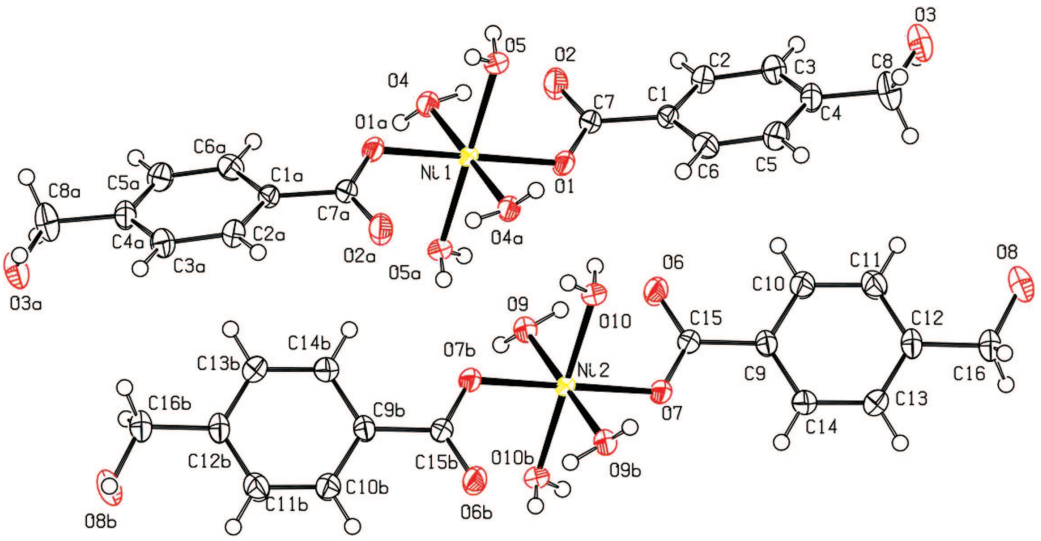
Lanlan Jin, Defu Tao, Rongyue Hu and Haixia Pang*

Crystal structure of tetraqua-bis(4-(hydroxymethyl)benzoato-κ*O*)nickel(II), $C_{16}H_{22}O_{10}Ni$



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Abstract

$C_{16}H_{22}O_{10}Ni$, monoclinic, $P2_1/c$ (no. 14), $a = 9.7643(12)$ Å, $b = 15.440(2)$ Å, $c = 13.6274(13)$ Å, $\beta = 122.235(6)°$, $V = 1737.5(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0382$, $wR_{ref}(F^2) = 0.1282$, $T = 297(2)$ K.

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The asymmetric unit of the title crystal structure containing two independent complexes is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Haixia Pang,** School of Materials and Chemical Engineering, Hubei University of Technology, Wuhan 430068, P.R. China; and State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, P.R. China, e-mail: m15623901779@163.com
Lanlan Jin: State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, P.R. China
Defu Tao and Rongyue Hu: School of Materials and Chemical Engineering, Hubei University of Technology, Wuhan 430068, P.R. China

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.12 × 0.10 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.17 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14021, 3784, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2822
$N(param)_{refined}$:	277
Programs:	Bruker [1], SHELX [2, 3]

Source of material

The title compound was synthesized by mixing 0.776 g (0.5 mmol) 4-hydroxymethylbenzoic acid, 0.145 g (0.5 mmol) $Ni(NO_3)_2{\cdot}6H_2O$, 12 mL ethyl alcohol absolute and 6 mL H_2O in a 50 mL beaker. After all the raw materials were dissolved, triethylamine was added dropwise to adjust the pH to 6. Then waiting for the solvent evaporate, green block crystals were separated out with 83% yield after about 20 days. Elemental analysis calculated for $C_{16}H_{22}O_{10}Ni$: C 44.35, H 5.17, O 36.81%; found C 44.40, H 5.12, O 36.95%. IR spectrum(cm^{-1}, KBr pellet): 3292(*m*), 1611(*m*), 1526(*m*), 1446(w), 1397(*s*), 1204(w), 1048(*s*), 987(w), 766(*s*), 503(*m*).

