Crystal structure of tetraaquafumaratonickel(II), $Ni(H_2O)_4(C_4H_2O_4)$

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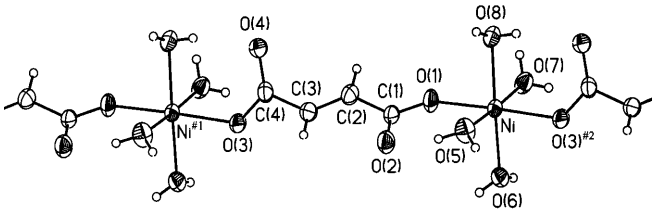

Symmetry codes: #1 = *x*-1, *y*, *z*-1; #2 = *x*+1, *y*, *z*+1

Abstract

$C_4H_{10}NiO_8$, monoclinic, $P12_1/c1$ (No. 14), a = 7.476(2) Å, b = 14.263(3) Å, c = 7.633(2) Å, β = 99.67(3)°, V = 802.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.067, T = 293 K.

Source of material

For the synthesis, 0.59 g (2.50 mmol) $NiCl_2 \cdot 6H_2O$ was added to a stirred methanolic aqueous solution of 0.17 g (2.50 mmol) imidazole and 0.29 g (2.50 mmol) fumaric acid in 50 ml CH_3OH/H_2O (1:1 v/v). The resulting mixture was further stirred for ca. 30 min to yield a pale green solution (pH = 3.94), which was then maintained at 323 K and faint green crystals were grown after two days.

Discussion

The Ni atoms in the title compound are each coordinated by six O atoms from four H_2O molecules and two carboxylate groups of different fumarate anions to complete slightly distorted octahedra with the carboxylate O atoms at the *trans* positions. The Ni—O bond distances vary from 2.044 Å to 2.088 Å. The cisoid O–Ni–O bond angles fall in the region 84.6 ° – 94.3° and the transoid ones in the region 174.7° – 178.2° exhibit trivial deviation from a linearity. The fumarate anions function as bis-monodentate ligands to bridge the six-coordinate Ni atoms to generate 1D $^1_\infty[Ni(H_2O)_4(C_4H_2O_4)_{2/2}]$ chains, which run along the [101] direction. The formed polymeric chains possess two strong intrachain hydrogen bonds between the water oxygen and uncoordinating carboxylate oxygen atoms with d(O–H···O) = 2.626 Å, 2.662 Å and ∠O–H···O = 158°, 164°. The coordinating water molecules donate hydrogen atoms to water and carboxylate oxygen atoms of the neighboring chains to form interchain hydrogen bonds (d(O–H···O) = 2.701 Å – 2.911 Å and ∠O–H···O = 164° – 176°), which are found to be responsible for supramolecular assembly of the polymeric chains. Due to formation of intrachain hydrogen bonds, the terminal carboxylate planes are rotated away by 13.0(4)°, 46.2(3)°, respectively, from the plane defined by the skeleton carbon atoms. As expected, the mean C—O bond distance to the coordinating O atom is 1.275(2) Å, significantly longer than that to the uncoordinating one (mean value: 1.244 Å). The central C—C bond length of 1.314(4) Å is considerably shorter than the terminal ones (mean value: 1.494(3) Å), suggesting double bond character.

Table 1. Data collection and handling.

Crystal:	pale green block, size 0.16 × 0.20 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	24.34 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2425, 1840
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1509
$N(param)_{refined}$:	159
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.731(4)	0.810(2)	0.272(4)	0.027(8)
H(3)	4*e*	0.483(4)	0.946(2)	0.274(4)	0.028(8)
H(5A)	4*e*	1.039(5)	1.040(3)	0.856(5)	0.05(1)
H(5B)	4*e*	0.927(5)	1.005(3)	0.716(5)	0.06(1)
H(6A)	4*e*	0.793(5)	0.854(2)	0.936(5)	0.04(1)
H(6B)	4*e*	0.896(4)	0.800(2)	1.000(4)	0.029(9)
H(7A)	4*e*	1.178(4)	0.690(2)	0.728(5)	0.034(9)
H(7B)	4*e*	1.182(5)	0.698(3)	0.892(5)	0.04(1)
H(8A)	4*e*	1.278(4)	0.922(2)	0.583(4)	0.020(7)
H(8B)	4*e*	1.353(5)	0.866(2)	0.700(5)	0.04(1)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	4*e*	1.07979(4)	0.86046(2)	0.79803(4)	0.0155(2)	0.0185(2)	0.0126(2)	0.0008(1)	–0.0006(1)	–0.0010(1)
O(1)	4*e*	0.8863(2)	0.8334(1)	0.5774(2)	0.0223(8)	0.0224(8)	0.0166(7)	0.0030(7)	–0.0052(6)	–0.0017(6)
O(2)	4*e*	0.7306(2)	0.9670(1)	0.5529(2)	0.0272(9)	0.0267(9)	0.0205(8)	0.0071(7)	–0.0037(7)	–0.0051(7)
C(1)	4*e*	0.7684(3)	0.8893(2)	0.4950(3)	0.015(1)	0.023(1)	0.014(1)	–0.0009(9)	–0.0002(8)	–0.0003(8)
C(2)	4*e*	0.6744(3)	0.8588(2)	0.3154(3)	0.022(1)	0.023(1)	0.016(1)	0.002(1)	0.0001(9)	–0.0030(9)
C(3)	4*e*	0.5308(3)	0.9024(2)	0.2305(3)	0.018(1)	0.025(1)	0.017(1)	0.000(1)	0.0002(9)	–0.004(1)
C(4)	4*e*	0.4362(3)	0.8790(2)	0.0479(3)	0.016(1)	0.021(1)	0.017(1)	0.0003(9)	–0.0010(8)	0.0014(8)
O(3)	4*e*	0.2634(2)	0.8769(1)	0.0292(2)	0.0151(8)	0.034(1)	0.0148(7)	–0.0024(7)	–0.0007(6)	–0.0028(7)
O(4)	4*e*	0.5247(2)	0.8646(2)	–0.0737(2)	0.0169(8)	0.056(1)	0.0183(8)	0.0036(8)	0.0007(7)	–0.0032(8)
O(5)	4*e*	1.0286(3)	1.0012(1)	0.7792(3)	0.027(1)	0.0197(9)	0.0278(9)	0.0005(7)	–0.0032(8)	–0.0045(8)
O(6)	4*e*	0.8917(3)	0.8464(1)	0.9657(2)	0.0156(9)	0.025(1)	0.0203(8)	0.0001(7)	0.0019(7)	0.0024(7)
O(7)	4*e*	1.1347(3)	0.7186(1)	0.8081(2)	0.0312(9)	0.0204(8)	0.0163(8)	0.0068(7)	0.0024(7)	0.0015(7)
O(8)	4*e*	1.2753(3)	0.8716(1)	0.6333(2)	0.0224(9)	0.0242(9)	0.0153(8)	–0.0010(7)	0.0001(7)	0.0020(7)

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