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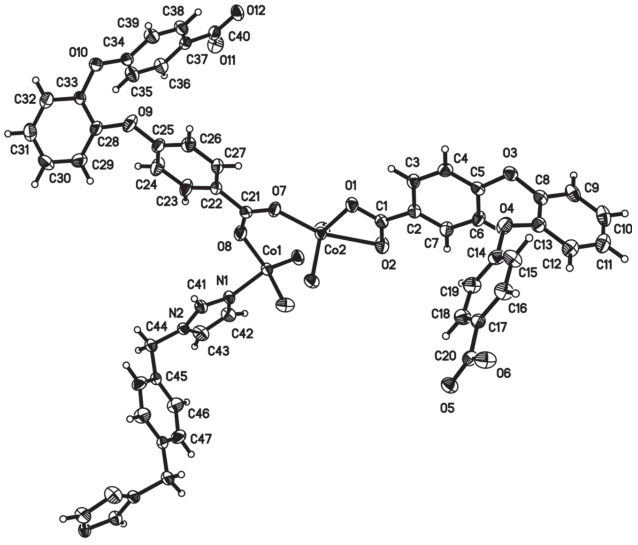
Crystal structure of poly[bis(μ_4-4,4′-(1,2-phenylenebis(oxy))dibenzoato-κ^4 *O*:*O*′:*O*″:*O*‴)bis(μ_3-4,4′-(1,2-phenylenebis(oxy))dibenzoato–κ^3*O*:*O*′:*O*″)(μ_2-1-(4-((1*H*-imidazol-1-yl)methyl)benzyl)-1*H*-imidazole-κ^2*N*:*N*′)tetracobalt(II)], $C_{94}H_{62}O_{24}N_4Co_4$



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Abstract

$C_{94}H_{62}O_{24}N_4Co_4$, triclinic, $P\bar{1}$, $a = 9.3604(11)$ Å, $b = 11.7945(14)$ Å, $c = 19.805(2)$ Å, $\alpha = 94.227(2)°$, $\beta = 98.390(2)°$, $\gamma = 98.965(2)°$, $V = 2126.2(4)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0540$, $wR_{ref}(F^2) = 0.1163$, $T = 293$ K.

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The crystal structure is shown in the figure, Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Pink, Block, size 0.19×0.22×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.47 cm^{-1}
Diffractometer, scan mode:	Bruker APEXII CCD, φ and ω scans
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11706, 8263
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5040
$N(param)_{refined}$:	568
Programs:	SHELXTL [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	2*i*	0.5841	0.4461	0.2019	0.049
H(4)	2*i*	0.8110	0.5566	0.2071	0.052
H(6)	2*i*	0.9862	0.3613	0.3424	0.055
H(7)	2*i*	0.7581	0.2493	0.3368	0.057
H(9)	2*i*	1.2928	0.4537	0.2812	0.062
H(10)	2*i*	1.4789	0.4756	0.3736	0.074
H(11)	2*i*	1.4630	0.5848	0.4727	0.074
H(12)	2*i*	1.2568	0.6665	0.4820	0.064
H(15)	2*i*	1.1265	0.8584	0.4476	0.072
H(16)	2*i*	1.0696	0.9391	0.5485	0.066
H(18)	2*i*	0.7812	0.6529	0.5560	0.061
H(19)	2*i*	0.8439	0.5721	0.4574	0.064
H(23)	2*i*	−0.3361	0.0819	0.1155	0.070
H(24)	2*i*	−0.5008	0.1638	0.0443	0.078
H(26)	2*i*	−0.1987	0.4472	0.0541	0.058
H(27)	2*i*	−0.0353	0.3640	0.1240	0.053
H(29)	2*i*	−0.6427	0.3186	0.0884	0.090
H(30)	2*i*	−0.8914	0.2530	0.0602	0.109
H(31)	2*i*	−1.0029	0.2392	−0.0520	0.106
