Crystal structure of poly[diaqua-4-carboxylatephenylacetate-κ^2*O,O'*-1,2-di-(4-pyridyl-κ*N*)-ethane-nickel(II) 0.33 hydrate, $Ni(C_9H_6O_4)(C_{12}H_{10}N_2)(H_2O)_2{\cdot}(H_2O)_{0.33}$, $C_{21}H_{20.66}N_2NiO_{6.33}$

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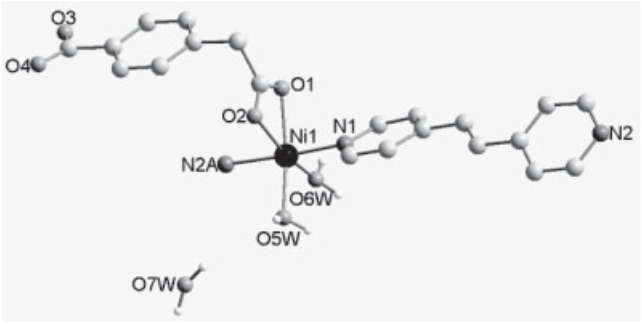

Abstract

$C_{21}H_{20.66}N_2NiO_{6.33}$, triclinic, $P\bar{1}$ (no. 2), a = 8.8119(9) Å, b = 11.367(1) Å, c = 11.689(2) Å, α = 108.992(2)°, β = 98.580(2)°, γ = 108.045(1)°, V = 1011.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.0329, $wR_{ref}(F^2)$ = 0.0935, T = 296 K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.14×0.19×0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.07 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7552, 3742
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3441
$N(param)_{refined}$:	280
Programs:	SHELX [9]

Source of material

The mixtures of 4-carboxyphenylacetic acid (H_2htpa, 0.1 mmol, 18.7 mg), 1,2-di(4-pyridyl)ethylene (*bpe*, 0.2 mmol, 36.8 mg), $Ni(OAc)_2{\cdot}4H_2O$ (0.1 mmol, 24.8 mg), and ethanol (3.5 ml), H_2O (3.5 ml) were sealed in a 23 ml Teflon-lined stainless steel autoclave, heated to 393K for 4 days, and then slowly cooled down to room temperature for crystallization. Green block-shaped crystals of the title compound were obtained.

Discussion

Inorganic-organic hybrid coordination polymeric frameworks have been widely studied, due to their potential application in the fields of magnetism, fluorescence, catalysis etc [1-6]. It is well known that organic ligands play crucial roles in the design and construction of desirable frameworks. Multi-carboxylate ligands combined with rigid and flexible carboxylate groups display unpredictable structure types, which can probably be attributed to very abundant coordination modes [7-8]. With the aim of the understanding of the coordination chemistry of flexible aromatic multi-carboxylate complexes, we have chosen 4-carboxyphenylacetic acid as a bridging ligand to construct new coordination polymers. Single-crystal X-ray analysis shows that the title compound is a 1D chain structure. The asymmetric unit contains one Ni(II) cation, one completely deprotonated *htpa* anions, one *bpe* molecule, two coordinating waters and one uncoordinated water as shown in Fig. 1. In this complex, the nickel atom is six-coordinated in a distorted octahedral manner [NiN_2O_4] by two N atoms from two *bpe* ligands, two oxygen atoms from one *htpa* anions and two coordinating water molecules, with respective bond lengths of 2.0866(17), 2.1109(17) and 2.0446(15)- 2.1615(15) Å. The –COO^- group in the 4 position remains uncoordinated, while the flexible –CH_2COO^- group adopts a chelating coordination mode to the Ni(II) atom. The Ni(II) ions are bridged by the *bpe* molecules to generate 1D chains along the established direction. The adjacent Ni···Ni atoms are separated by one *bpe* connector 13.548 Å. Several kinds of hydrogen bonding are observed in the crystal structure: (a) hydrogen bonds between coordinated water oxygen atoms and uncoordinated oxygen atoms of carboxylate (d(O···O): 2.695(2), 2.654(2) and 2.672(2) Å); (b) hydrogen bonding between coordinated water oxygen atoms and coordinated oxygen atoms of –CH_2COO^- groups (d(O···O): 2.789(2) Å); (c) hydrogen bonds between uncoordinated water oxygen atoms and coordinated oxygen atoms of *htpa* ligand (d(O···O): 3.490(5) Å); (d) hydrogen bonds between uncoordinated water oxygen atoms (O7W) and coordinated water oxygen atoms (O6W) (d(O7W···O6W): 2.957(5) Å). A 3D supramolecular network is formed through above hydrogen bondings.

