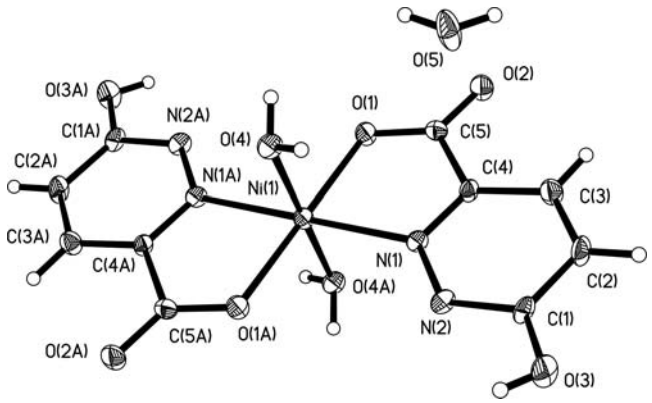
Crystal structure of diaquabis(6-hydroxy-3-pyridazinecarboxylato)-nickel(II) dihydrate, $Ni(H_2O)_2(C_5H_3N_2O_3)_2 \cdot 2H_2O$

Bo Xiao*[,I], Xia Zhang[II], Li-Jun Yang[I] and Yu-Ting Wang[III]

[I] Zhengzhou University of Light Industry, Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou 450002, Henan, P. R. China
[II] Zhengzhou University of Light Industry, School of Continuing Education, Zhengzhou 450002, Henan, P. R. China
[III] Henan Institute of Education, Department of Chemistry, Zhengzhou 450046, Henan, P. R. China

Received December 22, 2010, accepted and available on-line January 24, 2011; CCDC no. 1267/3340



Abstract

$C_{10}H_{14}N_4NiO_{10}$, triclinic, $P\bar{1}$ (no. 2), a = 6.2893(8) Å, b = 8.310(1) Å, c = 8.462(1) Å, α = 61.47(2)°, β = 81.41(1)°, γ = 80.90(1)°, V = 382.3 Å^3, Z = 1, $R_{gt(F)}$ = 0.059, $wR_{ref}(F^2)$ = 0.162, T = 296 K.

Source of material

A mixed solution of 6-hydroxy-3-pyridazinecarboxylic acid (0.05 mmol) and $NiCl_2 \cdot 6H_2O$ (5 mmol) in distilled water (10 ml) in the presence of excess 2,6-dimethylpyridine (ca. 0.05 ml for adjusting the pH value to the basic condition) was stirred for 5 min. The resulting solution was kept at room temperature. After about two weeks, green single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent with a yield of 35 %. Elemental analysis — found: H, 3.43 %; C, 29.32 %; N, 13.70 %; O, 44.01 %; calculated for $C_{10}H_{14}N_4NiO_{10}$: H, 3.42 %; C, 29.34 %; N, 13.69 %; O, 44.01 %.

Experimental details

All the hydrogen atoms were included in calculated positions and treated as riding with d(O—H) = 0.85 Å, d(C—H) = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C,O).

Discussion

The rational design and construction of coordination complexes based upon assembly of metal ions and multifunctional organic ligands is an interesting research field. This not only stems from their potential application as functional materials but also from their intriguing structural features [1-3]. In principle, the structural motifs of these molecular assemblies are defined by the metal centers and the chemical nature of organic ligands. The carboxylate groups have a strong ability to bond various metal ions and afford abundant coordination modes. Thus rigid carboxylate ligands have been widely used for the design and synthesis of a variety of structures [4]. Among these carboxylate-base complexes, nickel(II) representatives have attracted great attention since nickel has been recognized as a considerably important biological agent forming the active site of a variety of metalloproteins, such as hygrogenase (H_2-ase), carbon monoxide dehydrogenase (CODH), *S*-methyl-coenzyme M methyl-reductase (MCR) and urease [5,6]. In addition, their adducts with nitrogen have potential applications in area of organic conductors and magnetic materials [7].

The unit cell of the crystal structure of the title compound consists of the mononuclear nickel(II) complex $Ni(H_2O)_2(C_5H_3N_2O_3)_2$, and two lattice water molecules. Nickel(II) atom is located at the inversion center and is six-coordinated by two carboxylate oxygen atoms and two N donors from two 6-hydroxy-3-pyridazinecarboxylate ligands, and two O atoms from two coordinating water molecules in a distorted octahedral arrangement. N1, N1A, O1 and O1A atoms constitute the equatorial plane of the octahedron. The O4 and O4A atoms occupy the two axial positions. The axial Ni—O4 bond length is 2.067(3) Å. The bond lengths d(Ni—O1) = 2.023(3) Å and d(Ni—N1) = 2.124(4) Å are in normal range. The bond angles around the Ni(II) are in the range of 78.4(1)° - 180.0°.