H(32)	2*i*	−0.8675	0.2821	−0.1369	0.070
H(35)	2*i*	−0.5926	0.1378	−0.1231	0.061
H(36)	2*i*	−0.4210	0.0349	−0.1576	0.058
H(38)	2*i*	−0.1827	0.3259	−0.1986	0.059
H(39)	2*i*	−0.3529	0.4299	−0.1627	0.060
H(41)	2*i*	−0.3318	0.0207	0.2994	0.049
H(42)	2*i*	−0.2037	−0.2787	0.2999	0.061
H(43)	2*i*	−0.4331	−0.2972	0.3448	0.067
H(44A)	2*i*	−0.6326	−0.1604	0.3509	0.058
H(44B)	2*i*	−0.5921	−0.0358	0.3292	0.058
H(46)	2*i*	−0.4395	−0.1759	0.4710	0.071
H(47)	2*i*	−0.4061	−0.1046	0.5842	0.070

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.5033(5)	0.2596(4)	0.2623(2)	0.040(2)	0.042(3)	0.050(3)	0.009(2)	0.014(2)	0.008(2)
C(2)	2*i*	0.6481(4)	0.3339(3)	0.2684(2)	0.037(2)	0.028(2)	0.048(2)	0.004(2)	0.007(2)	0.007(2)
C(3)	2*i*	0.6648(4)	0.4282(3)	0.2298(2)	0.037(2)	0.037(2)	0.050(3)	0.008(2)	0.006(2)	0.008(2)
C(4)	2*i*	0.7999(4)	0.4942(4)	0.2331(2)	0.049(3)	0.036(2)	0.044(2)	0.004(2)	0.006(2)	0.012(2)
C(5)	2*i*	0.9186(4)	0.4693(3)	0.2743(2)	0.040(2)	0.029(2)	0.040(2)	−0.002(2)	0.011(2)	−0.002(2)
C(6)	2*i*	0.9052(4)	0.3777(4)	0.3139(2)	0.039(2)	0.041(3)	0.055(3)	0.004(2)	−0.004(2)	0.014(2)
C(7)	2*i*	0.7687(4)	0.3111(4)	0.3103(2)	0.041(2)	0.038(2)	0.062(3)	0.003(2)	0.004(2)	0.020(2)
C(8)	2*i*	1.1629(4)	0.5448(3)	0.3269(2)	0.040(2)	0.027(2)	0.050(3)	−0.008(2)	0.008(2)	0.003(2)
C(9)	2*i*	1.2853(5)	0.4960(4)	0.3217(3)	0.047(3)	0.037(3)	0.075(3)	0.003(2)	0.023(3)	0.008(2)
C(10)	2*i*	1.3966(5)	0.5098(4)	0.3765(3)	0.042(3)	0.039(3)	0.108(4)	0.008(2)	0.019(3)	0.019(3)
C(11)	2*i*	1.3865(5)	0.5745(4)	0.4359(3)	0.048(3)	0.046(3)	0.085(4)	−0.005(2)	−0.007(3)	0.025(3)
C(12)	2*i*	1.2637(5)	0.6241(4)	0.4414(2)	0.056(3)	0.041(3)	0.059(3)	0.002(2)	0.002(2)	0.002(2)
C(13)	2*i*	1.1514(4)	0.6103(4)	0.3865(2)	0.043(2)	0.041(3)	0.048(3)	0.001(2)	0.004(2)	0.006(2)
C(14)	2*i*	0.9931(5)	0.7059(4)	0.4449(2)	0.061(3)	0.053(3)	0.038(2)	0.020(2)	0.006(2)	0.000(2)
C(15)	2*i*	1.0589(5)	0.8168(4)	0.4704(2)	0.063(3)	0.057(3)	0.061(3)	0.002(3)	0.026(3)	0.002(3)
