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Crystal structure of *catena*-poly[triaqua-(1,3-di(1*H*-imidazol-1-yl)benzene- $\kappa^2 N:N'$)-(3-nitrophthalato- $\kappa^1 O$)cobalt(II)] – water (2/3), $C_{20}H_{22}N_5O_{10.5}Co$

Table 1: Data collection and handling.

Crystal:	Pink block
Size:	0.33 × 0.31 × 0.28 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.81 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	28.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13684, 4911, 0.030
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4241
$N(\text{param})_{\text{refined}}$:	334
Programs:	Olex2 [1], SHELX [2, 3], CrysAlis ^{PRO} [4]

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Abstract

$C_{20}H_{22}N_5O_{10.5}Co$, triclinic, $P\bar{1}$ (no. 2), $a = 7.9667(3)$ Å, $b = 11.5847(4)$ Å, $c = 13.5305(5)$ Å, $\alpha = 81.096(3)^\circ$, $\beta = 83.110(3)^\circ$, $\gamma = 69.997(4)^\circ$, $V = 1156.26(8)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0439$, $wR_{\text{ref}}(F^2) = 0.1096$, $T = 292(1)$ K.

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A part of the molecular structure is shown in the figure ($A = x$, $1 + y$, z). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Source of material

All chemical reagents were purchased without further purification. The 3-nitrobenzene-1,2-dicarboxylic acid and 1,3-bis(1-imidazolyl)benzene were purchased from Beijing Bailingwei Technology Co. All other chemical reagents were of analytical grade and obtained from the Tianjin Deen Chemical Reagent Co. The mixtures of 3-nitrobenzene-1,2-dicarboxylic acid (H_2 3-Nbdc 21.4 mg, 0.1 mmol), 1,3-bis(1-imidazolyl)benzene (bimb, 14.4 mg, 0.1 mmol), $Co(OAc)_2 \cdot 4 H_2O$ (24.9 mg, 0.1 mmol) and H_2O (6 mL) was placed in a 23 mL Teflon-lined autoclave at 393 K for 4 days, then cooled to room temperature. Purple block crystals were obtained in ca. 75% yield. **Elemental analysis** calcd. (%) for $C_{20}H_{22}N_5O_{10.5}Co$: C, 42.95; H, 3.96; N, 12.52. Found: C, 42.81; H, 4.02; N, 12.39.

Experimental details

Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using intrinsic phasing and refined with the SHELXL [3] refinement package. Hydrogen atoms were placed in their idealized positions and constrained to ride on their parent atoms. The U_{iso} of the H-atoms were constrained to 1.2 times U_{eq} of their bonding carbon atoms with C–H = 0.93 Å (aromatic) and 1.5 times U_{eq} for the hydrogen atoms at water with O–H = 0.85 Å.

Comment

Research projects related to coordination polymers are rapidly increasing in recent years not only for their diversities

