Crystal structure of (3,5-pyrazoledicarboxylato)-bis(diethylenediamine)cobalt(II) hexahydrate, $[\text{Co}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{C}_2\text{H}_8\text{N}_2)_2] \cdot 6\text{H}_2\text{O}$

Kai Shi, Hong-Jun Bai and Zeng-Lin Wang*

Key Laboratory of Applied Surface and Colloid Chemistry, Shaanxi Normal University, Ministry of Education, School of Chemistry and Material Science, Xi'an 710062, P. R. China

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Abstract

$\text{C}_{29}\text{H}_{30}\text{CoN}_6\text{O}_{10}$, monoclinic, $P12_1/c1$ (no. 14), $a = 7.2589(8)$ Å, $b = 11.783(1)$ Å, $c = 21.742(2)$ Å, $\beta = 91.628(2)^\circ$, $V = 1858.9$ Å³, $Z = 4$, $R(F) = 0.047$, $wR_{\text{ref}}(F^2) = 0.117$, $T = 185$ K.

Source of material

The intermediate complex bis(3,5-pyrazoledicarboxylic)cobalt(II) $[\text{Co}(\text{H}_2\text{pdc})_2]$ (H_2pdc = 3,5-pyrazoledicarboxylic acid) was prepared with some modification to the reported method [1]. $\text{Co}(\text{H}_2\text{pdc})_2$ (118.1 mg, 0.3 mmol) was dissolved in 10 ml water, followed by stirring for 5 min, then ethylenediamine (0.5 ml) was dropped into the solution. The resulting mixture was stirred for 1.5 h and then was filtered. Pink prismatic crystals were obtained from the mother liquor after several days at room temperature.

Experimental details

H atoms attached to C and N atoms were positioned geometrically and refined using a riding model with $d(\text{C}—\text{H}) = 0.95$ Å (CH) and 0.99 Å (CH_2); $d(\text{N}—\text{H}) = 0.88$ Å (NH) and 0.92 Å (NH_2); and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C or N})$. H atoms of water molecules were located in difference Fourier maps and fixed in the refinements, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O})$. The two H atoms at O6W were not found.

Discussion

The title compound consists of $[\text{Co}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{en})_2]$ (en = ethylenediamine) molecule and hydrogen bonded H_2O molecules. The Co^{2+} is six-coordinated in form of a distorted octahedron. Hpdc^{2-} bonds the metal ion through its carboxylate oxygen O1 and adjacent pyrazole nitrogen N1. Two ethylene-

diamine molecules bond the metal through their nitrogen atoms. The corresponding distances are $d(\text{Co}—\text{N1}) = 1.893(3)$ Å, $d(\text{Co}—\text{O1}) = 1.945(2)$ Å, $d(\text{Co}—\text{N3}) = 1.960(3)$ Å, $d(\text{Co}—\text{N4}) = 1.937(3)$ Å, $d(\text{Co}—\text{N5}) = 1.951(3)$ Å, $d(\text{Co}—\text{N6}) = 1.952(3)$ Å. The acute angle ($\text{O1}—\text{Co}—\text{N1}$) in the five-membered chelate ring is $83.7(1)^\circ$, and other acute angles around Co ($\angle\text{N3}—\text{Co}—\text{N4}$ and $\angle\text{N5}—\text{Co}—\text{N6}$) are $86.8(1)^\circ$ and $85.4(1)^\circ$, respectively. The coordination mode of Hpdc^{2-} is chelating bidentate, so the bond angles $\angle\text{N1}—\text{C2}—\text{C1} = 114.4(3)^\circ$ and $\angle\text{O1}—\text{C1}—\text{C2} = 113.8(3)^\circ$ are smaller than that of $\angle\text{N2}—\text{C4}—\text{C5} = 121.4(3)^\circ$ and $\angle\text{C4}—\text{C5}—\text{O3} = 118.9(3)^\circ$, respectively. There are various types of intermolecular hydrogen bonds in the complex ($\text{O1W}—\text{H1A} \cdots \text{O4}$, $\text{O2W}—\text{H2A} \cdots \text{O3}$, $\text{O4W}—\text{H4C} \cdots \text{O2}$, $\text{O5W}—\text{H5D} \cdots \text{O4}$), by which solvent water molecules were linked with $[\text{Co}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{en})_2]$.

