Crystal structure of hexaaqua-cobalt di(pyridine-2,5-dicarboxylato)-diaqua-cobalt tetrahydrate, $Co(H_2O)_6Co(C_7H_3NO_4)_2(H_2O)_2{\cdot}4(H_2O)$, $C_{14}H_{30}Co_2N_2O_{20}$

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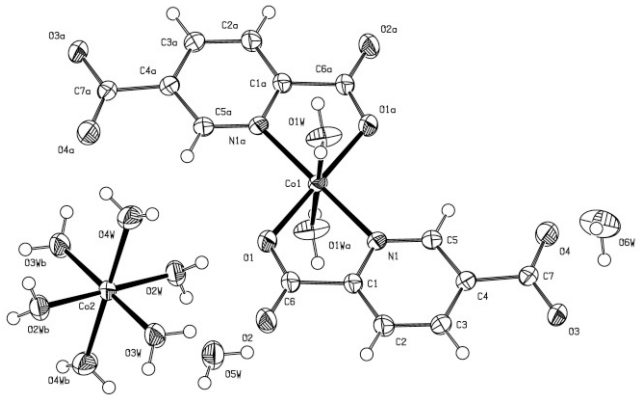

Abstract

$C_{14}H_{30}Co_2N_2O_{20}$, triclinic, $P\bar{1}$ (no. 2), a = 7.264(2) Å, b = 8.647(3) Å, c = 11.460(3) Å, α = 70.204(5)°, β = 85.143(5)°, γ = 70.168(5)°, V = 636.7 Å^3, Z = 1, $R_{gt}(F)$ = 0.0274, $wR_{ref}(F^2)$ = 0.0773, T = 293 K.

Table 1. Data collection and handling.

Crystal:	red blocks, size 0.15×0.33×0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.96 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEXII CCD, φ and ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3519, 2462
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2243
$N(param)_{refined}$:	200
Programs:	SHELXS-97 [9], PLATON [10]

Source of material

All reagents were commercially available and of analytical grade. 2,5-pyridinedicarboxylic acid (0.084 g, 0.5 mmol) was dissolved in the mixed solution of 10 ml CH_3CH_2OH and10 ml H_2O forming solution A, $CoCl_2{\cdot}6H_2O$ (0.234 g, 1 mmol) and $LaCl_3$ (0.1 g, 0.4 mmol) were dissolved in 20 ml H_2O forming solution B. Solution A was slowly added to solution B, and the mixture was adjusted to pH = 5.1 using 5 mol/L NaOH solution. The mixture was stirred and heated for one hour. The resulting solution was filtered and the filtrate evaporated at room temperature. Several weeks later, red block crystals of (I) were obtained.

Experimental details

The H atoms bonded to water were located in a difference synthesis and refined with distance restrains of O–H = 0.83Å and H–H = 1.37(2)Å and U_{iso}(H) = 1.2U_{eq}(O). The remaining H atoms were positioned geometrically, with C–H distances of 0.93Å, and were refined in a riding model with U_{iso}(H) = 1.2U_{eq}(C).

Discussion

Recently, many attentions focuse on the exploration of the construction of coordination polymers and supramolecular complexes based on the attractive and outstanding properties, which present potential exploitable application in many fields, such as catalysis, optical property, magnetism, gas storage, and molecular recognition [1-6]. The assembly reaction between a suitable transition metal and a fuctional organic ligand has usually been used as a successful strategy for preparing these coordination compounds [7, 8]. It is known that the transition metal Co^{2+} ions are able to be coordinated simultaneously in solution by both oxygen- and nitrogen-containing ligands. Various multifunctional carboxylic acids, such as pyridine-, benzene-, pyrazine-based carboxylic acids are widely used as organic ligands, as result of their rich coordination modes and strong H-bonding ability for the construction of transition metal complexes with supramolecular frameworks. Here, we have chosen the pyridine-2,5-dicarboxylic acid (dinic) as organic ligand to react with the Co^{2+} ions. Thus, we obtained a three-dimensional supramolecular framework $Co(H_2O)_6Co(C_7H_3N_1O_4)_2(H_2O)_2{\cdot}4(H_2O)$ formed by multiple O–H···O hydrogen bond interactions. The title complex, consists of a $[Co(H_2O)_6]^{2+}$ cation, a complex $[Co(C_7H_3N_1O_4)_2(H_2O)_2]^{2-}$ anion, and four crystal water molecules. Both Co^{2+} ions display six-coordinated octahedral coordination geometry. The Co1 polyhedron is defined by two oxygen atoms [Co1–O: 2.0752(15)Å] and two nitrogen atoms from the two dinic molecules [Co1–N: 2.1356(13)Å], and two coordinated water molecules [Co1–O_W 2.0410(17)Å]. The Co2 atom is coordinated by six water molecules with Co2–O_W distances in the range of 2.0590(18)-2.1280(17)Å. In the complex, the two dinic molecules are all dianionic to maintain electroneutrality. The presence of many water molecules in the complex leads to numerous hydrogen-bonding interactions, including intra- and inter-O–H···O hydrogen bond interactions. Coordinated and lattice water molecules act as donors and coordinated water molecules and oxygen atoms of the carboxylate groups act as acceptors, which consolidate a stacked arrangement leading to a three-dimensional supramolecular architecture.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1WA)	2*i*	1.366(3)	–0.082(2)	0.559(2)	0.054
H(1WB)	2*i*	1.312(4)	0.081(3)	0.472(2)	0.054
H(2WA)	2*i*	0.740(2)	0.022(3)	0.166(2)	0.042
H(2WB)	2*i*	0.908(3)	0.021(3)	0.209(2)	0.042
H(3WA)	2*i*	0.953(4)	0.296(3)	0.028(2)	0.051
H(3WB)	2*i*	0.912(4)	0.334(3)	–0.094(2)	0.051
H(4WA)	2*i*	1.311(4)	–0.014(3)	0.125(3)	0.052
H(4WB)	2*i*	1.345(3)	–0.166(2)	0.102(3)	0.052
H(5WA)	2*i*	0.425(4)	0.160(3)	0.222(2)	0.053
H(5WB)	2*i*	0.440(4)	0.204(3)	0.097(1)	0.053
H(6WA)	2*i*	0.3205	0.4458	0.9074	0.089
H(6WB)	2*i*	0.5292	0.4383	0.8997	0.089
H(2A)	2*i*	0.7755	0.6276	0.2557	0.038
H(3A)	2*i*	0.6659	0.7450	0.4139	0.036
H(5A)	2*i*	0.8315	0.2614	0.6576	0.031

