Crystal structure of tetraaqua-bis(2,4-dichlorophenoxy-acetato-κO)nickel(II) dihydrate, $Ni(H_2O)_4(C_8H_5Cl_2O_3)_2 \cdot 2H_2O$

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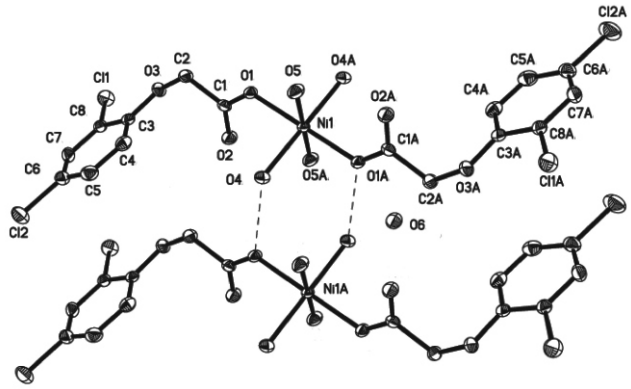
Received March 31, 2011, accepted and available on-line September 20, 2011; CCDC no. 1267/3488



Abstract

$C_{16}H_{22}Cl_4NiO_{12}$, monoclinic, *C*12/*c*1 (no. 15), a = 38.06(2) Å, b = 4.975(2) Å, c = 12.679(5) Å, β = 92.957(6)°, V = 2397.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.106, T = 294 K.

Source of material

A mixture of nickel acetate (0.10 mmol), 2,4-dichlorophenoxy acetic acid (0.25 mmol) and 4,4′-bipyridine (0.05 mmol) was added into the mixed solvent of C_2H_5OH/H_2O (volume ratio = 2:1), and the pH value of the mixture was adjusted to around 6.0 with dilute solution of NaOH. Then the reaction mixture was heated on a water bath for 12 h at 60 °C and then filtered. Green crystals were separated from the mother liquor by slow evaporation at room temperature after two weeks.

Experimental details

The hydrogen atoms H4, H5 and H7 bound to carbon atoms were positioned geometrically with d(C—H) = 0.93 Å and refined as riding, with U_{iso}(H) = 1.2 U_{eq}(C). The hydrogen atoms bound to oxygen atoms were located from difference Fourier map without further refinement.

Discussion

As flexible rigid aromatic carboxylate ligand, 2,4-dichlorophenoxy acetic acid can be used to construct organo-inorganic complex [1-4].

The asymmetric unit of the title crystal structure consists of four coordinating water molecules, two 2,4-dichlorophenoxy-acetate anions, two free water molecules and one nickel(II) ion. The title complex $Ni(H_2O)_4(C_8H_5Cl_2O_3)_2 \cdot 2H_2O$ is similar to the previously reported $Ni(C_8H_5Cl_2O_3)_2(H_2O)_4$ [5]. The coordinating 2,4-dichlorophenoxy-acetate anion acts as a monodentate ligand. The nickel(II) ion is six-coordinated (NiO_6). Its coordination polyhedron can be described as a distorted octahedron. The equatorial plane is formed by O1, O4, O1A and O4A from two 2,4-dichlorophenoxy-acetate anions and two water molecules. The axial positions are occupied by two O5 and O5A atoms from two other water molecules. The Ni—O distances are in the range of 2.052(2)-2.083(2) Å, being similar to the reported values [6]. There exist strong hydrogen bonding interactions in the title complex. Several kinds of hydrogen bonds are observed in the crystal structure: (a) hydrogen bonding between coordinated water oxygen atoms and uncoordinated oxygen atoms of 2,4-dichlorophenoxy-acetate (O5–H5A···O2 with the bond distance of 2.704(3) Å and bond angle of 156°); (b) hydrogen bonding between coordinated water oxygen atoms and coordinated oxygen atoms of 2,4-dichlorophenoxy-acetate (O4–H4A···O1 with the bond distances of 2.736(3) Å and bond angles of 162°); (c) hydrogen bonding between coordinated water oxygen atoms and uncoordinated water molecule (O4–H4B···O6 with the bond distance of 2.719(4) Å and bond angle of 159°); (d) hydrogen bonding between free water oxygen atoms and uncoordinated oxygen atoms of 2,4-dichlorophenoxy-acetate (O6–H6A···O2 with the bond distance of 2.884(4) Å and bond angle of 155°). Hydrogen bonds contribute to the stability of the crystal structure.

