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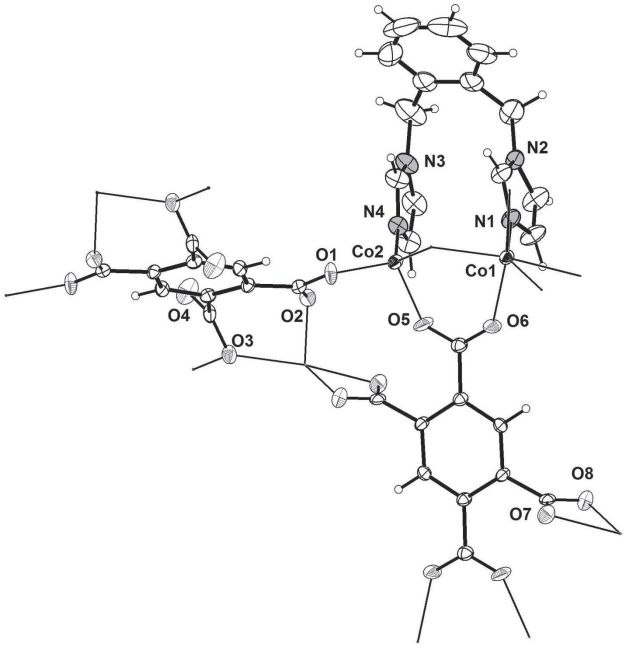
Crystal structure of poly-[(μ_6-benzene-1,2,4,5-tetracarboxylato)-(μ_2-1,2-bis(imidazol-1-ylmethyl)benzene)dicobalt(II)], $Co_2C_{24}H_{16}N_4O_8$



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Abstract

$Co_2C_{24}H_{16}N_4O_8$, triclinic, $P\bar{1}$ (no. 2), $a = 7.3859(13)$ Å, $b = 9.5719(17)$ Å, $c = 16.442(3)$ Å, $\alpha = 77.450(3)°$, $\beta = 85.065(3)°$, $\gamma = 84.844(3)°$, $V = 1127.4(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0457$, $wR_{ref}(F^2) = 0.1058$, $T = 296(2)$ K.

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A part of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.28 × 0.26 × 0.22 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	15.3 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, ω-scans
$2\theta_{max}$, completeness:	57°, >98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7302, 5323, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3694
$N(param)_{refined}$:	343
Programs:	Bruker SADABS, SMART, SAINT [9, 10], SHELX [11], OLEX2 [12]

Source of material

A mixture of $CoCl_2{\cdot}4H_2O$ (0.048 g, 0.2 mmol), 1,2-bis(imidazole-1-ylmethyl)benzene (1,2-BIB) (0.046 g 0.2 mmol), benzene-1,2,4,5-tetracarboxylic acid (BTA)(0.025 g, 0.1 mmol), NaOH (0.008 g, 0.2 mmol) and H_2O (10 mL) were stirred for about 30 min. The resulting solution was sealed in a Teflon-lined stainless autoclave and heated to 423 K for 3 days. The autoclave was cooled to ambient temperature spontaneously. Red single crystals (about 86%, based on Co input) were recovered by vacuum filtration and drying in air.

Experimental details

C-bound H atoms were geometrically placed (C—H = 0.95 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

Discussion

The design and synthesis of coordination polymers (CPs) and especially metal organic frameworks (MOFs) have developed rapidly owing to applications of these materials in a variety of fields [1, 2]. The 1, 2-bis(imidazole-1-ylmethyl)benzene (1,2-BIB) is an important semi-flexible N-donor ligand, and some fascinating archetypal structures

