Crystal structure of bisaqua-(4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole)-cobalt(II) terephthalate, $Co(H_2O)_2(C_{12}H_{10}N_6)(C_8H_4O_4)$

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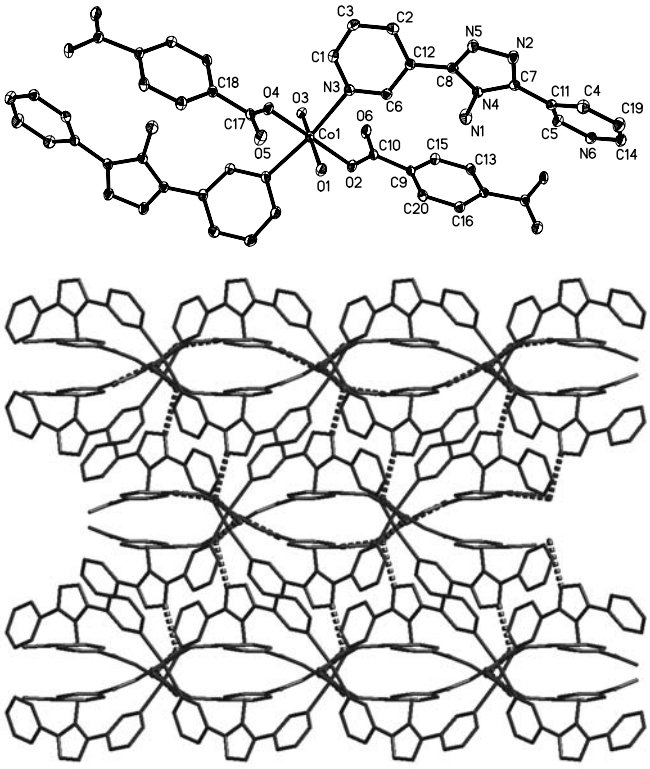

Abstract

$C_{20}H_{18}CoN_6O_6$, monoclinic, $P12_1/c1$ (no. 14), a = 9.7383(9) Å, b = 17.651(2) Å, c = 11.449(1) Å, β = 97.063(4)°, V = 1953.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.042, $wR_{ref}(F^2)$ = 0.106, T = 293 K.

Source of material

A mixture of $CoCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole (bpt, 0.240 g, 1 mmol), terephthalate (tp, 0.166 g, 1 mmol), and H_2O (15 g, 833 mmol) in the molar ratio 1.0 : 1.0 : 1.0 : 0.833 was heated to 160 °C and hold for 120 hours. After cooling to room temperature, large red block-like crystals of $Co(H_2O)_2$(bpt)(tp) were collected (yield, 85 % based on Co). Elemental analysis — found: C, 48.30 %; H, 3.65 %; N, 16.90 %; calculated for $C_{20}H_{18}N_6O_6Co$: C, 48.17 %; H, 3.68 %; N, 16.82 %.

Experimental details

All H atoms were positioned (d(N—H) = 0.90 Å and d(C—H) = 0.93 Å) and refined as riding, with U_{iso} = 1.2 U_{eq}(carrier). The water H atoms were located in a difference Fourier map, and were refined with distances restraints of d(O—H) = 0.85 Å; their displacement factors were fixed to those of parent atoms by a factor of 1.5.

Discussion

During the past decade, the rational design and synthesis of coordination polymers with well regulated network structures has attracted increasing interests for the sake of developing new functional materials with potential applications in the fields of catalysis, gas absorption, nonlinear optics, ion-exchange, luminescence, magnetism and so on [1-3]. To date, coordination polymers on the basis of polycarboxylate connectors have been extensively focused due to the versatile coordination capability as well as the sensitive character to acidity of such building blocks [4]. On the other hand, some analogous linkers derived from the proper modification of the classical 4,4′-bipyridine molecule have also been employed recently, which exhibit dissimilar backbone flexibility and thus give rise to profoundly steric effect on the direction of unexpected coordination architectures upon metal complexation [5].