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1W)	2*i*		0.2117	0.4034	0.1171	0.044
H(2W)	2*i*		0.3178	0.4968	0.0851	0.044
H(3W)	2*i*		0.0463	0.1399	0.0120	0.049
H(4W)	2*i*		0.0102	0.0492	–0.1087	0.049
H(2A)	2*i*		0.5534	0.1327	–0.3287	0.047
H(2B)	2*i*		0.6494	0.2898	–0.2744	0.047
H(4)	2*i*		0.3422	0.0236	–0.5300	0.046
H(5)	2*i*		0.1877	0.0319	–0.7017	0.046
H(7)	2*i*		0.3488	0.4323	–0.5239	0.054
H(8)	2*i*		0.5059	0.4245	–0.3536	0.053
H(10)	2*i*		0.5501	0.4350	0.1491	0.041
H(11)	2*i*		0.7233	0.4254	0.3083	0.043
H(13)	2*i*		0.4868	0.0240	0.1572	0.041
H(14)	2*i*		0.3117	0.0452	0.0066	0.038
H(15)	2*i*		0.7427	0.1296	0.3398	0.043
H(16)	2*i*		0.8072	0.3935	0.4814	0.042
H(18)	2*i*		0.9388	0.1246	0.4768	0.041
H(19)	2*i*		1.0918	0.1139	0.6448	0.040
H(20)	2*i*		1.0896	0.4506	0.8722	0.038
H(21)	2*i*		0.9377	0.4719	0.7094	0.041
H(5W)	2*i*	0.33	0.2941	0.7315	0.0621	0.318
H(6W)	2*i*	0.33	0.1557	0.7995	0.0640	0.318