Table 1. Data collection and handling.

Crystal:	green, size 0.10 × 0.10 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.13 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52.48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6107, 2381
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1804
$N(param)_{refined}$:	151
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7]

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

Atom	Site	x	y	z	U_{iso}
H(4A)	8*f*	0.2868	0.6778	1.0155	0.042
H(4B)	8*f*	0.3018	0.4895	1.0914	0.042
H(5A)	8*f*	0.2344	0.0790	1.1699	0.046
H(5B)	8*f*	0.2641	–0.0906	1.1479	0.046
H(2A)	8*f*	0.3572	–0.0999	0.9566	0.045
H(2B)	8*f*	0.3366	–0.2857	0.8750	0.045
H(4)	8*f*	0.3786	0.2977	0.9709	0.045
H(5)	8*f*	0.4246	0.5944	1.0047	0.054
H(7)	8*f*	0.4670	0.3740	0.7357	0.047
H(6A)	8*f*	0.3417	0.5934	0.1993	0.065
H(6B)	8*f*	0.3616	0.3552	0.1770	0.065

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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(1)	4*c*	¼	¼	1	0.0252(3)	0.0174(3)	0.0334(3)	0.0011(2)	0.0064(2)	0.0048(2)
Cl(1)	8*f*	0.42203(2)	–0.0288(2)	0.65350(7)	0.0495(5)	0.0473(6)	0.0401(5)	–0.0019(4)	0.0146(4)	–0.0044(4)
Cl(2)	8*f*	0.48447(3)	0.7381(2)	0.8980(1)	0.0586(7)	0.0479(6)	0.0941(8)	–0.0182(5)	–0.0229(6)	0.0060(6)
O(1)	8*f*	0.29169(5)	0.0250(4)	0.9539(2)	0.030(1)	0.023(1)	0.047(1)	0.0035(9)	0.015(1)	0.008(1)
O(2)	8*f*	0.31183(6)	0.2797(4)	0.8237(2)	0.038(1)	0.033(1)	0.053(1)	0.004(1)	0.014(1)	0.017(1)
O(3)	8*f*	0.37012(6)	–0.0417(4)	0.8096(2)	0.030(1)	0.033(1)	0.047(1)	–0.003(1)	0.014(1)	–0.001(1)
O(4)	8*f*	0.28308(6)	0.5519(4)	1.0595(2)	0.035(1)	0.024(1)	0.046(1)	–0.0022(9)	–0.001(1)	0.008(1)
O(5)	8*f*	0.25506(6)	0.0649(4)	1.1474(2)	0.040(1)	0.033(1)	0.043(1)	0.009(1)	0.008(1)	0.011(1)
C(1)	8*f*	0.31421(8)	0.0865(6)	0.8860(2)	0.030(2)	0.022(2)	0.039(2)	–0.005(1)	0.007(1)	0.000(1)
C(2)	8*f*	0.34526(8)	–0.1043(7)	0.8872(3)	0.033(2)	0.028(2)	0.053(2)	0.001(1)	0.019(2)	0.008(2)
C(3)	8*f*	0.39568(8)	0.1466(6)	0.8361(2)	0.030(2)	0.022(2)	0.037(2)	0.004(1)	0.004(1)	0.007(1)
C(4)	8*f*	0.39661(9)	0.3090(7)	0.9241(3)	0.041(2)	0.036(2)	0.036(2)	0.009(2)	0.008(2)	0.001(1)
C(5)	8*f*	0.4239(1)	0.4888(7)	0.9441(3)	0.054(2)	0.034(2)	0.044(2)	0.004(2)	–0.008(2)	–0.006(2)
C(6)	8*f*	0.45014(9)	0.5102(7)	0.8735(3)	0.039(2)	0.031(2)	0.054(2)	–0.003(2)	–0.009(2)	0.007(2)
C(7)	8*f*	0.44945(9)	0.3560(7)	0.7837(3)	0.028(2)	0.039(2)	0.049(2)	–0.003(2)	0.004(2)	0.010(2)
C(8)	8*f*	0.42242(8)	0.1736(6)	0.7654(2)	0.031(2)	0.027(2)	0.035(2)	0.002(1)	0.005(1)	0.003(1)
O(6)	8*f*	0.34835(7)	0.4828(6)	0.1531(2)	0.049(2)	0.064(2)	0.048(1)	0.016(1)	–0.003(1)	–0.009(1)

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