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The crystal structure of tetrakis(6-phenylpyridine-2-carboxylato-κ²N,O)-bis(1*H*-pyrazol-3-ylamine-κ²*N*:*N*)dicobalt(II) dihydrate, $C_{27}H_{23}N_5O_5Co$

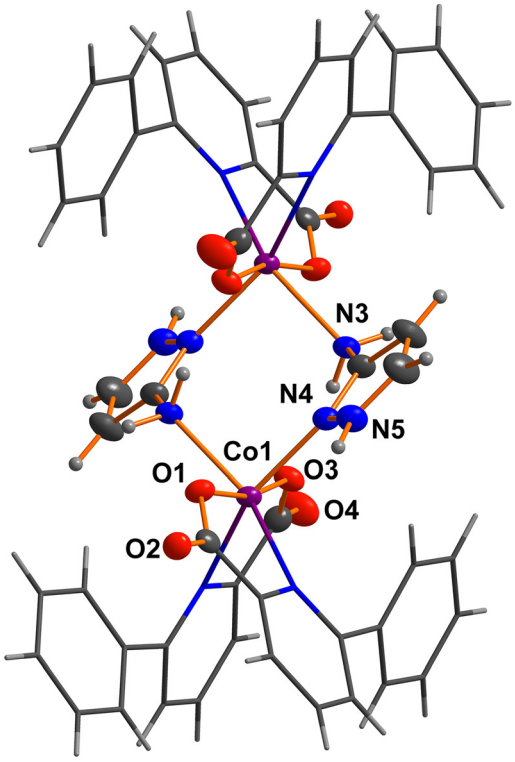

Figure 1: The molecular structure of the title complex.

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Abstract

$C_{27}H_{23}N_5O_5Co$, triclinic, $P\bar{1}$ (no. 2), a = 8.6503(7) Å, b = 11.1188(8) Å, c = 13.2711(11) Å, α = 79.185(7)°, β = 71.970(7)°, γ = 87.951(6)°, V = 1191.85(17) Å^3, Z = 2, $R_{gt}(F)$ = 0.0450, $wR_{ref}(F^2)$ = 0.1143, T = 200 K.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.13 × 0.11 × 0.09 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.77 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7764, 4188, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 3577
$N(param)_{refined}$:	346
Programs:	Bruker [1], Olex2 [2], SHELX [3], Diamond [4]

The molecular structure is shown in the figure (The hydrate water molecule was omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound has been synthesized by following method: 0.0498 g 6-phenylpyridine-2-carboxylic acid (0.25 mmol), 0.0208 g 1*H*-pyrazol-3-ylamine (0.25 mmol), 0.020 g NaOH (0.5 mmol), and 0.0623 g $Co(CH_3COO)_2{\cdot}4H_2O$ (0.25 mmol) were placed in a 100 mL flask containing 20 mL of an ethanol-water solution (v:v = 1:1) under stirring. Then the mixture was gradually heated up to 75 °C and maintained at this temperature for a further 5 h under constant stirring. The reactants were cooled to room temperature and filtered, and the filtrate was placed into a small conical flask to evaporate slowly. The yellow crystals of the title compound were received from the above solution in 20 days.

Experimental details

The hydrogen atoms were positioned geometrically (C–H = 0.93 Å, N–H = 0.86–0.89 Å and O–H = 0.85 Å). Their U_{iso} values were set to 1.2U_{eq} or 1.5U_{eq} of the parent atoms.