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}
Co1	0.25454(5)	0.97825(3)	0.71605(3)	0.02262(12)
O1	0.3734(2)	0.81986(17)	0.63609(13)	0.0265(4)
O1W	0.0031(2)	0.99004(18)	0.68291(15)	0.0333(5)
H1WA	−0.0347	1.0497	0.6371	0.050*
H1WB	0.0206	0.9262	0.6542	0.050*
O2	0.6564(3)	0.75304(19)	0.67751(14)	0.0340(5)
O2W	0.2818(3)	1.08045(18)	0.57155(14)	0.0331(5)
H2WA	0.3914	1.0694	0.5776	0.050*
H2WB	0.2796	1.0394	0.5251	0.050*
O3	0.4027(4)	0.7471(3)	0.25631(17)	0.0562(7)
O3W	0.5167(3)	0.96472(19)	0.75216(15)	0.0338(5)
H3WA	0.5866	0.8991	0.7295	0.051*
H3WB	0.5609	1.0091	0.7081	0.051*
O4	0.4576(4)	0.5514(3)	0.25696(18)	0.0599(7)
O5	0.3727(3)	0.91764(17)	0.42306(14)	0.0300(4)
O6	0.1826(2)	0.81047(18)	0.44482(15)	0.0320(4)
N1	0.2348(3)	0.8561(2)	0.84602(16)	0.0274(5)
N2	0.2260(3)	0.6824(2)	0.93752(15)	0.0257(5)
N3	0.1558(3)	0.3087(2)	0.85077(16)	0.0266(5)
N4	0.1645(3)	0.1528(2)	0.77208(17)	0.0303(5)
C8	0.3350(3)	0.8191(2)	0.44114(18)	0.0238(5)
C1	0.5349(3)	0.7557(2)	0.62464(18)	0.0223(5)
C2	0.5896(3)	0.6733(2)	0.54270(19)	0.0223(5)
C3	0.7382(4)	0.5666(3)	0.5540(2)	0.0283(6)
H3	0.8041	0.5511	0.6097	0.034*
C4	0.7895(4)	0.4836(3)	0.4845(2)	0.0344(7)
H4	0.8882	0.4122	0.4939	0.041*
C5	0.6949(4)	0.5065(3)	0.4013(2)	0.0330(6)
H5	0.7262	0.4499	0.3548	0.040*
C6	0.5522(4)	0.6151(3)	0.38784(19)	0.0274(6)
C7	0.4931(3)	0.7006(2)	0.45745(18)	0.0216(5)
N5	0.4631(3)	0.6401(3)	0.29371(18)	0.0375(6)
C9	0.2386(4)	0.7420(3)	0.84424(19)	0.0279(6)
H9	0.2487	0.7066	0.7857	0.034*
C10	0.2191(5)	0.8703(3)	0.9459(2)	0.0384(7)
H10	0.2120	0.9425	0.9707	0.046*
C11	0.2153(5)	0.7648(3)	1.0032(2)	0.0386(7)
H11	0.2071	0.7506	1.0729	0.046*
C12	0.2350(3)	0.5561(2)	0.96273(18)	0.0229(5)
C13	0.1847(3)	0.4970(2)	0.89560(19)	0.0241(5)
H13	0.1413	0.5396	0.8348	0.029*
C14	0.2002(3)	0.3733(2)	0.92060(19)	0.0246(5)
C15	0.2576(4)	0.3105(3)	1.0128(2)	0.0329(6)
H15	0.2622	0.2287	1.0303	0.040*
C16	0.3076(4)	0.3707(3)	1.0782(2)	0.0346(7)
H16	0.3475	0.3289	1.1399	0.042*
C17	0.2991(4)	0.4928(3)	1.0531(2)	0.0289(6)
H17	0.3365	0.5321	1.0968	0.035*
C18	0.0334(4)	0.3556(3)	0.7789(2)	0.0321(6)
H18	−0.0395	0.4375	0.7654	0.038*
C19	0.0396(4)	0.2596(3)	0.7317(2)	0.0319(6)
H19	−0.0299	0.2647	0.6796	0.038*
C20	0.2311(4)	0.1862(3)	0.8428(2)	0.0316(6)
H20	0.3196	0.1321	0.8826	0.038*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
O5W	0.0029(3)	0.7673(2)	0.64010(17)	0.0451(6)
H5WA	−0.1013	0.7633	0.6574	0.068*
H5WB	0.0240	0.7811	0.5771	0.068*
O4W ^a	−0.2322(6)	0.9674(4)	0.8870(3)	0.0389(10)
H4WA ^a	−0.3067	0.9666	0.8473	0.058*
H4WB ^a	−0.1626	0.9731	0.8351	0.058*

^aOccupancy: 0.5.

