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Crystal structure of *catena*-poly[tetraaqua-bis(μ_2 -2-(4-carboxylatophenoxy)benzoato- $\kappa^2 O:O'$)-pentakis(pyridine- $\kappa^1 N$)dinickel(II)], $C_{53}H_{47}N_5Ni_2O_{13}$

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Abstract

$C_{53}H_{47}N_5O_{13}Ni_2$, monoclinic, $C2/c$ (no. 15), $a = 24.0549(15)$ Å, $b = 14.5539(4)$ Å, $c = 18.8986(11)$ Å, $\beta = 130.953(10)^\circ$, $V = 4996.9(7)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0435$, $wR_{ref}(F^2) = 0.1158$, $T = 293(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Green block
Size:	$0.24 \times 0.22 \times 0.18$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.82 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max} , completeness:	26.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11813, 5099, 0.028
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3948
$N(\text{param})_{\text{refined}}$:	371
Programs:	Olex2 [1], SHELX [2], CrysAlis ^{PRO} [3]

A part of the title crystal structure is shown in the figure (The disorder of one of the pyridine ligands is omitted for clarity. The asymmetric unit is shown as ellipsoid representations). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of $NiCl_2 \cdot 6 H_2O$ (0.238 g, 1 mmol), 2-(4-carboxyphenoxy)benzoic acid (H_2oba , 0.258 g, 1 mmol) and distilled water (15 mL) was added into a 25 mL stainless steel reactor with a Teflon liner. After the addition of two drops of pyridine (py), the reactor was heated to 160°C for 96 h and cooled to room temperature in 24 h. Green block crystals of the title complex were obtained in 46% yield (based on H_2oba ligand).

Experimental details

H atoms bonded to C atoms from organic ligands were positioned geometrically and refined using a riding model, with $C-H = 0.93$ Å, with $U_{\text{iso}}(H) = 1.2$ times $U_{\text{eq}}(C)$.

