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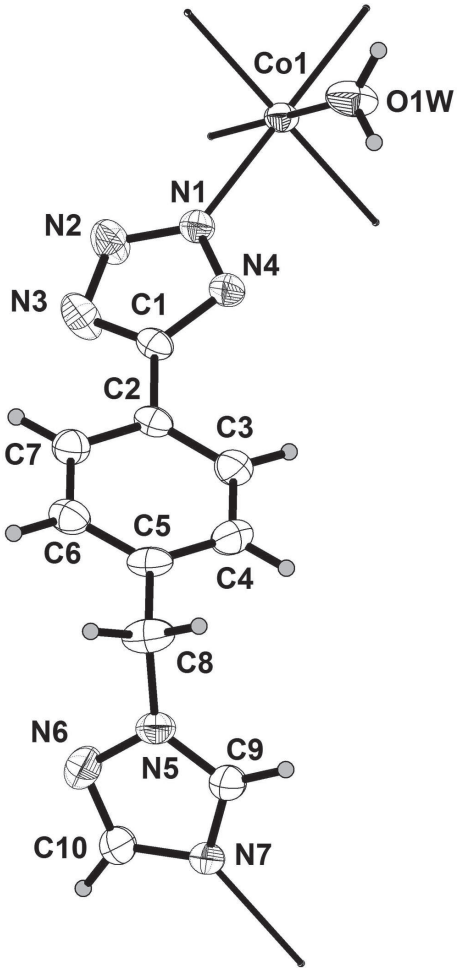
Crystal structure of diaqua-*catena*-poly[diaqua-bis(μ_2-5-(4-(1H-1,2,4-triazol-1-yl)phenyl)tetrazol-2-ido-$\kappa^2N:N'$)cobalt(II)] dihydrate, $C_{20}H_{24}CoN_{14}O_4$



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Abstract

$C_{20}H_{24}CoN_{14}O_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.797(2)$ Å, $b = 8.766(3)$ Å, $c = 9.709(3)$ Å, $\alpha = 73.554(7)°$, $\beta = 86.460(7)°$, $\gamma = 78.537(7)°$, $V = 623.7(3)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0303$, $wR_{ref}(F^2) = 0.0752$, $T = 293(2)$ 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:	Orange block
Size:	0.35 × 0.31 × 0.27 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	7.5 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
$2\theta_{max}$, completeness:	50.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4013, 2205, 0.019
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2028
$N(param)_{refined}$:	181
Programs:	Bruker programs [1], SHELX [2]

Source of material

All reagents used in these syntheses were of analytical grade and used as purchased without further purification. The title compound was synthesized by hydrothermal methods. The mixtures of 1-(tetrazo-5-yl)-4-(1,2,4-triazol-1-ylmethyl)benzene (*ttmb*)(0.1 mmol, 22.7 mg), $Co(OAC)_2{\cdot}2H_2O$ (0.1 mmol, 24.9 mg), NaOH (0.1 mmol), and H_2O (6.0 ml) were placed in a 23 ml Teflon liner stainless steel reactor. The vessel was heated to 393 K for 4 days, and then slowly cooled to room temperature. Orange crystals were obtained, and further crystals were filtered off, washed, and dried under ambient conditions. Yield 56%.