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.97356(6)	0.20552(5)	0.69818(3)	0.01958(12)
Co2	0.52786(6)	0.24612(4)	0.77168(3)	0.01901(12)
O1	0.3776(3)	0.1168(3)	0.85465(14)	0.0284(6)
O2	0.1343(3)	0.2298(2)	0.79471(13)	0.0243(5)
O3	−0.2199(3)	0.1467(3)	0.80040(13)	0.0273(5)
O4	−0.3165(4)	0.2724(3)	0.89311(16)	0.0414(7)
O5	0.5147(3)	0.1919(3)	0.66590(15)	0.0357(6)
O6	0.8000(3)	0.1405(3)	0.62196(15)	0.0338(6)
O7	0.8361(3)	−0.2341(2)	0.40639(14)	0.0277(5)
O8	0.8304(3)	−0.0250(2)	0.32035(14)	0.0292(6)
N1	0.9002(4)	0.4218(3)	0.67857(17)	0.0293(7)
N2	0.8709(5)	0.6465(3)	0.6898(2)	0.0380(8)
N3	0.4485(5)	0.6773(3)	0.7657(2)	0.0452(9)
N4	0.4497(4)	0.4555(3)	0.75251(18)	0.0293(7)
C1	0.8631(7)	0.5072(4)	0.6030(2)	0.0514(12)
H1	0.8518	0.4743	0.5546	0.062*
C2	0.8454(7)	0.6452(4)	0.6087(3)	0.0588(14)
H2	0.8206	0.7243	0.5661	0.071*
C3	0.9062(5)	0.5108(4)	0.7282(2)	0.0337(9)
H3	0.9322	0.4823	0.7839	0.040*
C4	0.8694(7)	0.7777(4)	0.7230(3)	0.0585(14)
H4A	0.7796	0.8487	0.6956	0.070*
H4B	0.9878	0.8167	0.7100	0.070*
C5	0.8261(6)	0.7508(4)	0.8154(3)	0.0440(11)
C6	0.9678(7)	0.7111(5)	0.8661(4)	0.0608(14)
H6	1.0862	0.7064	0.8419	0.073*
C7	0.9410(10)	0.6787(6)	0.9502(4)	0.083(2)
H7	1.0402	0.6521	0.9828	0.100*
C8	0.7716(13)	0.6848(6)	0.9868(4)	0.089(2)
H8	0.7535	0.6601	1.0446	0.107*
C9	0.6258(9)	0.7271(5)	0.9390(4)	0.0740(17)
H9	0.5092	0.7330	0.9649	0.089*
C10	0.6494(6)	0.7616(4)	0.8520(3)	0.0468(11)
C11	0.4874(7)	0.7995(4)	0.8015(4)	0.0697(17)
H11A	0.3826	0.8250	0.8365	0.084*
H11B	0.5098	0.8819	0.7568	0.084*
C12	0.3714(6)	0.6798(4)	0.6941(3)	0.0538(13)
H12	0.3267	0.7611	0.6572	0.065*
C13	0.3710(6)	0.5434(4)	0.6858(3)	0.0449(11)
H13	0.3249	0.5136	0.6420	0.054*
C14	0.4939(5)	0.5405(4)	0.7987(3)	0.0382(10)
H14	0.5503	0.5091	0.8486	0.046*
C15	0.2079(4)	0.1408(3)	0.85219(19)	0.0200(7)
C16	0.0955(4)	0.0644(3)	0.92556(18)	0.0174(6)
C17	−0.0938(4)	0.0868(3)	0.93520(18)	0.0189(7)
C18	−0.1850(4)	0.0228(3)	1.00859(19)	0.0198(7)
H18	−0.3111	0.0384	1.0143	0.024*
C19	−0.2126(4)	0.1787(4)	0.87221(19)	0.0225(7)
C20	0.6331(4)	0.1410(3)	0.61963(19)	0.0208(7)
C21	0.5612(4)	0.0703(3)	0.55715(18)	0.0179(6)
C22	0.6821(4)	0.0173(3)	0.49966(19)	0.0197(7)
H22	0.8056	0.0296	0.4996	0.024*
C23	0.6248(4)	−0.0526(3)	0.44278(18)	0.0180(7)
C24	0.7692(4)	−0.1082(4)	0.38491(19)	0.0209(7)

based on the 1,2-BIB ligand are reported [3, 4]. 1, 2, 4, 5-benzenetetracarboxylate (BTA) have also been extensively employed in the preparation of CPs [5]. Furthermore, it has been shown that the combination of carboxylate linkers along with semi-flexible N-donor ligands is a good choice for the construction of new CPs [6–8].

As shown in Figure, the asymmetric unit of the title compound contains two unique Co(II) atoms, one 1,2-BIB ligand, and two halves of BTA ligands. The Co1 center is six-coordinated with a distorted-octahedral geometry, defined by five oxygen atoms from three different BTA ligands, and one nitrogen atom from one 1,2-BIB ligand. The Co—N is 2.054(3) Å, and Co—O lengths are in the range of 1.969(2)–2.209(2) Å, which is comparable to values reported for related Co(II) complexes [4]. The Co2 atom is surrounded by one nitrogen donor from one 1,2-BIB ligand, as well as three oxygen atoms from different BTA anions, which exhibits a slightly distorted tetrahedron coordination sphere. The Co—O bond lengths range between 1.933(2) and 2.058(2) Å, while the Co—N bond length is 1.999(3) Å, which are in the normal ranges [4]. Both cyrstallographically independent BTA ligands are coordinated in an octa-dentate, coordination mode. They are located around different inversion centres of the triclinic space group (*cf*. the figure). Two symmetry-related carboxylate groups containing (O7, O8) of a BTA ligand are coordinated to two Co(II) atoms in chelating mode, while the other carboxylat groups are coordinated to four metal atoms in bridge-monodentate mode. The symmetry-related carboxylate groups (O1, O2) of the crystallographically independent BTA ligand act as a μ_2-bridging function to connect two metal atoms in monodentated mode. Each of the two symmetry-related carboxylate groups of this second BTA ligand connect two metal atoms by its O3 and O3′ atom (*cf*. the figure). All these coordinations result in a two dimensional grid structure.

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