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	2*i*		0.25573(3)	0.26112(2)	–0.07708(2)	0.0255(2)	0.0225(2)	0.0177(2)	0.0087(1)	0.0002(1)	0.0095(1)
N(1)	2*i*		0.4113(2)	0.2418(2)	0.0629(2)	0.0297(9)	0.0299(9)	0.0211(8)	0.0118(8)	0.0012(7)	0.0118(7)
N(2)	2*i*		1.1080(2)	0.2806(2)	0.7759(2)	0.0272(9)	0.0279(9)	0.0229(9)	0.0100(7)	0.0008(7)	0.0125(7)
O(1)	2*i*		0.3319(2)	0.1333(1)	–0.2122(1)	0.0327(8)	0.0254(7)	0.0264(8)	0.0111(6)	0.0029(6)	0.0102(6)
O(2)	2*i*		0.4727(2)	0.3517(1)	–0.1309(1)	0.0326(8)	0.0267(8)	0.0259(8)	0.0091(6)	0.0041(6)	0.0106(6)
O(3)	2*i*		0.0538(2)	0.1352(2)	–0.8342(2)	0.065(1)	0.0315(9)	0.0274(9)	0.0068(8)	0.0026(8)	0.0106(7)
O(4)	2*i*		0.1854(3)	0.3581(2)	–0.7468(2)	0.075(1)	0.0304(9)	0.0318(9)	0.0186(9)	0.0145(9)	0.0150(7)
O(5W)	2*i*		0.2341(2)	0.4227(1)	0.0555(1)	0.0362(8)	0.0272(7)	0.0219(7)	0.0105(6)	0.0031(6)	0.0091(6)
O(6W)	2*i*		0.0449(2)	0.1327(2)	–0.0629(1)	0.0342(8)	0.0295(8)	0.0278(8)	0.0048(6)	0.0023(6)	0.0137(6)
C(1)	2*i*		0.4458(3)	0.2347(2)	–0.2093(2)	0.028(1)	0.030(1)	0.022(1)	0.0129(9)	0.0007(8)	0.0111(9)
C(2)	2*i*		0.5400(3)	0.2181(3)	–0.3070(2)	0.038(1)	0.047(1)	0.034(1)	0.019(1)	0.012(1)	0.014(1)
C(3)	2*i*		0.4421(3)	0.2229(2)	–0.4228(2)	0.042(1)	0.040(1)	0.028(1)	0.014(1)	0.015(1)	0.013(1)
C(4)	2*i*		0.3446(3)	0.1064(2)	–0.5286(2)	0.050(1)	0.031(1)	0.035(1)	0.017(1)	0.014(1)	0.013(1)
C(5)	2*i*		0.2510(3)	0.1112(2)	–0.6318(2)	0.053(2)	0.027(1)	0.028(1)	0.011(1)	0.009(1)	0.0061(9)
C(6)	2*i*		0.2503(3)	0.2335(2)	–0.6323(2)	0.047(1)	0.029(1)	0.024(1)	0.010(1)	0.014(1)	0.0112(9)
C(7)	2*i*		0.3474(4)	0.3495(2)	–0.5259(2)	0.068(2)	0.027(1)	0.032(1)	0.011(1)	0.012(1)	0.012(1)
C(8)	2*i*		0.4418(4)	0.3450(2)	–0.4232(2)	0.058(2)	0.030(1)	0.029(1)	0.004(1)	0.006(1)	0.008(1)
C(9)	2*i*		0.1557(3)	0.2434(2)	–0.7456(2)	0.050(1)	0.034(1)	0.026(1)	0.016(1)	0.017(1)	0.013(1)
C(10)	2*i*		0.5353(3)	0.3515(2)	0.1522(2)	0.036(1)	0.031(1)	0.032(1)	0.010(1)	–0.002(1)	0.016(1)
C(11)	2*i*		0.6409(3)	0.3464(2)	0.2476(2)	0.034(1)	0.035(1)	0.030(1)	0.006(1)	–0.006(1)	0.016(1)
C(12)	2*i*		0.6252(3)	0.2230(2)	0.2538(2)	0.032(1)	0.040(1)	0.026(1)	0.016(1)	0.0038(9)	0.017(1)
C(13)	2*i*		0.5002(3)	0.1091(2)	0.1590(2)	0.043(1)	0.031(1)	0.029(1)	0.018(1)	0.002(1)	0.013(1)
C(14)	2*i*		0.3963(3)	0.1225(2)	0.0677(2)	0.036(1)	0.029(1)	0.024(1)	0.0118(9)	–0.0020(9)	0.0088(9)
C(15)	2*i*		0.7321(3)	0.2119(3)	0.3553(2)	0.036(1)	0.044(1)	0.034(1)	0.020(1)	0.002(1)	0.021(1)
C(16)	2*i*		0.8149(3)	0.3105(2)	0.4677(2)	0.037(1)	0.042(1)	0.031(1)	0.020(1)	0.002(1)	0.020(1)
C(17)	2*i*		0.9175(3)	0.3001(2)	0.5720(2)	0.026(1)	0.036(1)	0.027(1)	0.0123(9)	0.0038(9)	0.0174(9)
C(18)	2*i*		0.9679(3)	0.1925(2)	0.5563(2)	0.038(1)	0.039(1)	0.022(1)	0.019(1)	–0.0027(9)	0.0072(9)
C(19)	2*i*		1.0602(3)	0.1870(2)	0.6581(2)	0.038(1)	0.033(1)	0.028(1)	0.019(1)	–0.002(1)	0.010(1)
C(20)	2*i*		1.0594(3)	0.3844(2)	0.7915(2)	0.038(1)	0.031(1)	0.024(1)	0.016(1)	0.0003(9)	0.0093(9)
C(21)	2*i*		0.9671(3)	0.3975(2)	0.6938(2)	0.040(1)	0.033(1)	0.033(1)	0.019(1)	0.004(1)	0.015(1)
O(7W)	2*i*	0.33	0.2189(6)	0.7587(6)	0.0410(6)	0.146(4)	0.232(6)	0.306(7)	0.114(4)	0.075(5)	0.122(6)

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