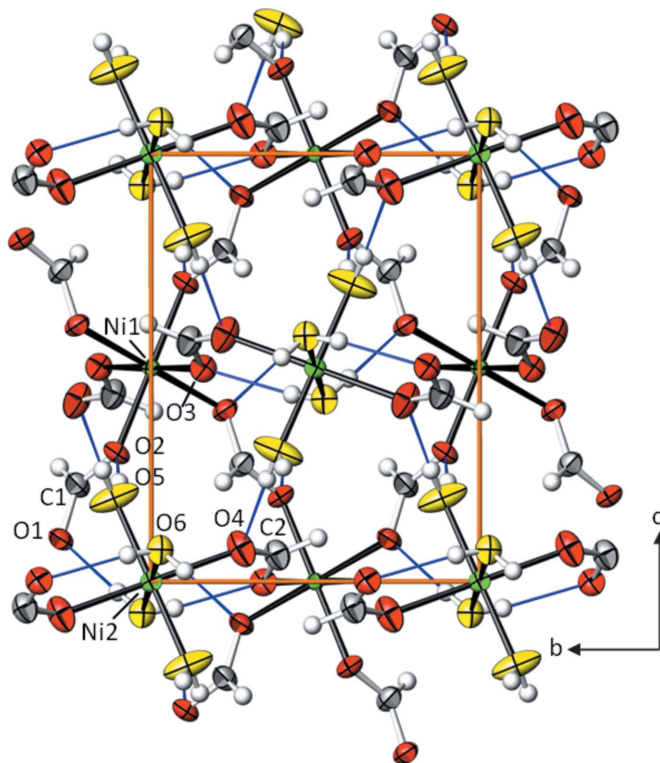


Figure 1
The crystal structure of Ni(HCOO)₂·2H₂O in a projection along $[\bar{1}00]$. Displacement ellipsoids are drawn at the 97% probability level. Ni atoms are green, C atoms grey, formate O atoms red, water O atoms yellow. H atoms are shown as white spheres of arbitrary radius; O—H...O hydrogen bonding is indicated by thin blue lines.

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

D—H...A	D—H	H...A	D...A	D—H...A
O6—H5...O3 ⁱ	0.787 (18)	1.985 (18)	2.7312 (9)	158.1 (16)
O5—H3...O2	0.89 (2)	1.87 (2)	2.7522 (9)	171.2 (19)
O5—H4...O4 ⁱ	0.832 (18)	1.898 (18)	2.7271 (10)	174.1 (17)
O6—H6...O1 ⁱⁱ	0.837 (18)	1.926 (18)	2.7610 (9)	175.5 (16)

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

anions (O1–O3 and symmetry-related counterparts), whereas Ni2 is bound to four O atoms of two pairs of water molecules (O5, O6 and symmetry-related counterparts) and two formate anions (O4 and its symmetry-related counterpart). Relevant bond lengths and a comparison with the previous determination are collated in Table 1. In general, bond lengths and angles are similar to related divalent first-row transition metal formates (Viertelhaus *et al.*, 2005).

Each of the two formate anions bridges two Ni²⁺ cations, thus creating a three-dimensional framework. O—H...O hydrogen bonds of medium strength and with nearly linear O—H...O angles between water molecules as donor groups and each of the formate carboxylate O atoms as acceptor groups help to consolidate this arrangement (Fig. 1, Table 2). In comparison with the previous determination, the H-atom positions are unambiguous and were clearly discernible from difference maps.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Ni(HCOO) ₂ (H ₂ O) ₂]
M_r	184.78
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	8.5806 (4), 7.0202 (3), 9.2257 (4)
β (°)	97.551 (1)
V (Å ³)	550.91 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	3.48
Crystal size (mm)	0.12 × 0.10 × 0.02
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2015)
T_{\min}, T_{\max}	0.667, 0.748
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	44072, 3433, 2591
R_{int}	0.036
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.907
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.021, 0.049, 1.04
No. of reflections	3433
No. of parameters	101
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.52, -0.55

Computer programs: APEX3 and SAINT (Bruker, 2015), SHELXL2016 (Sheldrick, 2015), ATOMS (Dowty, 2006) and publCIF (Westrip, 2010). Coordinates from previous determination.

Synthesis and crystallization

Crystals of the title compound were harvested from a saturated aqueous solution of nickel formate (Königswarter & Ebell, Chemische Fabrik GmbH, Germany) that was stored in a closed glass bottle for several months.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Starting coordinates for refinement were taken from the previous determination (Krogmann & Mattes, 1963).