Table 1. Data collection and handling.

Crystal:	pink prismatic, size $0.12 \times 0.12 \times 0.17$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	9.84 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	51.42°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	9807, 3518
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3148
$N(\text{param})_{\text{refined}}$:	235
Programs:	SHELXS-97 [2], SHELXL-97 [3], SHELXTL [4]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.5229	0.9315	0.3012	0.041
H(1B)	4e	0.4996	1.0462	0.3144	0.041
H(2A)	4e	0.8684	0.4304	0.0904	0.042
H(2B)	4e	0.7802	0.4637	0.1495	0.042
H(3C)	4e	0.1887	0.6284	0.1861	0.049
H(3D)	4e	0.0481	0.5667	0.1592	0.049
H(4C)	4e	0.2885	0.8113	0.4971	0.058
H(4D)	4e	0.2675	0.9267	0.5181	0.058
H(5C)	4e	0.9910	0.7954	0.3509	0.088
H(5D)	4e	0.8042	0.7638	0.3325	0.088
H(2)	4e	0.2901	0.5394	0.2673	0.022
H(3A)	4e	−0.1423	0.5007	0.4253	0.025
H(3B)	4e	−0.0624	0.5787	0.3790	0.025
H(4A)	4e	0.1727	0.3640	0.2855	0.023
H(4B)	4e	0.0417	0.2838	0.3144	0.023
H(5A)	4e	0.4121	0.3144	0.3578	0.023
H(5B)	4e	0.4539	0.3568	0.4213	0.023
H(6A)	4e	−0.0521	0.3246	0.4647	0.026
H(6B)	4e	−0.0397	0.2498	0.4095	0.026
H(3)	4e	0.5129	0.7570	0.3903	0.024

* Correspondence author (e-mail: wangzl@snnu.edu.cn)

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(6C)	4e	−0.3045	0.5065	0.3263	0.032
H(6D)	4e	−0.2640	0.3824	0.3544	0.032
H(7A)	4e	−0.1523	0.3828	0.2542	0.032
H(7B)	4e	−0.0390	0.4979	0.2675	0.032

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(8A)	4e	0.4297	0.1741	0.4417	0.031
H(8B)	4e	0.2730	0.1583	0.3886	0.031
H(9A)	4e	0.1226	0.1535	0.4823	0.032
H(9B)	4e	0.2234	0.2684	0.5048	0.032

