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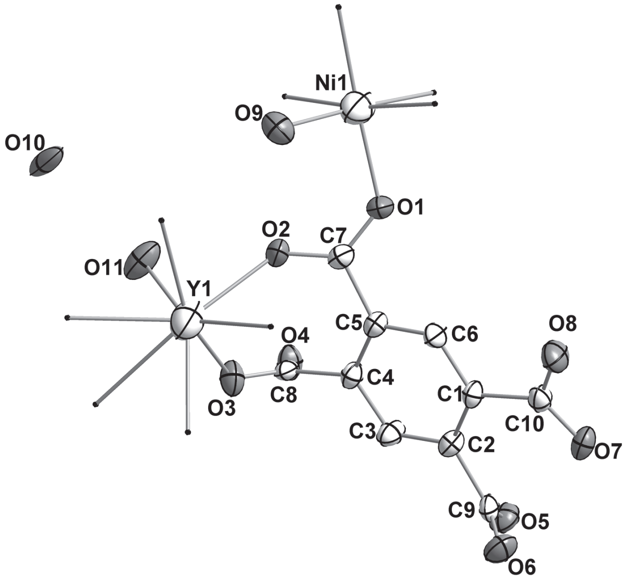
Crystal structure of poly[tetraaqua-bis(μ_6-benzene-1,2,4,5-tetracarboxylato)nickel(II) diyttrium(III)]dihydrate, $C_{20}H_{16}NiO_{22}Y_2$



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Abstract

$C_{20}H_{16}NiO_{22}Y_2$, monoclinic $C2/c$ (no. 15), $a = 17.8995(9)$ Å, $b = 7.5278(4)$ Å, $c = 19.9682(10)$ Å, $\beta = 109.592(1)°$, $V = 2534.8(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0298$, $wR_{ref}(F^2) = 0.0744$, $T = 296(2)$ K.

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The crystal structure 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.

Table 1: Data collection and handling.

Crystal:	Prism, colorless
Size:	$0.20 \times 0.05 \times 0.05$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.39 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
$2\theta_{max}$, completeness:	24.7°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15219, 3161, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2806
$N(param)_{refined}$:	204
Programs:	Bruker programs [1], SHELX [2]

Source of material

Crystals of $C_{20}H_{16}NiO_{22}Y_2$ were synthesized hydrothermally from a mixture of 1,2,4,5-benzenetetracarboxylic acid (H_4Btec), $Ni(NO_3)_2{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$, HCl, KOH and water. In a typical synthesis, 0.02 g $Ni(NO_3)_2{\cdot}6H_2O$, 0.02 g $Y(NO_3)_3{\cdot}6H_2O$ and 0.1 g H_4 Btec were dissolved in a mixture of 10 ml water at constant stirring, whose pH value was then adjusted to 3.5 by HCl and KOH. Finally, the mixture was kept in a 20 mL Teflon–lined steel autoclave at 453 K for 5 days. The autoclave was slowly cooled to room temperature at a rate of 2 °C/h. Colorless prism crystals of the title compound were obtained.

Experimental details

All hydrogen atoms were placed on calculated positions using a riding model (AFIX 3 option for oxygen bonded hydrogen atoms and AFIX 43 for carbon bonded hydrogen atoms).

Discussion

The study of coordination polymers (CPs) has gained great recognition as an important interface between synthetic chemistry and material science, and provides a solid foundation for understanding how functions can be achieved [3–5]. Crystal engineering considerations provide powerful tools for the design and synthesis of novel and interesting CPs, and the advances in theory and practice of molecular crystallography have increased the speed and scope of structure determination enormously. It is well known that selection of suitable organic ligands is crucial for constructing extended

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

Atom	x	y	z	U_{iso}*/U_{eq}
Y1	1.02076(2)	0.71783(3)	0.07257(2)	0.01318(8)
Ni1	1.0000	1.24023(6)	0.2500	0.01153(11)
C1	0.69975(14)	0.8490(3)	0.07232(13)	0.0135(5)
C2	0.69448(14)	0.6634(3)	0.07373(13)	0.0130(5)
C3	0.76365(15)	0.5641(3)	0.10022(14)	0.0151(5)
H3	0.7605	0.4409	0.1015	0.018*
C4	0.83764(14)	0.6462(3)	0.12496(13)	0.0127(5)
C5	0.84282(14)	0.8312(3)	0.12729(13)	0.0134(5)
C6	0.77349(15)	0.9301(3)	0.10010(14)	0.0149(5)
H6	0.7766	1.0534	0.1005	0.018*
C7	0.91965(15)	0.9289(3)	0.16235(13)	0.0137(5)
C8	0.90892(14)	0.5261(3)	0.15008(13)	0.0124(5)
C9	0.61761(14)	0.5611(3)	0.04820(14)	0.0142(5)
C10	0.62817(15)	0.9664(3)	0.05058(13)	0.0149(5)
O1	0.91367(11)	1.0677(3)	0.19464(10)	0.0188(4)
O2	0.98359(11)	0.8674(3)	0.15860(10)	0.0182(4)
O3	0.95135(11)	0.5124(3)	0.11086(10)	0.0183(4)
O4	0.91893(11)	0.4409(2)	0.20586(10)	0.0172(4)
O5	0.60463(11)	0.4583(3)	0.09240(11)	0.0190(4)
O6	0.57375(11)	0.5777(3)	−0.01510(11)	0.0218(4)
O7	0.55980(11)	0.8984(3)	0.04208(10)	0.0186(4)
O8	0.63550(11)	1.1295(3)	0.04488(11)	0.0216(4)
O9	1.05414(12)	1.2283(2)	0.17457(11)	0.0201(4)
O10	1.2733(3)	0.7025(9)	0.2358(3)	0.132(2)
O11	1.11603(12)	0.6248(3)	0.18115(11)	0.0256(5)
H11A	1.1665	0.6589	0.1982	0.031*
H10A	1.2515	0.7943	0.2477	0.038*
H6A	1.0325	1.2948	0.1389	0.031*
H10B	1.2743	0.5758	0.2456	0.038*
H6B	1.0552	1.1257	0.1580	0.031*
H11B	1.0929	0.5607	0.2036	0.031*