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)	1*b*	1	0	½	0.0255(2)	0.0163(2)	0.0252(2)	–0.0039(2)	–0.0040(2)	–0.0069(2)
Co(2)	1*a*	1	0	0	0.0303(2)	0.0233(2)	0.0227(2)	–0.0047(2)	–0.0013(2)	–0.0105(2)
O(1)	2*i*	0.9967(2)	0.1244(2)	0.3099(1)	0.0428(9)	0.0228(7)	0.0283(8)	–0.0056(6)	–0.0027(6)	–0.0116(6)
O(2)	2*i*	0.9146(3)	0.3819(2)	0.1601(1)	0.077(1)	0.0292(8)	0.0232(8)	–0.0055(8)	–0.0029(8)	–0.0086(7)
O(3)	2*i*	0.6019(2)	0.7450(2)	0.6372(1)	0.0440(9)	0.0244(8)	0.0293(8)	–0.0027(7)	0.0006(7)	–0.0118(6)
O(4)	2*i*	0.7113(3)	0.4759(2)	0.7677(2)	0.080(1)	0.0359(9)	0.0235(8)	0.0069(9)	0.0039(8)	–0.0056(7)
O(1W)	2*i*	1.2741(2)	0.0041(2)	0.5219(2)	0.0290(9)	0.0280(9)	0.066(1)	–0.0096(7)	–0.0124(8)	0.0021(8)
O(2W)	2*i*	0.8597(2)	–0.0195(2)	0.1681(2)	0.0377(9)	0.0410(9)	0.0314(8)	–0.0113(7)	0.0016(7)	–0.0197(7)
O(3W)	2*i*	0.9740(3)	0.2556(2)	–0.0314(2)	0.069(1)	0.0256(8)	0.0290(8)	–0.0083(8)	–0.0058(8)	–0.0104(7)
O(4W)	2*i*	1.2625(3)	–0.0758(2)	0.1053(2)	0.0365(9)	0.040(1)	0.053(1)	–0.0020(7)	–0.0126(8)	–0.0223(8)
O(5W)	2*i*	0.4553(3)	0.1218(2)	0.1634(2)	0.045(1)	0.051(1)	0.040(1)	–0.0122(8)	0.0060(8)	–0.0250(8)
O(6W)	2*i*	0.4425(3)	0.3730(3)	0.9425(2)	0.052(1)	0.089(2)	0.054(1)	–0.014(1)	–0.005(1)	0.001(1)
N(1)	2*i*	0.8781(2)	0.2681(1)	0.4858(1)	0.0278(9)	0.0178(8)	0.0243(8)	–0.0043(7)	–0.0026(7)	–0.0063(6)
C(1)	2*i*	0.8613(2)	0.3768(2)	0.3677(1)	0.030(1)	0.023(1)	0.023(1)	–0.0072(8)	–0.0027(8)	–0.0091(8)
C(2)	2*i*	0.7844(3)	0.5553(2)	0.3378(1)	0.048(1)	0.022(1)	0.022(1)	–0.0086(9)	–0.0022(9)	–0.0050(8)
C(3)	2*i*	0.7205(3)	0.6250(3)	0.4321(2)	0.042(1)	0.0176(9)	0.028(1)	–0.0047(9)	–0.0035(9)	–0.0061(8)
C(4)	2*i*	0.7385(3)	0.5149(3)	0.5541(2)	0.024(1)	0.0223(9)	0.026(1)	–0.0055(8)	–0.0004(8)	–0.0081(8)
C(5)	2*i*	0.8188(3)	0.3363(3)	0.5761(2)	0.030(1)	0.0209(9)	0.0228(9)	–0.0061(8)	–0.0011(8)	–0.0052(8)
C(6)	2*i*	0.9301(3)	0.2892(3)	0.2704(2)	0.036(1)	0.025(1)	0.025(1)	–0.0065(9)	–0.0033(8)	–0.0111(8)
C(7)	2*i*	0.6791(3)	0.5826(3)	0.6622(2)	0.027(1)	0.025(1)	0.024(1)	–0.0024(8)	0.0015(8)	–0.0086(8)

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