Comment

The rational design and syntheses of coordination polymers have gained great interest in the field of crystal engineering due to their ability to provide diverse assemblies with fascinating structures and material properties, which might serve as functional materials [4, 5]. Selection of appropriate multidentate ligands to link metal ions is a key strategy for the building coordination polymers [6]. Semi-rigid V-shaped multi-carboxylate ligands with two benzene rings,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Ni1	0.500000	0.87005(3)	0.250000	0.03627(14)
Ni2	0.750000	0.250000	0.500000	0.03673(14)
O1	0.71442(11)	0.37256(13)	0.50992(14)	0.0468(5)
O2	0.62291(12)	0.33412(14)	0.50636(17)	0.0614(6)
O3	0.62026(12)	0.76706(13)	0.53712(15)	0.0552(5)
O4	0.59471(10)	0.86722(13)	0.39178(12)	0.0425(4)
O5	0.61561(14)	1.01427(15)	0.43038(14)	0.0758(8)
O6	0.81460(10)	0.32048(13)	0.48195(13)	0.0466(5)
H6A	0.839642	0.362534	0.524335	0.070*
H6B	0.842562	0.303344	0.469745	0.070*
O7	0.500000	1.0107(2)	0.250000	0.0646(9)
H7A ^a	0.482610	1.031762	0.195900	0.097*
H7B ^a	0.544710	1.031762	0.288129	0.097*
N1	0.500000	0.7271(2)	0.250000	0.0404(7)
N2	0.56372(12)	0.87271(17)	0.21008(15)	0.0449(6)
N3	0.66255(13)	0.24995(16)	0.35244(16)	0.0460(6)
C1	0.62607(14)	0.93112(19)	0.45043(18)	0.0406(6)
C2	0.68211(15)	0.90593(19)	0.55287(19)	0.0430(6)
C3	0.73958(16)	0.9669(2)	0.6145(2)	0.0538(8)
H3	0.742630	1.020973	0.590982	0.065*
C4	0.79204(18)	0.9492(3)	0.7092(2)	0.0635(9)
H4	0.830135	0.990759	0.748543	0.076*
C5	0.7880(2)	0.8706(3)	0.7452(2)	0.0741(11)
H5	0.823228	0.858637	0.809058	0.089*
C6	0.7317(2)	0.8092(2)	0.6867(2)	0.0720(11)
H6	0.728749	0.755835	0.711148	0.086*
C7	0.67971(17)	0.8268(2)	0.5920(2)	0.0523(8)
C8	0.63459(16)	0.6758(2)	0.53405(19)	0.0476(7)
C9	0.69305(17)	0.6483(2)	0.5420(2)	0.0530(8)
H9	0.726414	0.691402	0.552780	0.064*
C10	0.70206(16)	0.5564(2)	0.5340(2)	0.0497(7)
H10	0.741333	0.537886	0.538634	0.060*
C11	0.65329(15)	0.49095(19)	0.51923(18)	0.0422(6)
C12	0.59469(17)	0.5205(2)	0.5111(2)	0.0522(7)
H12	0.561182	0.477847	0.500550	0.063*
C13	0.58525(18)	0.6125(2)	0.5184(2)	0.0546(8)
H13	0.545568	0.631577	0.512672	0.066*
C14	0.66364(16)	0.39104(19)	0.51087(19)	0.0431(6)
C15	0.43738(15)	0.6795(2)	0.2031(2)	0.0481(7)
H15	0.393244	0.711568	0.169838	0.058*
C16	0.43552(18)	0.5853(2)	0.2020(2)	0.0606(9)
H16	0.391034	0.554106	0.169081	0.073*
C17	0.500000	0.5382(3)	0.250000	0.0656(13)
H17	0.500000	0.474251	0.250004	0.079*
C18 ^b	0.5891(6)	0.2680(9)	0.3142(7)	0.070(4)
H18 ^b	0.579498	0.273476	0.354372	0.084*
C18A ^c	0.6361(3)	0.3292(3)	0.3056(3)	0.0635(15)
H18A ^c	0.657425	0.383654	0.338890	0.076*
C19 ^b	0.5352(7)	0.2770(8)	0.2244(8)	0.088(4)
H19 ^b	0.490175	0.300757	0.201469	0.106*
C19A ^c	0.5787(3)	0.3340(4)	0.2106(3)	0.084(2)
H19A ^c	0.562121	0.390143	0.179369	0.101*
C20	0.5459(2)	0.2503(3)	0.1620(3)	0.0971(15)
H20 ^c	0.501366	0.249737	0.100592	0.117*
H20A ^b	0.509131	0.256138	0.097407	0.117*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C21 ^b	0.6127(6)	0.2161(10)	0.2025(9)	0.104(4)
H21 ^b	0.623087	0.195838	0.165634	0.125*
C21A ^c	0.5806(3)	0.1722(4)	0.2070(3)	0.0781(19)
H21A ^c	0.567362	0.117205	0.174365	0.094*
C22 ^b	0.6631(8)	0.2112(13)	0.2939(9)	0.087(6)
H22 ^b	0.703908	0.174832	0.317890	0.104*
C22A ^c	0.6366(3)	0.1749(4)	0.3029(4)	0.0644(16)
H22A ^c	0.657214	0.119397	0.334303	0.077*
C23	0.62028(17)	0.9286(3)	0.2503(2)	0.0593(9)
H23	0.633652	0.964470	0.300089	0.071*
C24	0.6606(2)	0.9370(3)	0.2228(3)	0.0788(12)
H24	0.699650	0.978220	0.252741	0.095*
C25	0.6425(2)	0.8842(3)	0.1514(3)	0.0815(12)
H25	0.668329	0.888980	0.130668	0.098*
C26	0.5853(2)	0.8235(3)	0.1103(2)	0.0776(12)
H26	0.572404	0.785082	0.062266	0.093*
C27	0.54722(18)	0.8203(3)	0.1413(2)	0.0607(9)
H27	0.508086	0.779402	0.112703	0.073*

^aOccupancy: 0.5, ^bOccupancy: 0.294(6), ^cOccupancy: 0.706(6).

which contain a non-metallic atom (C, O, S), are excellent candidates since they can freely twist to meet the requirements of the coordination geometries of metal atoms in the assembly process [7, 8]. In recent years, some coordination polymers with interesting structural diversity ranging from 0D to 3D have been successfully constructed from a combination of the V-shaped 2-(4-carboxyphenoxy)benzoic acid (H₂oba) and pyridine-based ligands [9, 10].

The X-ray diffraction analysis shows that the asymmetric unit of the title complex contains two crystallographic independent Ni(II) ions (each of them located on a special position), one oba^{2−} ligand, two coordinated water as well as two and a half coordinated py ligands. The Ni1 ion sitting on the 2-fold axis is coordinated with three N atoms of the coordinated py ligands and three O atoms from two oba^{2−} ligands and one coordinated water, which shape a distorted octahedral coordination environment; Ni2 ion also locates on the 2-fold axis revealing the similar octahedral coordination environment which is finished by two coordinated water, two carboxylato O atoms and two pyridyl N atoms. The Ni and N2 ions are connected with each other *via* the oba^{2−} ligands, which creates the 1D chain-like network of the title complex with the Ni2–Ni2 separation of 9.218(3) Å. The structure of the title compound is similar to the Co(II)-based compound in which the adjacent Co(II) ions are connected by the 4,4'-bipyridine and oba^{2−} ligand to result in a 2D layered network [9].

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