CPs. The benzene-1,2,4,5-tetracarboxylate (btec) ligand is a remarkably versatile building block for the construction of supramolecular architectures due to its four rigid carboxyl groups and various coordination modes in the self-assembly reaction [6–8]. And it can provide directional conformation of network structures *via* non-covalent contacts like hydrogen bonding and aromatic stacking. We deem that the association between btec ligand, Ni^{2+} and Y^{3+} cations may afford new CPs. Single-crystal structure determination shows that the compound $C_{20}H_{16}NiO_{22}Y_2$ crystallizes in the monoclinic space group $C2/c$ and features a three-dimensional framework. There is one half of a Ni^{2+} located at a two-fold axis, a Y^{3+}ion, a btec^{4-} anion, two coordinated water molecules and one water molecule in the asymmetric unit. The Ni^{2+} ion is 6-coordinated by four O atoms from four btec^{4-} anions, and two oxygen from two aqua ligands. This coordination geometry can be described as a NiO_6 octahedron with Ni–O bond distances ranging from 2.0376(18) to 2.0753(18) Å and the O—Ni—O bond angles varying from 84.74(8) to 91.88(8)°. The larger Y^{3+} ion, is surrounded by seven O atoms from btec^{4-} ligand and one oxygen from an aqua ligand, forming YO_8 geometry with the Y—O bonds ranging from 2.2710(19) to 2.632(2) Å. For btec^{4-} ligand, it connects with four Ni^{2+} and two Y^{3+} metal centers to form a three-dimensional metal-organic coordination polymer.

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References

1. Bruker: APEX2, SAINT and SADABS. Brucker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Yu, Y.; Guo, Y.; Yang, L.; Niu, Y.: Crystal structure of two-dimensional coordination polymer poly-μ$_2$-azido-aqua-(μ$_2$-pyrazine-2-carboxylato-κ^3*O*,*N*:*N′*)nickel(II), $C_5H_5N_5O_3Ni$. Z. Kristallogr. NCS **231** (2016) 1163–1164.
4. Zhao, E.-X.; Li, F.-F.; Zhao, D.: Hydrothermal syntheses, crystal structures and characteristics of two new isostructural Ni(II) coordination polymers. Chin. J. Struct. Chem. **35** (2016) 1764–1769.
5. Karmakar, A.; Hazra, S.: Synthesis, structure and thermal study of a new 3-aminopyrazine-2-carboxylate based zinc(II) coordination polymer. Z. Kristallogr. Cryst. Mater. **230** (2015) 413–419.
6. Ma, F.-X.; Zhao, D.; Yang, R.-J.; Huang, M.: Crystal structure of poly-tetraaquabis(μ$_8$-benzene-1,2,4,5-tetracarboxylato-1κ^{3}O^4:O^6:O^8: 2κ^{4}O^2:O^2:O^5:O^5:3κ^{4}O^1:O^3:O^5:O^7)(di-μ$_3$-hydroxido)-pentazinc(II) decahydrate, $C_{20}H_{34}O_{32}Zn_5$. Z. Kristallogr. NCS **231** (2016) 897–899.
7. Yang, L. L.: A new Zn(II) coordination polymer with (3,4)-connected 3,4T10 topological net based on pyromellitic acid and *N*-donor ligand: synthesis, crystal structure, and luminescent property. Synth. React. Inorg. Metal-Org. Nano-Metal Chem. **46** (2016) 1198–1201.
8. Freslon, S.; Luo, Y.; Daiguebonne, C.; Calvez, G.; Bernot, K.; Guillou, O.: Brightness and color tuning in a series of lanthanide-based coordination polymers with benzene-1,2,4,5-tetracarboxylic acid as a ligand. Inorg. Chem. **55** (2016) 794–802.