In the crystal structure of the title compound, the asymmetric unit consists of a cobalt ion, one half of bpt ligand, one half of tp ligand and two coordinated water molecules. The cobalt ion is surrounded by four oxygen donors from two tp and two water ligands in the basal plane and two pyridyl nitrogen atoms from bpt in *trans*-arrangement at the apical sites, displaying a distorted octahedral geometry. The Co—O and Co—N bond distances are in the range 2.022(2) - 2.151(2) Å and 2.215(2) - 2.263(2) Å, which are comparable with literature data [6-8]. Each carboxylate group of tp behaves in monodentate fashion. Thus, bpt and tp ligands both act as μ_2-bridging ligands linking adjacent two cobalt atoms to generate a one-dimensional structure. This one-dimensional coordination polymer structure presents double S-shape single chains when viewed from the c direction. Three types of hydrogen bonds (N1–H1C···O5 (symmetry code: x+1,y,z), d(N···O) = 3.068(3) Å; O1–H1D···O5, d(O-O) = 2.657(3) Å and O3–H3C···O6, d(O···O) = 2.611(2) Å) connect the discrete $Co(H_2O)_2$(bpt)(tp) chains into a two-dimensional layer, which are further extended by two kinds of bonds (O1–H1F···O3 (symmetry code: x,–y+1/2,z+1/2), d(O···O) = 2.750(2) Å and O3–H3B···N5 (symmetry code: x,–y+1/2,z + 1/2), d(O···N) = 2.830(3) Å) into a three-dimensional supramolecular architecture.

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Table 1. Data collection and handling.

Crystal:	red block, size 0.10 × 0.20 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.35 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14995, 4478
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3975
$N(param)_{refined}$:	298
Programs:	SHELXS-97 [9], SHELXL-97 [10], SHELXTL [11]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	–2.2000	0.3652	–0.8856	0.038
H(2A)	4*e*	–1.9533	0.5299	–0.7431	0.040
H(3A)	4*e*	–2.1246	0.4884	–0.8875	0.044
H(4A)	4*e*	–1.5720	0.5429	–0.2341	0.041
H(5A)	4*e*	–1.4495	0.3603	–0.4007	0.031
H(6A)	4*e*	–1.9503	0.3221	–0.6003	0.029
H(13A)	4*e*	–1.4613	0.1695	–0.5092	0.031
H(14A)	4*e*	–1.2439	0.4216	–0.1022	0.037
H(15A)	4*e*	–1.6347	0.1518	–0.6637	0.032
H(16A)	4*e*	–1.7468	0.1827	–0.2839	0.034
H(19A)	4*e*	–1.3883	0.5233	–0.0880	0.045
H(20A)	4*e*	–1.9198	0.1690	–0.4396	0.035
H(1C)	4*e*	–1.6508	0.3472	–0.5664	0.052
H(1B)	4*e*	–1.6386	0.3147	–0.4665	0.052
H(1E)	4*e*	–2.3108	0.2817	–0.5835	0.044
H(1F)	4*e*	–2.1916	0.2480	–0.5276	0.044
H(3B)	4*e*	–2.1457	0.1357	–0.9135	0.038
H(3D)	4*e*	–2.0273	0.1788	–0.8837	0.038

