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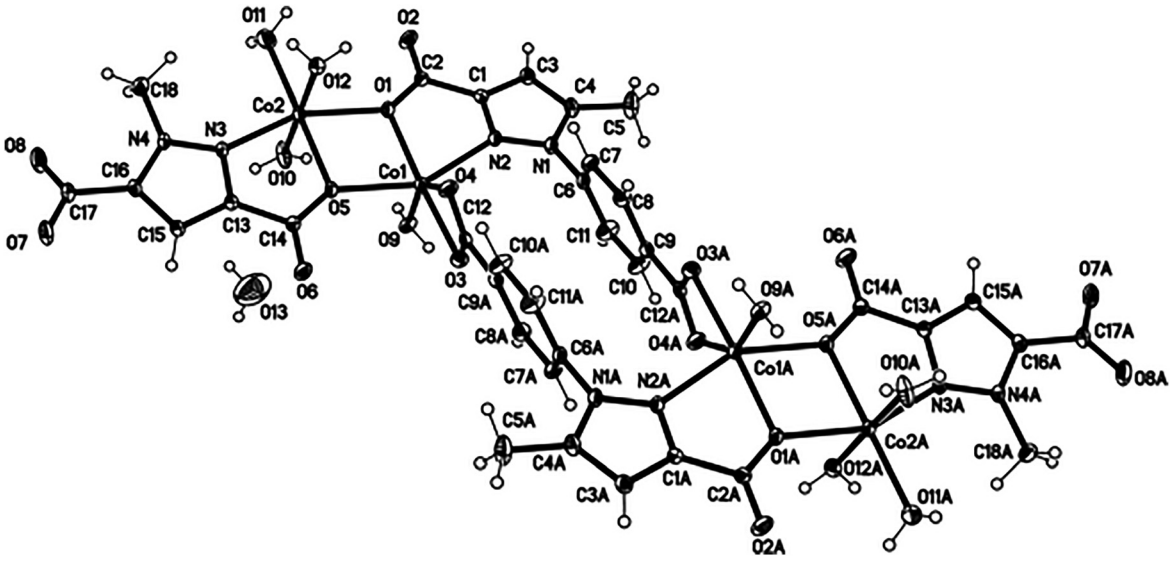
Crystal structure of bis{tetraaqua-[μ_3-1-(4-carboxylatophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate-κ^4*N*,*O*,*O*′,*O*″] [μ_2-1-methyl-1*H*-pyrazole-3,5-dicarboxylate-κ^3*N*,*O*:*O*]dicobalt(II)} dihydrate, $C_{36}H_{44}Co_4N_8O_{26}$



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Abstract

$C_{36}H_{44}Co_4N_8O_{26}$, triclinic, $P\bar{1}$ (no. 2), a = 6.6434(4) Å, b = 9.3788(5) Å, c = 18.5581(10) Å, α = 86.262(2)°, β = 89.642(2)°, γ = 84.726(2)°, V = 1148.96(11) Å^3, Z = 1, $R_{gt}(F)$ = 0.0258, $\omega R_{ref}(F^2)$ = 0.0679, T = 298(2) K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Red block
Size	0.20 × 0.10 × 0.10 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.52 mm^{-1}
Diffractometer, scan mode:	D8/APEX2, φ and ω
θ_{max}, completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20,297, 4047, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 3625
$N(param)_{refined}$:	362
Programs:	Bruker [1], SHELX [2–4]

Source of material

All chemicals were of analytical reagent grade and used without further purification. A mixture of $CoCl_2{\cdot}3H_2O$ (23.79 mg), 1-methyl-1*H*-pyrazole-3,5-dicarboxylic acid (8.50 mg), 1-(4-carboxyphenyl)-5-methyl-1*H*-pyrazole-3-carboxylic acid (12.31 mg) and acetonitrile/water (7 ml, 4:3 *v*/*v*) was placed in a 10 ml of Teflon-lined stainless steel autoclave. The mixture was heated under autogenous