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	4e	0.14516(6)	0.41762(4)	0.39186(2)	0.0161(2)	0.0156(2)	0.0145(2)	−0.0011(2)	0.0036(2)	0.0005(2)
O(1)	4e	0.2114(3)	0.4892(2)	0.4700(1)	0.023(1)	0.022(1)	0.013(1)	−0.002(1)	0.0041(9)	−0.0008(9)
O(2)	4e	0.3412(3)	0.6446(2)	0.5101(1)	0.027(1)	0.027(1)	0.018(1)	−0.001(1)	0.002(1)	−0.005(1)
O(3)	4e	0.4495(4)	0.7003(2)	0.2029(1)	0.035(2)	0.024(1)	0.021(1)	−0.003(1)	0.005(1)	0.005(1)
O(4)	4e	0.6184(4)	0.8063(2)	0.2681(1)	0.030(1)	0.023(1)	0.032(1)	−0.006(1)	0.011(1)	0.001(1)
O(1W)	4e	0.4624(4)	0.9830(2)	0.3263(1)	0.045(2)	0.023(1)	0.035(2)	−0.001(1)	0.011(1)	0.003(1)
O(2W)	4e	0.8851(4)	0.4409(2)	0.1288(1)	0.036(2)	0.034(2)	0.035(2)	0.003(1)	−0.003(1)	−0.002(1)
O(3W)	4e	0.0908(4)	0.6396(2)	0.1617(2)	0.038(2)	0.027(2)	0.057(2)	0.006(1)	−0.018(2)	0.000(1)
O(4W)	4e	0.2389(5)	0.8805(3)	0.4872(1)	0.071(2)	0.037(2)	0.036(2)	0.003(2)	−0.008(2)	0.001(1)
O(5W)	4e	0.9142(5)	0.7391(3)	0.3487(2)	0.050(2)	0.042(2)	0.127(4)	−0.021(2)	−0.040(2)	0.041(2)
O(6W)	4e	0.3531(9)	0.0454(3)	0.5639(2)	0.217(6)	0.038(2)	0.088(3)	−0.016(3)	−0.100(4)	0.011(2)
N(1)	4e	0.2798(4)	0.5394(2)	0.3584(1)	0.019(1)	0.018(1)	0.016(1)	−0.002(1)	0.004(1)	0.001(1)
N(2)	4e	0.3222(4)	0.5724(2)	0.3023(1)	0.020(1)	0.020(2)	0.014(1)	−0.002(1)	0.004(1)	−0.000(1)
N(3)	4e	−0.0857(4)	0.5039(2)	0.3880(1)	0.020(1)	0.018(2)	0.023(2)	0.001(1)	0.005(1)	0.003(1)
N(4)	4e	0.0749(4)	0.3589(3)	0.3114(1)	0.019(1)	0.022(2)	0.017(1)	−0.002(1)	0.004(1)	−0.002(1)
N(5)	4e	0.3654(4)	0.3227(2)	0.3965(1)	0.018(1)	0.022(2)	0.018(1)	−0.001(1)	0.002(1)	−0.002(1)
N(6)	4e	0.0271(4)	0.2950(3)	0.4365(1)	0.022(2)	0.019(2)	0.023(2)	−0.001(1)	0.008(1)	0.002(1)
C(1)	4e	0.3029(4)	0.5825(3)	0.4653(2)	0.017(2)	0.023(2)	0.016(2)	0.001(1)	0.002(1)	−0.001(1)
C(2)	4e	0.3508(5)	0.6110(3)	0.4016(2)	0.019(2)	0.020(2)	0.017(2)	−0.002(1)	0.004(1)	−0.002(1)
C(3)	4e	0.4472(5)	0.6950(3)	0.3723(2)	0.022(2)	0.019(2)	0.019(2)	−0.002(1)	0.004(1)	−0.004(1)
C(4)	4e	0.4256(5)	0.6678(3)	0.3099(2)	0.019(2)	0.014(2)	0.020(2)	−0.000(1)	0.004(1)	0.001(1)
C(5)	4e	0.5025(5)	0.7286(3)	0.2566(2)	0.022(2)	0.015(2)	0.023(2)	0.005(1)	0.007(1)	0.002(1)
C(6)	4e	−0.2060(5)	0.4528(3)	0.3392(2)	0.018(2)	0.029(2)	0.031(2)	0.001(2)	−0.004(2)	0.003(2)
C(7)	4e	−0.0835(5)	0.4267(3)	0.2862(2)	0.028(2)	0.030(2)	0.022(2)	−0.002(2)	−0.006(2)	0.003(2)
C(8)	4e	0.3191(5)	0.2091(3)	0.4219(2)	0.025(2)	0.020(2)	0.032(2)	0.001(2)	−0.000(2)	0.003(2)
C(9)	4e	0.1726(5)	0.2271(3)	0.4685(2)	0.030(2)	0.022(2)	0.028(2)	−0.001(2)	0.002(2)	0.008(2)

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