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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	0.49294 (4)	0.31008 (3)	0.61683 (3)	0.01887 (15)
O1	0.6220 (2)	0.18818 (17)	0.52693 (15)	0.0223 (4)
O2	0.6744 (2)	−0.00853 (17)	0.51837 (15)	0.0241 (4)
O3	0.3907 (2)	0.46017 (18)	0.67507 (15)	0.0242 (5)
O4	0.3396 (3)	0.5777 (2)	0.79980 (18)	0.0375 (6)
N1	0.5570 (3)	0.3045 (2)	0.77585 (17)	0.0183 (5)
N2	0.3726 (3)	0.1335 (2)	0.70471 (17)	0.0186 (5)
N3	0.3055 (3)	0.5654 (2)	0.49406 (18)	0.0209 (5)
H3A	0.320700	0.551263	0.558554	0.025*
H3B	0.213862	0.606595	0.500734	0.025*
N4	0.3475 (3)	0.3495 (2)	0.50726 (18)	0.0214 (5)
N5	0.3006 (3)	0.2610 (2)	0.46418 (19)	0.0274 (6)
H5	0.328575	0.185799	0.474301	0.033*
C1	0.4729 (3)	0.3911 (3)	0.8275 (2)	0.0204 (6)
C2	0.4512 (3)	0.3934 (3)	0.9349 (2)	0.0279 (7)
H2	0.392887	0.455407	0.967061	0.034*
C3	0.5174 (4)	0.3025 (3)	0.9932 (2)	0.0336 (8)
H3	0.502869	0.300622	1.065901	0.040*
C4	0.6054 (4)	0.2143 (3)	0.9415 (2)	0.0310 (7)
H4	0.651833	0.152426	0.979466	0.037*
C5	0.6258 (3)	0.2167 (3)	0.8328 (2)	0.0218 (6)
C6	0.7304 (3)	0.1267 (3)	0.7765 (2)	0.0218 (6)
C7	0.7266 (4)	0.0051 (3)	0.8262 (3)	0.0332 (8)
H7	0.651011	−0.021332	0.893530	0.040*
C8	0.8332 (5)	−0.0775 (3)	0.7774 (3)	0.0435 (9)
H8	0.828712	−0.159124	0.811258	0.052*
C9	0.9464 (4)	−0.0382 (3)	0.6782 (3)	0.0405 (9)
H9	1.020561	−0.093013	0.646028	0.049*
C10	0.9504 (4)	0.0809 (3)	0.6266 (3)	0.0357 (8)
H10	1.025050	0.106474	0.558859	0.043*
C11	0.8431 (3)	0.1628 (3)	0.6757 (2)	0.0262 (7)
H11	0.846407	0.243750	0.640517	0.031*
C12	0.3946 (3)	0.4857 (3)	0.7640 (2)	0.0238 (6)
C13	0.5959 (3)	0.0735 (3)	0.5618 (2)	0.0190 (6)
C14	0.4560 (3)	0.0397 (3)	0.6644 (2)	0.0199 (6)
C15	0.4210 (3)	−0.0809 (3)	0.7131 (2)	0.0248 (7)
H15	0.481159	−0.143167	0.682459	0.030*
C16	0.2952 (4)	−0.1077 (3)	0.8083 (2)	0.0289 (7)
H16	0.268560	−0.188412	0.842949	0.035*
C17	0.2102 (4)	−0.0131 (3)	0.8509 (2)	0.0288 (7)
H17	0.126389	−0.029551	0.915762	0.035*
C18	0.2484 (3)	0.1076 (3)	0.7977 (2)	0.0223 (6)
C19	0.1523 (3)	0.2081 (3)	0.8431 (2)	0.0230 (6)
C20	0.1152 (4)	0.2094 (3)	0.9535 (2)	0.0295 (7)
H20	0.155658	0.148799	0.996501	0.035*
C21	0.0202 (4)	0.2987 (3)	0.9992 (3)	0.0337 (8)
H21	−0.001831	0.298669	1.072336	0.040*
C22	−0.0424 (4)	0.3880 (3)	0.9371 (3)	0.0373 (8)
H22	−0.108748	0.447336	0.968275	0.045*
C23	−0.0059 (4)	0.3890 (3)	0.8280 (3)	0.0379 (8)
H23	−0.046366	0.450235	0.785551	0.045*
C24	0.0904 (3)	0.2995 (3)	0.7811 (2)	0.0293 (7)
H24	0.113525	0.300839	0.707638	0.035*
C25	0.2783 (3)	0.4509 (3)	0.4709 (2)	0.0217 (6)
C26	0.1872 (4)	0.4273 (3)	0.4064 (3)	0.0324 (8)
H26	0.127291	0.482469	0.372547	0.039*
C27	0.2053 (4)	0.3056 (3)	0.4039 (3)	0.0358 (8)
H27	0.159630	0.261291	0.366945	0.043*
O5	0.1389 (3)	0.7012 (2)	0.6789 (2)	0.0395 (6)
H5A	0.194914	0.666534	0.718207	0.059*
H5B	0.201114	0.745526	0.622613	0.059*