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.66778 (4)	0.97162 (3)	0.78788 (2)	0.01982 (10)
Co2	0.35973 (4)	0.82898 (3)	0.67826 (2)	0.02136 (11)
N1	0.6016 (3)	1.28006 (19)	0.86620 (9)	0.0225 (4)
N2	0.5469 (3)	1.17501 (19)	0.82572 (9)	0.0218 (4)
N3	0.4444 (3)	0.61450 (18)	0.65212 (9)	0.0218 (4)
N4	0.3857 (3)	0.51414 (19)	0.61090 (10)	0.0228 (4)
O1	0.3899 (2)	1.01804 (15)	0.73253 (8)	0.0250 (3)
O2	0.1498 (2)	1.19325 (17)	0.69983 (10)	0.0347 (4)
O3	0.9426 (2)	0.94360 (17)	0.84150 (8)	0.0259 (3)
O4	0.6853 (2)	0.85687 (18)	0.89722 (8)	0.0300 (4)
O5	0.6376 (2)	0.78030 (15)	0.73479 (8)	0.0230 (3)
O6	0.8945 (2)	0.60952 (17)	0.75290 (10)	0.0372 (4)
O7	0.6324 (3)	0.16567 (16)	0.58259 (9)	0.0354 (4)
O8	0.3871 (3)	0.28348 (19)	0.51632 (9)	0.0420 (5)
O9	0.8147 (3)	1.05724 (18)	0.69944 (9)	0.0272 (4)
H9A	0.755 (4)	1.099 (3)	0.6636 (16)	0.041*
H9B	0.910 (5)	1.100 (3)	0.7041 (15)	0.041*
O10	0.4990 (3)	0.9012 (2)	0.58680 (10)	0.0419 (5)
H10A	0.525 (5)	0.983 (4)	0.5791 (18)	0.063*
H10B	0.534 (5)	0.853 (4)	0.5557 (18)	0.063*
O11	0.0800 (3)	0.8644 (2)	0.62734 (12)	0.0458 (5)
H11A	0.080 (6)	0.881 (4)	0.588 (2)	0.069*
H11B	−0.005 (6)	0.916 (4)	0.6459 (19)	0.069*
O12	0.2070 (3)	0.7633 (2)	0.77004 (9)	0.0306 (4)
H12A	0.157 (5)	0.829 (3)	0.7901 (16)	0.046*
H12B	0.122 (5)	0.715 (3)	0.7644 (16)	0.046*
C1	0.3926 (3)	1.2360 (2)	0.78555 (11)	0.0195 (4)
C2	0.2998 (3)	1.1452 (2)	0.73472 (11)	0.0207 (4)
C3	0.3454 (3)	1.3784 (2)	0.80075 (11)	0.0236 (5)
H3	0.2436	1.4425	0.7800	0.028*
C4	0.4809 (4)	1.4045 (2)	0.85283 (11)	0.0250 (5)
C5	0.5043 (5)	1.5358 (3)	0.89196 (15)	0.0453 (7)
H5A	0.4585	1.5216	0.9408	0.068*
H5B	0.4254	1.6161	0.8683	0.068*
H5C	0.6440	1.5543	0.8919	0.068*
C6	0.7384 (3)	1.2442 (2)	0.92584 (11)	0.0219 (5)
C7	0.6727 (3)	1.1625 (2)	0.98403 (12)	0.0266 (5)
H7	0.5431	1.1324	0.9843	0.032*
C8	0.8006 (3)	1.1255 (2)	1.04207 (12)	0.0267 (5)
H8	0.7568	1.0703	1.0815	0.032*
C9	0.9936 (3)	1.1703 (2)	1.04177 (11)	0.0220 (4)
C10	1.0563 (4)	1.2544 (3)	0.98329 (13)	0.0344 (6)
H10	1.1850	1.2859	0.9833	0.041*
C11	0.9294 (4)	1.2923 (3)	0.92479 (13)	0.0356 (6)
H11	0.9717	1.3490	0.8856	0.043*
C12	0.8680 (3)	0.8778 (2)	0.89619 (11)	0.0225 (5)
C13	0.6274 (3)	0.5655 (2)	0.67772 (11)	0.0205 (4)
C14	0.7322 (3)	0.6566 (2)	0.72584 (12)	0.0220 (5)
C15	0.6866 (3)	0.4314 (2)	0.65280 (12)	0.0230 (5)
H15	0.8065	0.3746	0.6629	0.028*
C16	0.5295 (3)	0.4007 (2)	0.60995 (11)	0.0208 (4)
C17	0.5113 (3)	0.2743 (2)	0.56610 (11)	0.0238 (5)
C18	0.1852 (4)	0.5329 (3)	0.57843 (16)	0.0411 (7)
H18A	0.1005	0.6010	0.6041	0.062*
H18B	0.1274	0.4426	0.5809	0.062*
H18C	0.1955	0.5675	0.5288	0.062*
O13	0.9803 (5)	0.8594 (5)	0.48894 (18)	0.1423 (16)
H13A	1.0758	0.8364	0.4635	0.213*
H13B	0.8810	0.8219	0.4785	0.213*