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	4*e*	–2.19606(3)	0.21968(2)	–0.74108(2)	0.0165(2)	0.0259(2)	0.0209(2)	–0.0008(1)	–0.0029(1)	0.0001(1)
C(1)	4*e*	–2.1324(3)	0.3814(1)	–0.8264(2)	0.030(1)	0.034(1)	0.029(1)	–0.004(1)	–0.004(1)	0.002(1)
C(2)	4*e*	–1.9854(3)	0.4803(1)	–0.7428(2)	0.035(1)	0.024(1)	0.038(1)	–0.002(1)	–0.002(1)	0.004(1)
C(3)	4*e*	–2.0869(3)	0.4555(2)	–0.8285(2)	0.041(2)	0.030(1)	0.036(1)	–0.001(1)	–0.010(1)	0.010(1)
C(4)	4*e*	–1.5121(3)	0.5023(1)	–0.2391(2)	0.036(1)	0.023(1)	0.041(1)	0.006(1)	–0.005(1)	–0.003(1)
C(5)	4*e*	–1.4384(2)	0.3933(1)	–0.3369(2)	0.026(1)	0.028(1)	0.023(1)	0.0029(9)	–0.0004(9)	0.0002(9)
C(6)	4*e*	–1.9850(2)	0.3559(1)	–0.6588(2)	0.022(1)	0.025(1)	0.026(1)	0.0020(9)	0.0015(9)	0.0018(9)
C(7)	4*e*	–1.6488(2)	0.4682(1)	–0.4261(2)	0.023(1)	0.020(1)	0.027(1)	0.0011(9)	–0.0005(9)	0.0019(8)
C(8)	4*e*	–1.8249(2)	0.4583(1)	–0.5633(2)	0.022(1)	0.019(1)	0.030(1)	0.0004(8)	0.0025(9)	0.0030(8)
C(9)	4*e*	–1.7957(2)	0.1610(1)	–0.5680(2)	0.020(1)	0.020(1)	0.029(1)	–0.0019(8)	–0.0039(9)	0.0012(9)
C(10)	4*e*	–1.9070(2)	0.1627(1)	–0.6713(2)	0.022(1)	0.021(1)	0.031(1)	–0.0015(9)	–0.0040(9)	0.0000(9)
C(11)	4*e*	–1.5319(2)	0.4528(1)	–0.3348(2)	0.023(1)	0.024(1)	0.027(1)	–0.0010(9)	–0.0008(9)	0.0048(9)
C(12)	4*e*	–1.9316(2)	0.4297(1)	–0.6552(2)	0.021(1)	0.024(1)	0.026(1)	0.0005(9)	0.0010(9)	0.0009(9)
C(13)	4*e*	–1.5534(2)	0.1699(1)	–0.4953(2)	0.017(1)	0.029(1)	0.032(1)	0.0007(9)	0.0010(9)	–0.0007(9)
C(14)	4*e*	–1.3168(3)	0.4294(1)	–0.1614(2)	0.031(1)	0.029(1)	0.030(1)	–0.000(1)	–0.007(1)	0.000(1)
C(15)	4*e*	–1.6573(2)	0.1596(1)	–0.5880(2)	0.023(1)	0.030(1)	0.027(1)	0.0008(9)	0.0007(9)	–0.0039(9)
C(16)	4*e*	–1.7244(2)	0.1784(1)	–0.3602(2)	0.022(1)	0.036(1)	0.027(1)	–0.002(1)	0.0022(9)	0.004(1)
C(17)	4*e*	–2.4728(2)	0.2993(1)	–0.7847(2)	0.020(1)	0.023(1)	0.030(1)	–0.0024(9)	–0.0029(9)	–0.0005(9)
C(18)	4*e*	–2.5862(2)	0.3192(1)	–0.8814(2)	0.021(1)	0.019(1)	0.028(1)	–0.0003(8)	–0.0021(9)	–0.0020(8)
C(19)	4*e*	–1.4032(3)	0.4906(1)	–0.1520(2)	0.047(2)	0.025(1)	0.036(1)	0.003(1)	–0.009(1)	–0.006(1)
C(20)	4*e*	–1.8278(2)	0.1694(1)	–0.4535(2)	0.017(1)	0.036(1)	0.034(1)	–0.0017(9)	0.0018(9)	0.003(1)
N(1)	4*e*	–1.7074(3)	0.3389(1)	–0.5113(2)	0.045(1)	0.018(1)	0.063(2)	0.007(1)	–0.010(1)	–0.002(1)
N(2)	4*e*	–1.7019(2)	0.5364(1)	–0.4446(2)	0.030(1)	0.023(1)	0.039(1)	0.0020(8)	–0.0113(9)	–0.0007(8)
N(3)	4*e*	–2.0837(2)	0.3317(1)	–0.7427(2)	0.0226(9)	0.026(1)	0.0272(9)	–0.0012(8)	0.0020(8)	0.0003(8)
N(4)	4*e*	–1.7228(2)	0.4175(1)	–0.4992(2)	0.0231(9)	0.0171(9)	0.030(1)	0.0012(7)	–0.0008(8)	0.0013(7)
N(5)	4*e*	–1.8129(2)	0.5302(1)	–0.5317(2)	0.030(1)	0.021(1)	0.039(1)	0.0018(8)	–0.0087(9)	–0.0002(8)
N(6)	4*e*	–1.3332(2)	0.3809(1)	–0.2519(2)	0.023(1)	0.028(1)	0.027(1)	0.0027(8)	–0.0008(8)	0.0025(8)
O(1)	4*e*	–2.2617(2)	0.2418(1)	–0.5788(1)	0.0252(8)	0.0381(9)	0.0235(8)	–0.0010(7)	–0.0015(7)	–0.0025(7)
O(2)	4*e*	–2.0305(2)	0.1669(1)	–0.6463(1)	0.0179(8)	0.039(1)	0.0303(8)	0.0024(7)	–0.0038(7)	0.0040(7)
O(3)	4*e*	–2.1151(2)	0.17997(9)	–0.8966(1)	0.0237(8)	0.0268(8)	0.0246(8)	–0.0021(6)	–0.0022(6)	0.0001(6)
O(4)	4*e*	–2.3630(2)	0.2755(1)	–0.8212(2)	0.0184(8)	0.040(1)	0.0283(8)	0.0041(7)	–0.0026(7)	0.0043(7)
O(5)	4*e*	–2.4934(2)	0.3056(1)	–0.6800(2)	0.0289(9)	0.051(1)	0.0282(9)	0.0060(8)	–0.0012(7)	–0.0025(8)
O(6)	4*e*	–1.8734(2)	0.1622(1)	–0.7731(2)	0.0246(9)	0.054(1)	0.0292(9)	–0.0014(8)	–0.0035(7)	–0.0023(8)

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