All the molecules participate in intermolecular hydrogen bonds, d(O5–H4W···N2) = 2.690(6) Å, ∠O5–H4W···N2 = 153.9°, d(O5–H3W···O1) = 2.690(5) Å, ∠O5–H3W···O1 = 149.5°, d(O4–H2W···O3) = 2.763(5) Å, ∠O4–H2W···O3 = 177.0°, d(O4–H1W···O2) = 2.667(5) Å, ∠O4–H1W···O2 = 159.6°, d(O3–H3D···O5) = 2.771(5) Å, ∠O3–H3D···O5 = 132.1°, which further stabilize the 2D framework.

Table 1. Data collection and handling.

Crystal:	green block, size 0.12 × 0.18 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.33 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2282, 1421
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1172
$N(param)_{refined}$:	115
Programs:	SHELXS-97, SHELXL-97 [8]

* Correspondence author (e-mail: boxiao@zzuli.edu.cn)

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3D)	2*i*	–0.2897	0.6475	0.4993	0.060
H(1W)	2*i*	0.3163	–0.0712	0.8220	0.045
H(2W)	2*i*	0.1981	0.0728	0.6935	0.045
H(3W)	2*i*	0.5906	0.1717	0.7159	0.080
H(4W)	2*i*	0.6301	0.3533	0.6761	0.080
H(2)	2*i*	0.0869	0.7853	0.6419	0.039
H(3)	2*i*	0.3131	0.5694	0.8500	0.036

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)	1*a*	0	0	0	0.0246(5)	0.0146(5)	0.0248(5)	–0.0014(3)	–0.0100(3)	–0.0013(4)
O(1)	2*i*	0.2592(5)	0.0323(5)	1.0941(5)	0.030(2)	0.018(2)	0.032(2)	–0.001(1)	–0.013(1)	–0.002(2)
O(2)	2*i*	0.4488(6)	0.2425(5)	1.0862(5)	0.035(2)	0.028(2)	0.046(2)	0.001(2)	–0.024(2)	–0.013(2)
O(3)	2*i*	–0.2308(6)	0.7078(5)	0.5305(5)	0.051(2)	0.021(2)	0.035(2)	–0.002(2)	–0.025(2)	0.003(2)
O(4)	2*i*	0.1889(5)	–0.0276(5)	0.7908(4)	0.031(2)	0.021(2)	0.029(2)	0.001(1)	–0.009(1)	–0.003(2)
O(5)	2*i*	0.5680(7)	0.2871(6)	0.6490(6)	0.064(3)	0.024(2)	0.060(3)	–0.013(2)	–0.039(2)	0.002(2)
N(1)	2*i*	0.0041(6)	0.2905(5)	0.8609(5)	0.023(2)	0.015(2)	0.018(2)	0.001(2)	–0.008(2)	0.001(2)
N(2)	2*i*	–0.1294(6)	0.4191(6)	0.7368(5)	0.031(2)	0.017(2)	0.021(2)	0.003(2)	–0.012(2)	0.002(2)
C(1)	2*i*	–0.1040(8)	0.6032(7)	0.6461(6)	0.036(3)	0.013(2)	0.020(2)	0.003(2)	–0.009(2)	0.000(2)
C(2)	2*i*	0.0668(8)	0.6610(7)	0.6950(7)	0.044(3)	0.014(3)	0.033(3)	–0.004(2)	–0.012(2)	–0.002(2)
C(3)	2*i*	0.1992(8)	0.5342(7)	0.8187(7)	0.031(3)	0.026(3)	0.031(3)	–0.005(2)	–0.009(2)	–0.009(2)
C(4)	2*i*	0.1606(7)	0.3468(7)	0.8997(6)	0.026(2)	0.015(2)	0.021(2)	0.000(2)	–0.008(2)	–0.004(2)
C(5)	2*i*	0.3047(7)	0.1948(7)	1.0384(6)	0.021(2)	0.026(3)	0.029(3)	–0.001(2)	–0.005(2)	–0.012(2)

Acknowledgments. This work was supported by the Natural Science Research Assistance Program from the Education Department of Henan Province (grant nos. 2009A430024 and 2009A150007), and the Base and Cutting-edge Technology Research Project of Henan Province (no. 092300410033), the Foundation for Young Backbone Teacher of Henan Colleges and Universities in 2008 (grant no.198).

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