Comment

The studying on the structure and properties of metal complexes has been one of the scientific hotspots [5–9]. 6-Phenylpyridine-2-carboxylate is a bidentate ligand with very strong coordination capacity, some complexes using it as a ligand have been synthesized and structurally characterized in previous studies of our group [10–14]. In this paper, another new dinuclear Co(II) complex has been synthesized using $Co(CH_3COO)_2{\cdot}4H_2O$, 1*H*-pyrazol-3-ylamine, 6-phenylpyridine-2-carboxylic acid, and NaOH. The results of structural analysis show that the dinuclear Co(II) complex contains two Co(II) ions, four 6-phenylpyridine-2-carboxylate ligands, two 1*H*-pyrazol-3-ylamine ligands (Figure 1). Two Co(II) ions are bridged by nitrogen atoms of two 1*H*-pyrazol-3-ylamine ligands. Each Co(II) ion is six-coordinated with two nitrogen atoms and two oxygen atoms of two different 6-phenylpyridine-2-carboxylate ligands, and two nitrogen atoms of two different 1*H*-pyrazol-3-ylamine ligands, forming a distorted CoN_4O_2 octahedron with O1 and O3 atoms in the axial position (O1–Co1–O3, 166.67(8)°). The Co–N distances are 2.178(2)–2.332(2) Å (Co1–N1, 2.332(2) Å; Co1–N2, 2.199(2) Å; Co1–N3a, 2.223(2) Å; Co1–N4, 2.178(2) Å) and the Co–O distances are 2.0299(19)–2.0446(19) Å (Co1–O1, 2.0446(19) Å, and Co1–O3, 2.0299(19) Å). The complex molecules are connected to each other through N–H···O hydrogen bonds between the 1*H*-pyrazol-3-ylamine molecules and the 6-phenylpyridine-2-carboxylate ligands to form a 1D chained structure.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. SAINT and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2000.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Brandenburg K. *DIAMOND*. Visual Crystal Structure Information System (ver. 3.2); Crystal Impact: Bonn, Germany, 2012.
5. Williams C.-K., Nozaki K. Metal complexes for catalytic polymerizations. *Inorg. Chem.* 2020, *59*, 957–959.
6. Chipman J.-A., Berry J.-F. Paramagnetic metal-metal bonded heterometallic complexes. *Chem. Rev.* 2020, *120*, 2409–2447.
7. Balch A.-L., Winkler K. Electrochemistry of fullerene/transition metal complexes: three decades of progress. *Coord. Chem. Rev.* 2021, *438*, 213623.
8. Liang J., Sun D.-J., Yang Y.-Y., Li M.-X., Li H., Chen L.-X. Discovery of metal-based complexes as promising antimicrobial agents. *Eur. J. Med. Chem.* 2021, *224*, 113696.
9. Wang L.-H., Wang Z.-J., Zhao M.-L., Tai X.-S., Ouyang J., Li Y.-F., Zhang W., Jia W.-L. Synthesis, crystal structure of tetra-nuclear macrocyclic Zn(II) complex and its application as catalyst for oxidation of benzyl alcohol. *Bull. Chem. React. Eng. Catal.* 2021, *16*, 839–846.
10. Tai X.-S., Liang L., Li X.-T., Cao S.-H., Wang L.-H. Crystal structure of diaqua-bis(μ_2-6-phenylpyridine-2-carboxylate-$\kappa^3N,O:O$)-bis(6-phenylpyridine-2-carboxylato-κ^2N,O)lead(II)-*N,N*-dimethylformamide-water (1/2/4), $C_{54}H_{58}N_6O_{16}Pb_2$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1199–1201.
11. Tai X.-S., Wang Z.-J., Ouyang J., Li Y.-F., Zhang W., Jia W.-L., Wang L.-H. The crystal structure of [(phenantroline-κ^2N,N')-bis(6-phenylpyridine-2-carboxylate-κ^2N,O) cobalt(II)] monohydrate, $C_{36}H_{26}N_4O_5Co$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1309–1311.
12. Wang L.-H., Liang L., Li X.-T., Cao S.-H., Tai X.-S. The crystal structure of bis(6-phenylpyridine-2-carboxylato-κ^2N,O)copper(II), $C_{24}H_{16}N_2O_4Cu$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1251–1253.
13. Wang L.-H., Wang Z.-J., Ouyang J., Tai X.-S. The crystal structure of bis(6-phenylpyridine-2-carboxylate-κ^2N,O)-(2,2′-bipyridine-κ^2N,N')zinc(II) monohydrate, $C_{34}H_{26}N_4O_5Zn$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1297–1299.
14. Tai X.-S., Zhang L.-L., Liu L.-L., Cao S.-H., Wang L.-H. The crystal structure of bis(ethanol-κO)-bis(6-aminopicolinato-κ^2N,O) manganese(II), $C_{16}H_{22}O_6N_4Mn$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 551–552.