of structures and their strong thermal and chemical stabilities, but also for their characteristics of both polymers and coordination compounds at the same time, which make them increasingly attractive application prospects in many fields [5–11]. Among the carboxylate ligands, nitrobenzene-1,2-dicarboxylates have gained attention as *O*-donor ligands in constructing coordination polymers not only because of their good coordination capabilities, but also because of the existence of a electron-withdrawing group (−NO₂), which can enrich the structural and functional diversities of coordination polymers [10]. In our previous work, we had synthesized a number of CPs with interesting 1D to 3D structures and excellent properties such as fluorescent, magnetic and photochemical properties based on 4-nitrobenzene-1,2-dicarboxylates [10, 12–15] and 3-nitrobenzene-1,2-dicarboxylate [16–18]. In the *N*-donor ligands, the imidazolyl ligands are often used to mediate the structures and properties of coordination polymers together with the *O*-donor ligands [19, 20]. The organic molecule 1,3-di(1*H*-imidazol-1-yl)benzene (bimb) is one of the most common *N*-donor ligands to combine with *O*-donor ligands to construct a series of coordination polymers with interesting structures and excellent properties [21].

The asymmetric unit contains one Co(II) ion, one 3-Nbdc dianion, one bimb molecule, three coordinated water molecules, one and a half guest water molecules, as shown in the figure (A: *x*, 1 + *y*, *z*). The Co(II) ion is coordinated by one carboxylic oxygen atom from one 3-Nbdc dianion, another three oxygen atoms from three coordinated water molecules and two nitrogen atoms from two symmetry-related bimb ligands. The hexa-coordinated Co(II) ion forms a slightly distorted octahedral [CoN₂O₄] geometry with the four atoms (N1, N4, O1, O2W) in the equatorial plane and two atoms (O1W, O3W) in the axial position. The Co—O bond lengths are in the range from 2.0595(18) to 2.1516(19) Å, whilst the Co—N bond lengths are 2.106(2) and 2.128(2) Å, respectively. The adjacent Co(II) neighbours are connected by bimb molecules adopting exobidentate coordination mode to form one dimensional chain structure with the Co···Co separation of 11.5847(2) Å. In the 3-Nbdc anion, only one carboxyl group participates in the coordination of cobalt ions adopting a monodentate coordination mode. So the 3-Nbdc anions are

suspended as parallel pendent arms on both sides of the chain. As a result of the presence of three coordinated water molecules (O1W, O2W and O3W) and two free water molecules (O4W and O5W) in the compound, there are three kinds of hydrogen bonds. Firstly, there are the oxygen atoms in coordinated waters as donors and the carboxylate oxygen atoms as acceptors (O(1W)—H(1WA)···O(6): $d = 2.748(3)$ Å; O(2W)—H(2WA)···O(5): $d = 2.770(3)$ Å; O(2W)—H(2WB)···O(5): $d = 2.830(3)$ Å; O(3W)—H(3WA)···O(2): $d = 2.627(3)$ Å; O(3W)—H(3WB)···O(5): $d = 2.752(3)$ Å). Secondly, the hydrogen bonding interactions are between free water oxygen atoms acting as donors and the carboxylate oxygen atoms in 3-Nbdc dianion as acceptors (O(5W)—H(5WA)···O(2): $d = 2.803(3)$ Å; O(5W)—H(5WB)···O(6): $d = 2.907(3)$ Å). Thirdly, it is between free water oxygen atoms and coordinated water oxygen atoms (O(4W)—H(4WA)···O(3W): $d = 2.875(4)$ Å; O(4W)—H(4WB)···O(1W): $d = 3.174(5)$ Å; O(1W)—H(1WB)···O(5W): $d = 2.732(3)$ Å). Adjacent chains are pairwise linked by H-bonds. At the same time, there exist strong interchain face-face π - π interactions between parallel benzene rings of 3-Nbdc dianions in the chain pair. The centroid-centroid distance and the dihedral angle between benzene rings are $3.5473(1)$ Å and 0° respectively. Chain pairs are extended by H-bonds to form a two-dimensional layer. There exist interlayer face-face π - π interactions between two parallel benzene rings of bimb ligands. The centroid-centroid distance and the dihedral angle between two benzene rings are $3.7032(2)$ Å and 0° respectively. Individual layers stack together in an -AAA- motif along the c direction forming its entire three-dimensional supramolecular structure.

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