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The crystal structure of [(2,2'-bipyridine- k^2N,N)-bis(6-phenylpyridine-2-carboxylato- k^2N,O)cobalt(II)]-monohydrate, $C_{36}H_{26}N_4O_5Co$

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Abstract

$C_{36}H_{26}N_4O_5Co$, monoclinic, $C2/c$ (no. 15), $a = 29.3826(17)$ Å, $b = 10.3153(5)$ Å, $c = 19.9407(12)$ Å, $\beta = 107.263(6)^\circ$, $V = 5771.6(6)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0341$, $wR_{ref}(F^2) = 0.0777$, $T = 200$ K.

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Table 1: Data collection and handling.

Crystal:	Red block
Size	$0.14 \times 0.11 \times 0.09$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.65 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	25.0° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11790, 5081, 0.025
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4369
$N(\text{param})_{\text{refined}}$:	400
Programs:	Bruker [1], Olex2 [2], SHELX [3], Diamond [4]

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
Co1	0.37802 (2)	0.42972 (2)	0.30897 (2)	0.01825 (9)
O1	0.36059 (5)	0.49317 (16)	0.49866 (8)	0.0372 (4)
O2	0.38739 (5)	0.50687 (14)	0.40542 (7)	0.0266 (3)
O3	0.36283 (5)	0.59292 (13)	0.24949 (7)	0.0262 (3)
O4	0.39226 (5)	0.77367 (13)	0.21700 (8)	0.0293 (4)
N1	0.37359 (6)	0.30813 (15)	0.22105 (8)	0.0211 (4)
N2	0.38644 (6)	0.23334 (16)	0.35189 (9)	0.0214 (4)
N3	0.30505 (5)	0.41056 (15)	0.32057 (8)	0.0189 (4)
N4	0.45040 (5)	0.51432 (15)	0.32317 (8)	0.0191 (4)
C1	0.50075 (7)	0.3418 (2)	0.38825 (11)	0.0247 (5)
C2	0.48848 (7)	0.2465 (2)	0.33719 (12)	0.0304 (5)
H2	0.474744	0.269763	0.290478	0.036*
C3	0.49644 (8)	0.1168 (2)	0.35490 (15)	0.0434 (6)
H3	0.488338	0.053396	0.320224	0.052*
C4	0.51642 (9)	0.0824 (3)	0.42418 (17)	0.0530 (8)
H4	0.521417	−0.004634	0.436416	0.064*
C5	0.52905 (9)	0.1767 (3)	0.47548 (15)	0.0493 (7)
H5	0.542441	0.152782	0.522164	0.059*
C6	0.52194 (8)	0.3065 (2)	0.45799 (12)	0.0369 (6)
H6	0.531252	0.369776	0.492596	0.044*
C7	0.49307 (7)	0.4804 (2)	0.36802 (10)	0.0224 (4)
C8	0.52907 (7)	0.5707 (2)	0.39357 (12)	0.0304 (5)
H8	0.557729	0.545708	0.425621	0.036*
C9	0.52217 (8)	0.6974 (2)	0.37129 (13)	0.0356 (6)
H9	0.545932	0.758954	0.388162	0.043*
C10	0.47936 (7)	0.7313 (2)	0.32344 (12)	0.0297 (5)
H10	0.474130	0.815590	0.306322	0.036*
C11	0.44455 (7)	0.63836 (19)	0.30150 (10)	0.0196 (4)
C12	0.39626 (7)	0.67217 (19)	0.25174 (10)	0.0209 (4)
C13	0.39173 (8)	0.2008 (2)	0.41865 (11)	0.0291 (5)
H13	0.400681	0.264945	0.452849	0.035*
C14	0.38456 (9)	0.0769 (2)	0.43926 (13)	0.0383 (6)
H14	0.387819	0.058613	0.486116	0.046*
C15	0.37257 (8)	−0.0185 (2)	0.38965 (13)	0.0408 (6)
H15	0.367103	−0.102612	0.402189	0.049*
C16	0.36870 (8)	0.0111 (2)	0.32107 (12)	0.0330 (5)
H16	0.361428	−0.053126	0.286811	0.040*
C17	0.37575 (7)	0.13793 (19)	0.30349 (10)	0.0220 (5)
C18	0.37301 (7)	0.17853 (19)	0.23139 (10)	0.0221 (5)
C19	0.37138 (8)	0.0910 (2)	0.17826 (12)	0.0320 (5)
H19	0.371103	0.002305	0.186486	0.038*
C20	0.37017 (9)	0.1372 (2)	0.11292 (12)	0.0387 (6)
H20	0.369031	0.079774	0.076497	0.046*
C21	0.37066 (8)	0.2687 (2)	0.10190 (12)	0.0357 (6)
H21	0.369960	0.301582	0.058186	0.043*
C22	0.37220 (7)	0.3504 (2)	0.15700 (11)	0.0273 (5)
H22	0.372284	0.439339	0.149412	0.033*
C23	0.35611 (7)	0.4801 (2)	0.43545 (11)	0.0247 (5)
C24	0.30949 (7)	0.42413 (19)	0.38934 (10)	0.0205 (4)
C25	0.27426 (7)	0.3887 (2)	0.41862 (12)	0.0301 (5)
H25	0.278336	0.401460	0.466212	0.036*
C26	0.23288 (7)	0.3339 (2)	0.37609 (12)	0.0335 (5)
H26	0.208918	0.306882	0.394631	0.040*
C27	0.22788 (7)	0.3203 (2)	0.30573 (12)	0.0285 (5)
H27	0.200326	0.283316	0.276225	0.034*