Acknowledgements

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full crystallographic data

IUCrData (2018). 3, x180428 [https://doi.org/10.1107/S2414314618004285]

Redetermination of nickel(II) formate dihydrate

Matthias Weil

Poly[*diaquadi-μ-formato-nickel(II)*]

Crystal data

[Ni(CHO₂)₂(H₂O)₂]
 $M_r = 184.78$
 Monoclinic, $P2_1/c$
 $a = 8.5806$ (4) Å
 $b = 7.0202$ (3) Å
 $c = 9.2257$ (4) Å
 $\beta = 97.551$ (1)°
 $V = 550.91$ (4) Å³
 $Z = 4$

$F(000) = 376$
 $D_x = 2.228$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9891 reflections
 $\theta = 2.4$ – 39.9 °
 $\mu = 3.48$ mm⁻¹
 $T = 100$ K
 Plate, green
 0.12 × 0.10 × 0.02 mm

Data collection

Bruker APEXII CCD
 diffractometer
 ω - and φ -scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2015)
 $T_{\min} = 0.667$, $T_{\max} = 0.748$
 44072 measured reflections

3433 independent reflections
 2591 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 40.1$ °, $\theta_{\min} = 2.4$ °
 $h = -15 \rightarrow 15$
 $k = -12 \rightarrow 12$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.049$
 $S = 1.04$
 3433 reflections
 101 parameters
 0 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0181P)^2 + 0.2503P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.52$ e Å⁻³
 $\Delta\rho_{\min} = -0.55$ e Å⁻³

Special details

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

Refinement. H atoms bound to O atoms were located from a difference map and were refined freely.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.500000	1.000000	0.500000	0.00423 (3)
Ni2	0.000000	1.000000	0.000000	0.00564 (3)
O1	0.40966 (7)	1.27481 (9)	0.09909 (7)	0.00780 (10)
O2	0.40368 (7)	1.10493 (9)	0.30080 (7)	0.00783 (10)
O3	0.29319 (7)	0.84112 (9)	0.49822 (7)	0.00847 (10)
O4	0.06317 (8)	0.72530 (10)	0.07671 (8)	0.01179 (11)
O5	0.08832 (8)	1.11264 (12)	0.19580 (8)	0.01638 (14)
O6	-0.21606 (8)	0.97254 (10)	0.07381 (7)	0.00910 (10)
C1	0.46712 (10)	1.22417 (12)	0.22586 (9)	0.00844 (12)
H1	0.563988	1.279365	0.267077	0.010*
C2	0.17660 (10)	0.61599 (12)	0.06198 (10)	0.00963 (13)
H2	0.174105	0.491537	0.102054	0.012*
H5	-0.2593 (18)	1.071 (3)	0.0623 (17)	0.023 (4)*
H3	0.188 (2)	1.098 (3)	0.2325 (18)	0.039 (5)*
H4	0.036 (2)	1.148 (3)	0.2609 (19)	0.033 (5)*
H6	-0.278 (2)	0.898 (3)	0.0248 (18)	0.031 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.00443 (5)	0.00435 (5)	0.00395 (5)	-0.00014 (4)	0.00061 (4)	-0.00003 (4)
Ni2	0.00466 (5)	0.00628 (6)	0.00601 (6)	0.00038 (4)	0.00083 (4)	-0.00025 (5)
O1	0.0087 (2)	0.0080 (2)	0.0065 (2)	-0.00071 (19)	0.00013 (18)	0.00185 (18)
O2	0.0081 (2)	0.0087 (2)	0.0066 (2)	-0.00015 (19)	0.00077 (18)	0.00260 (19)
O3	0.0065 (2)	0.0094 (2)	0.0098 (2)	-0.00125 (19)	0.00243 (18)	-0.00016 (19)
O4	0.0090 (2)	0.0106 (3)	0.0168 (3)	0.0033 (2)	0.0056 (2)	0.0040 (2)
O5	0.0071 (2)	0.0307 (4)	0.0112 (3)	-0.0001 (3)	0.0010 (2)	-0.0095 (3)
O6	0.0071 (2)	0.0090 (3)	0.0113 (3)	-0.00036 (19)	0.00169 (19)	-0.00004 (19)
C1	0.0084 (3)	0.0081 (3)	0.0084 (3)	-0.0013 (2)	-0.0006 (2)	0.0017 (2)
C2	0.0082 (3)	0.0089 (3)	0.0120 (3)	0.0016 (2)	0.0023 (2)	0.0013 (3)