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.5000	0.5000	0.01846(14)
Ni2	0.0000	0.5000	0.5000	0.01906(14)
C1	0.6262(3)	0.37121(15)	0.81716(18)	0.0213(5)
C2	0.7006(3)	0.29902(15)	0.8859(2)	0.0257(5)
H2	0.7162	0.2500	0.8533	0.031*
C3	0.7521(3)	0.29852(17)	1.00220(19)	0.0281(6)
H3	0.8025	0.2496	1.0470	0.034*
C4	0.7290(3)	0.37060(16)	1.05225(19)	0.0262(5)
C5	0.6525(3)	0.44297(16)	0.9833(2)	0.0298(5)
H5	0.6358	0.4916	1.0159	0.036*
C6	0.6013(3)	0.44350(15)	0.8677(2)	0.0274(5)
H6	0.5498	0.4922	0.8228	0.033*
C7	0.5848(3)	0.37660(15)	0.69445(19)	0.0218(5)
C8	0.7787(4)	0.37497(17)	1.1784(2)	0.0392(7)
H8B	0.8359	0.4290	1.2114	0.047*
H8C	0.6817	0.3759	1.1814	0.047*
C9	0.1340(3)	0.37310(15)	0.82159(19)	0.0231(5)
C10	0.2696(3)	0.33027(16)	0.9099(2)	0.0302(6)
H10	0.3432	0.3058	0.8945	0.036*
C11	0.2968(3)	0.32344(17)	1.0202(2)	0.0327(6)
H11	0.3891	0.2954	1.0783	0.039*
C12	0.1869(3)	0.35833(15)	1.04478(19)	0.0261(5)
C13	0.0490(3)	0.39856(16)	0.9563(2)	0.0294(5)
H13	−0.0272	0.4205	0.9709	0.035*
C14	0.0235(3)	0.40647(16)	0.8469(2)	0.0288(5)
H14	−0.0689	0.4345	0.7890	0.035*
C15	0.1111(3)	0.38522(14)	0.70446(19)	0.0219(5)
C16	0.2146(3)	0.35842(17)	1.1650(2)	0.0333(6)
H16A	0.2254	0.4178	1.1914	0.040*
H16B	0.1205	0.3337	1.1611	0.040*
O1	0.5001(2)	0.44050(10)	0.63485(13)	0.0257(4)
O2	0.6384(2)	0.31991(11)	0.65764(14)	0.0328(4)
O3	0.8777(2)	0.30601(12)	1.24781(15)	0.0366(5)
H3A	0.825(4)	0.2611(14)	1.227(3)	0.055*
O4	0.5628(2)	0.38537(10)	0.45498(14)	0.0237(4)
H4A	0.593(3)	0.3556(15)	0.5133(13)	0.036*
H4B	0.498(3)	0.3580(15)	0.3968(14)	0.036*
O5	0.7417(2)	0.52949(13)	0.60911(14)	0.0257(4)
H5A	0.762(4)	0.5705(12)	0.582(2)	0.039*
H5B	0.794(4)	0.4864(12)	0.617(3)	0.039*
O6	0.2007(2)	0.34526(12)	0.68045(14)	0.0344(4)
O7	0.00156(19)	0.43819(10)	0.63521(13)	0.0252(4)
O8	0.3537(2)	0.31143(12)	1.24719(15)	0.0346(4)
H8A	0.331(4)	0.262(2)	1.239(3)	0.052*
O9	0.0724(2)	0.38485(11)	0.45843(14)	0.0250(4)
H9A	0.124(3)	0.3599(15)	0.5221(12)	0.037*
H9B	0.014(3)	0.3511(14)	0.4054(15)	0.037*
O10	0.2394(2)	0.53301(12)	0.60926(14)	0.0255(4)
H10A	0.289(4)	0.4874(11)	0.623(3)	0.038*
H10B	0.270(3)	0.5694(13)	0.582(2)	0.038*

Experimental details

Hydrogen atoms were added using the standard options of the SHELX system.

Comment

Carboxylates are often used as a ligands to construct coordination polymers. This is because the carboxylate group can be bonded to metal ions in a variety of ways. It can be also self-assembled into a multinuclear secondary structural unit with metal ions to further construct coordination polymer networks of various structures. The carboxyl- and carboxylate rich coordination mode and diverse coordination chemistry are favored by coordination chemists and crystal engineering scholars [4, 5]. And the carboxyl oxygen atoms can form hydrogen bonds with a solvent molecule such as water, thereby assembling a supramolecular structure to form a supramolecular compound having a special property [6]. According to the theory of coordination chemistry, it is predicted that these ligands can coordinate with almost all metals on the periodic table. The skeleton structure can be completely preserved. These features are very useful to design and construct molecules in accordance with pre-designed specific morphologies and structures [7]. But in some cases mononuclear complexes and oligomeric ones are obtained.

In this paper we report the synthesis and crystal structure of a mononuclear Ni(II) complex under solvent conditions. There are two halves of the title complexes in one asymmetric unit. In the coordination of the complex, the Ni1(II) atom adopts a distorted octahedral coordination configuration, and the coordination is derived from two carboxylate groups and oxygen atoms of four water molecules. The two symmetry-related oxygen atoms O4 in the water molecules are at the top of the octahedron, the oxygen atom O1, O1a, O5a and O5 are in the equatorial plane. In addition, another Ni2(II) atom also has the same coordination mode. In the complex, the Ni1—O1 bond length is 2.0542(15) Å, the Ni1—O5 bond length is 2.0600(17) Å, the Ni1—O4 bond length is 2.0702(16) Å, and the Ni2—O10 bond length is 2.0556(17) Å, the bond length of Ni2—O7 is 2.0678(15) Å, and the bond length of the Ni2—O9 bond is 2.1000(17) Å, which is slightly longer than that reported in [8–10]. The O—Ni—O angles are almost orthogonal. The remaining bond lengths and angles are all within the normal range. Due to the four coordinated water molecules acting as the hydrogen-bonding donors and acceptors, a complex three-dimensional hydrogen-bonded network is formed.

The title structure shows a translational pseudosymmetry (92%; *a*/2). The aryl moieties of the two independent complexes are significantly tilted to each other and the absence of

difference electron density in this region rules out a smaller unit cell [11].

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