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C28	0.26386 (7)	0.36166 (18)	0.27835 (11)	0.0213 (4)
C29	0.25562 (7)	0.36050 (19)	0.20145 (11)	0.0229 (5)
C30	0.26489 (7)	0.4712 (2)	0.16832 (11)	0.0278 (5)
H30	0.278860	0.542675	0.195011	0.033*
C31	0.25359 (8)	0.4764 (2)	0.09619 (12)	0.0369 (6)
H31	0.259664	0.551339	0.074406	0.044*
C32	0.23323 (8)	0.3703 (2)	0.05616 (12)	0.0382 (6)
H32	0.225604	0.373781	0.007473	0.046*
C33	0.22433 (9)	0.2600 (2)	0.08832 (13)	0.0415 (6)
H33	0.211018	0.188257	0.061373	0.050*
C34	0.23500 (8)	0.2546 (2)	0.16062 (12)	0.0345 (6)
H34	0.228338	0.179814	0.182007	0.041*
O5	0.36053 (7)	0.7566 (2)	0.06873 (9)	0.0535 (5)
H5A	0.369542	0.750866	0.113268	0.080*
H5B	0.359665	0.678614	0.054576	0.080*

Source of material

The title compound was synthesized by the one-pot method according to the following procedure: 6-phenylpyridine-2-carboxylic acid (0.0996 g, 0.5 mmol), NaOH (0.020 g, 0.5 mmol), $Co(CH_3COO)_2 \cdot 4H_2O$ (0.1245 g, 0.5 mmol), and 2,2'-bipyridine (0.078 g, 0.5 mmol) were dissolved in a mixed solvent of 20 mL of water and ethanol (v:v = 1:1) at room temperature. The solution immediately turns light amaranth. The reaction mixture then continued to react with stirring for 4.5 h at 75 °C. Then the reaction mixture was cooled to room temperature and filtered. The light red crystals of the title compound were obtained from the above filtrate after 10 days.

Experimental details

Coordinates of hydrogen atoms were refined using different models. The hydrogen atoms were positioned geometrically ($C-H = 0.93 \text{ \AA}$ and $O-H = 0.85 \text{ \AA}$). Their U_{iso} values were set to $1.2U_{eq}$ or $1.5U_{eq}$ of the parent atoms.

Comment

Many studies have shown that some metal complexes show excellent potential applications [5]. As an important class of metal complexes, cobalt(II) complexes have also especially shown excellent properties in many aspects such as catalytic for the electrochemical reduction of CO_2 , DNA binding and antibacterial activity, magnetic property and redox property,

large zero-field splittings, and single-ion magnets [6–8]. 2,2'-Bipyridine plays a significant role as a second ligand in many complexes [9]. Some complexes of Mn(II), Pb(II), Cu(II), Zn(II) and Co(II) have been synthesized and structural characterized with 6-phenylpyridine-2-carboxylate as an excellent ligand in our group [10–14]. In this paper, we present a new Co(II) complex, which was synthesized using $Co(CH_3COO)_2 \cdot 4H_2O$, 2,2'-bipyridine, 6-phenylpyridine-2-carboxylic acid, and NaOH.

Analysis of the crystal structure data shows that the Co(II) complex contains a Co(II) ion, two 6-phenylpyridine-2-carboxylate ligands, a 2,2'-bipyridine ligand, and a lattice water molecule (see the Figure). The Co(II) ion adopts a distorted octahedral coordination mode by coordinating with two carboxylate oxygen atoms (O2 and O3), two pyridine nitrogen atoms (N3 and N4) of two different 6-phenylpyridine-2-carboxylate ligands and two nitrogen atoms (N2 and N1) of one 2,2'-bipyridine ligand. The bond angles around Co(II) are $101.97(6)^\circ$ (N1–Co1–N3), $78.48(6)^\circ$ (O2–Co1–N3), $82.54(6)^\circ$ (O2–Co1–N4) and $99.06(6)^\circ$ (N1–Co1–N4), respectively, indicating N1, N3, N4 and O2 atoms are at the equatorial plane. And the bond angle of N2–Co1–O3 is $167.71(6)^\circ$, showing N2 and O3 atoms are in the axial position. The Co–N distances fall in the range of $2.1280(16)$ – $2.2378(15)$ Å (Co1–N1), $2.1280(16)$ Å, (Co1–N2), $2.1844(16)$ Å, (Co1–N3), $2.2325(16)$ Å, Co1–N4, $2.2378(15)$ Å and the Co–O distances are $2.0233(14)$ Å (Co1–O2) and $2.0313(14)$ Å (Co1–O3), respectively. The dihedral angles between of ring 1 (C1–C2–C3–C4–C5–C6) and ring 2 (C7–C8–C9–C10–C11–N4), ring 3 (C29–C30–C31–C32–C33–C34) and ring 4 (C24–C25–C26–C27–C28–N3) are 133.4° and 132.4° , respectively, which indicates that each 6-phenylpyridine-2-carboxylate ligand is not coplanar. The complex molecules form 1D chained structure through hydrogen bonds between the water molecule and the 6-phenylpyridine-2-carboxylate ligand.

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