pressure at 433 K for 72 h and then cooled to room temperature. Red block crystals were collected by filtration, washed with H_2O, and dried in air with 63% yield.

Experimental details

The multi-scan program SADABS [1] was used for absorption correction. The structures were solved by direct methods and refined using SHELXS-97 [2, 3] and SHELXL-2014/7 [4]. Hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, with C—H = 0.96 Å and U_{iso}(H) = 1.2U_{eq}(C). Hydrogen atoms attached to O atoms were located from difference Fourier maps and refined using U_{iso}(H) = 1.5U_{eq}(O).

Comment

Polycarboxylate ligands have been shown to be building blocks in the design of coordination polymers with desired topologies due to their rich coordination modes. For example, the aromatic polycarboxylate ligands, such as pyridine-, pyrazole-, pyrazine-, imidazole- and benzenecarboxylates have been widely used to construct different coordination polymers because of the diversity of coordination modes and sensitivity to pH [5–7]. Among them, pyrazole-3,5-dicarboxylate is one of the excellent N/O mixed ligands for the construction of various coordination polymers due to its unique coordination behaviors [8]. In order to search for new coordination polymers based on pyrazole-3,5-dicarboxylates the title complex has been synthesized and characterized.

The asymmetric unit of the title complex **1**, consists of two Co^{II} cations, one deprotonated 1-(4-carboxyphenyl)-5-methyl-1*H*-pyrazole-3-carboxylate anion, one deprotonated 1-methyl-1*H*-pyrazole-3,5-dicarboxylate anion, four coordinated water molecules and one lattice water molecule. The coordination geometries of the Co^{II} cations are both distorted octahedra but the two Co^{II} cations have different coordination environments. The $Co1^{II}$ cation is coordinated by one N atom from one 1-(4-carboxylatephenyl)-5-methyl-1*H*-pyrazole-3-carboxylate ligand, five O atoms from one coor-

dinated water molecule, one 1-methyl-1*H*-pyrazole-3, 5-dicarboxylate ligand and two 1-(4-carboxylatephenyl)-5-methyl-1*H*-pyrazole-3-carboxylate ligands. The six-coordinated $Co2^{II}$ cation is surrounded by one N atom from one 1-methyl-1*H*-pyrazole-3,5-dicarboxylate ligand and five O atoms from three coordinated water molecules, one 1-methyl-1*H*-pyrazole-3,5-dicarboxylate ligand and one 1-(4-carboxylatephenyl)-5-methyl-1*H*-pyrazole-3-carboxylate ligand (see the Figure). The bond lengths of Co—O range from 2.0631 (16) to 2.2329(17) Å, which are all within the normal ranges [9, 10]. Interestingly, in the structure, the neighboring cobalt ions bridged by two O atoms from carboxylates groups of pyrazole-carboxylate of two ligands form Co_2O_2 units. The ligand 1-(4-carboxylatephenyl)-5-methyl-1*H*-pyrazole-3-carboxylate is the same as in the Cd compound $[CdL(H_2O)]\cdot 1DMF\cdot 1.5H_2O$ [11]. However the ligand exhibits a different coordination mode, in which the carboxylate group of pyrazole-carboxylate adopts μ_2-η^1:η^1 bidentate mode while exhibits η^1:η^0 monodentate mode in **1**. In the crystal, intermolecular O—H···O hydrogen bonds involving the carboxylate oxygen atoms and water molecules link the tetranuclear complexes into a three-dimensional network.

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

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