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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}
Co1	0.0000	0.5000	−0.5000	0.02585(13)
N1	0.2481(2)	0.3879(2)	−0.39937(17)	0.0307(4)
N2	0.3920(2)	0.3390(3)	−0.46331(19)	0.0451(5)
N3	0.5193(2)	0.2756(3)	−0.3649(2)	0.0485(5)
N4	0.2769(2)	0.3586(2)	−0.25854(18)	0.0333(4)
N5	0.8944(2)	0.1295(2)	0.33860(18)	0.0339(4)
N6	1.0521(3)	0.1377(3)	0.2737(3)	0.0620(7)
N7	0.9939(2)	0.3072(2)	0.41005(18)	0.0316(4)
C1	0.4444(2)	0.2892(2)	−0.2408(2)	0.0298(4)
C2	0.5342(2)	0.2287(2)	−0.1019(2)	0.0299(4)
C3	0.4767(3)	0.2932(3)	0.0109(3)	0.0400(5)
H3	0.3829	0.3800	−0.0021	0.048*
C4	0.5576(3)	0.2295(3)	0.1427(2)	0.0430(5)
H4	0.5181	0.2741	0.2178	0.052*
C5	0.7569(3)	0.0380(3)	0.0510(2)	0.0368(5)
H5	0.8524	−0.0472	0.0634	0.044*
C6	0.6762(3)	0.1013(2)	−0.0812(2)	0.0343(5)
H6	0.7174	0.0582	−0.1569	0.041*
C7	0.6975(3)	0.0997(2)	0.1646(2)	0.0354(5)
C8	0.7827(3)	0.0268(3)	0.3092(3)	0.0454(6)
H8A	0.6930	0.0122	0.3829	0.054*
H8B	0.8526	−0.0789	0.3125	0.054*
C9	0.8626(3)	0.2305(3)	0.4180(2)	0.0369(5)
H9	0.7615	0.2460	0.4724	0.044*
C10	1.1053(3)	0.2450(3)	0.3213(3)	0.0493(6)
H10	1.2128	0.2760	0.2954	0.059*
O1W	−0.1399(2)	0.3845(2)	−0.32325(16)	0.0466(4)
H1WA	−0.1212	0.3788	−0.2364	0.070*
H1WB	−0.2409	0.3611	−0.3209	0.070*
O2W	0.0117(3)	0.6243(3)	0.06959(19)	0.0625(5)
H2WA	0.0034	0.6924	−0.0129	0.094*
H2WB	−0.0889	0.6264	0.1090	0.094*

Experimental details

Hydrogen atoms were placed in calculated positions using the riding model except for those bound to water molecules, which were initially located in a difference Fourier map and included in the final refinement by use of geometrical restraints with the O–H distances being fixed at 0.85 Å and U_{iso}(H) equivalent to 1.5 times of U_{eq}(O).

Discussion

Over the past decades, there has been much interest in the fabrication of coordination polymers (CPs) because of fascinating structural diversities and framework topologies, as well as their potential applications in the fields of ion-exchange, adsorption, catalysis, magnetism, and luminescence, and so on [3–7]. Structural design of CPs owing the expected functions is still not easy, and there remains a great challenge to truly understand the factors that affect their formation [8]. It is known that the structures of such complexes can often be adjusted by the intelligent selection of organic ligands with suitable shape, functionality, flexibility, and symmetry, and the coordination geometry of the metal ions, the reaction conditions, and so on [9], and much attention has been focusing on tuning the frameworks through rational selection of structurally related ligands. Among them, tetrazole-based ligands have attracted much attention because its four nitrogen electron-donating atoms allows it to serve as either a multidentate ligand or a bridging building block in supramolecular assemblies [10]. However, ligands based on tetrazole-based ligands as building blocks for constructing coordination complexes have been less studied. In recent times we have elected such technique to form coordination polymers that use tetrazole-based ligands to link metal centers. These CPs provided a class of compounds displaying interesting chemical and physical properties such as second harmonic generation (SHG), fluorescence, ferroelectric, dielectric behaviors and magnetic interaction properties and so on [11–14].

The asymmetric unit of the title crystal structure contains one half of a Co atom, one *ttmb* anion, one ligated water and one guest water molecules. The Co(II) ion is coordinated by four nitrogen atoms belonging to four *ttmb* molecules and two oxygen atoms from two ligated water molecules defining a distorted CoN_4O_2 octahedral geometry. The Co—N bond lengths are 2.12 and 2.14 Å and the Co—O bond length is 2.09 Å. Extension of the structure through the two pairs of bisymmetric *ttmb* molecules results in a one-dimensional double-stranded chain running along the *c* direction. There exist hydrogen bonds between ligated water molecules and uncoordinated nitrogen atoms in *ttmb* (O1W—H1W···N3). These hydrogen bonds connect adjacent chains to form a 2D open bilayer structure. The 2D bilayer form channels, which are occupied by free water molecules connected by hydrogen-bonding including of O1W—H1W···O2W, O2W—H2W···N6 and O2W—H2W···N4. Furthermore, a wide range of 159.3–169.5° for the O—H···—O angles provides flexibility to the water molecules in this environment so that they can be accommodated in the channels. The adjacent 2D bilayers stack in a slightly off-set parallel fashion.

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