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

Ni1—O1 ⁱ	2.0302 (6)	Ni2—O4 ^{iv}	2.1007 (7)
Ni1—O1 ⁱⁱ	2.0302 (6)	O1—C1	1.2593 (10)
Ni1—O2	2.0503 (6)	O2—C1	1.2546 (10)
Ni1—O2 ⁱⁱⁱ	2.0504 (6)	O3—C2 ^v	1.2618 (10)
Ni1—O3 ⁱⁱⁱ	2.0942 (6)	O4—C2	1.2607 (10)
Ni1—O3	2.0942 (6)	O5—H3	0.89 (2)
Ni2—O5 ^{iv}	2.0255 (7)	O5—H4	0.832 (18)
Ni2—O5	2.0256 (7)	O6—H5	0.787 (18)
Ni2—O6	2.0663 (6)	O6—H6	0.837 (18)
Ni2—O6 ^{iv}	2.0664 (6)	C1—H1	0.9500
Ni2—O4	2.1006 (7)	C2—H2	0.9500

O1 ⁱ —Ni1—O1 ⁱⁱ	180.00 (3)	O6—Ni2—O4	90.36 (3)
O1 ⁱ —Ni1—O2	89.49 (2)	O6 ^{iv} —Ni2—O4	89.64 (3)
O1 ⁱⁱ —Ni1—O2	90.51 (2)	O5 ^{iv} —Ni2—O4 ^{iv}	90.47 (3)
O1 ⁱ —Ni1—O2 ⁱⁱⁱ	90.51 (2)	O5—Ni2—O4 ^{iv}	89.53 (3)
O1 ⁱⁱ —Ni1—O2 ⁱⁱⁱ	89.49 (2)	O6—Ni2—O4 ^{iv}	89.64 (3)
O2—Ni1—O2 ⁱⁱⁱ	180.00 (4)	O6 ^{iv} —Ni2—O4 ^{iv}	90.36 (3)
O1 ⁱ —Ni1—O3 ⁱⁱⁱ	87.42 (2)	O4—Ni2—O4 ^{iv}	180.0
O1 ⁱⁱ —Ni1—O3 ⁱⁱⁱ	92.58 (2)	C1—O1—Ni1 ^{vi}	120.79 (5)
O2—Ni1—O3 ⁱⁱⁱ	93.27 (2)	C1—O2—Ni1	125.50 (6)
O2 ⁱⁱⁱ —Ni1—O3 ⁱⁱⁱ	86.73 (2)	C2 ^v —O3—Ni1	126.31 (6)
O1 ⁱ —Ni1—O3	92.58 (2)	C2—O4—Ni2	133.73 (6)
O1 ⁱⁱ —Ni1—O3	87.42 (2)	Ni2—O5—H3	121.7 (12)
O2—Ni1—O3	86.73 (2)	Ni2—O5—H4	126.1 (12)
O2 ⁱⁱⁱ —Ni1—O3	93.27 (2)	H3—O5—H4	110.0 (16)
O3 ⁱⁱⁱ —Ni1—O3	180.0	Ni2—O6—H5	107.5 (12)
O5 ^{iv} —Ni2—O5	180.00 (2)	Ni2—O6—H6	114.6 (11)
O5 ^{iv} —Ni2—O6	90.62 (3)	H5—O6—H6	103.0 (16)
O5—Ni2—O6	89.38 (3)	O2—C1—O1	123.70 (8)
O5 ^{iv} —Ni2—O6 ^{iv}	89.38 (3)	O2—C1—H1	118.1
O5—Ni2—O6 ^{iv}	90.62 (3)	O1—C1—H1	118.1
O6—Ni2—O6 ^{iv}	180.0	O4—C2—O3 ^{vii}	125.14 (8)
O5 ^{iv} —Ni2—O4	89.53 (3)	O4—C2—H2	117.4
O5—Ni2—O4	90.47 (3)	O3 ^{vii} —C2—H2	117.4

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H5 \cdots O3 ^{viii}	0.787 (18)	1.985 (18)	2.7312 (9)	158.1 (16)
O5—H3 \cdots O2	0.89 (2)	1.87 (2)	2.7522 (9)	171.2 (19)
O5—H4 \cdots O4 ^{viii}	0.832 (18)	1.898 (18)	2.7271 (10)	174.1 (17)
O6—H6 \cdots O1 ^{iv}	0.837 (18)	1.926 (18)	2.7610 (9)	175.5 (16)

Symmetry codes: (iv) $-x, -y+2, -z$; (viii) $-x, y+1/2, -z+1/2$.