C(16)	2*i*	1.0233(5)	0.8654(4)	0.5302(2)	0.066(3)	0.041(3)	0.053(3)	−0.002(2)	0.012(2)	−0.004(2)
C(17)	2*i*	0.9188(4)	0.8045(3)	0.5628(2)	0.038(2)	0.036(2)	0.041(2)	0.003(2)	0.006(2)	0.009(2)
C(18)	2*i*	0.8520(5)	0.6943(4)	0.5347(2)	0.052(3)	0.045(3)	0.050(3)	−0.007(2)	0.009(2)	0.008(2)
C(19)	2*i*	0.8894(5)	0.6459(4)	0.4759(2)	0.062(3)	0.044(3)	0.049(3)	−0.004(2)	0.007(2)	−0.001(2)
C(20)	2*i*	0.8861(5)	0.8540(4)	0.6287(2)	0.042(2)	0.039(3)	0.040(2)	0.009(2)	0.003(2)	0.006(2)
C(21)	2*i*	−0.0648(5)	0.1624(4)	0.1754(2)	0.042(3)	0.058(3)	0.042(2)	0.019(2)	0.013(2)	0.016(2)
C(22)	2*i*	−0.1691(4)	0.2139(4)	0.1273(2)	0.036(2)	0.057(3)	0.044(2)	0.018(2)	0.007(2)	0.013(2)
C(23)	2*i*	−0.3083(5)	0.1558(4)	0.1032(3)	0.041(3)	0.049(3)	0.084(4)	0.008(2)	−0.003(2)	0.027(3)
C(24)	2*i*	−0.4076(5)	0.2045(4)	0.0613(3)	0.045(3)	0.055(3)	0.088(4)	0.002(2)	−0.012(3)	0.022(3)
C(25)	2*i*	−0.3656(5)	0.3151(4)	0.0450(2)	0.045(3)	0.055(3)	0.043(2)	0.017(2)	−0.001(2)	0.008(2)
C(26)	2*i*	−0.2267(5)	0.3738(4)	0.0671(2)	0.051(3)	0.039(3)	0.056(3)	0.014(2)	0.008(2)	0.009(2)
C(27)	2*i*	−0.1293(4)	0.3238(4)	0.1084(2)	0.037(2)	0.045(3)	0.052(3)	0.012(2)	0.006(2)	0.005(2)
C(28)	2*i*	−0.6068(5)	0.3339(4)	−0.0073(2)	0.045(3)	0.057(3)	0.046(3)	0.023(2)	0.003(2)	0.008(2)
C(29)	2*i*	−0.6875(6)	0.3098(5)	0.0428(3)	0.079(4)	0.116(5)	0.044(3)	0.052(4)	0.016(3)	0.019(3)
C(30)	2*i*	−0.8360(7)	0.2722(6)	0.0261(3)	0.079(4)	0.140(6)	0.084(4)	0.054(4)	0.053(4)	0.051(4)
C(31)	2*i*	−0.9021(6)	0.2631(6)	−0.0409(3)	0.047(3)	0.124(6)	0.110(5)	0.032(3)	0.025(3)	0.054(4)
C(32)	2*i*	−0.8220(5)	0.2887(4)	−0.0914(3)	0.049(3)	0.066(3)	0.061(3)	0.017(3)	0.000(2)	0.012(3)
C(33)	2*i*	−0.6734(4)	0.3242(4)	−0.0748(2)	0.042(2)	0.044(3)	0.046(3)	0.021(2)	0.014(2)	0.010(2)
C(34)	2*i*	−0.4885(4)	0.2936(4)	−0.1405(2)	0.043(2)	0.045(3)	0.039(2)	0.016(2)	0.011(2)	0.006(2)
C(35)	2*i*	−0.5102(5)	0.1755(4)	−0.1384(2)	0.047(3)	0.038(3)	0.071(3)	0.006(2)	0.021(2)	0.007(2)
C(36)	2*i*	−0.4076(4)	0.1144(4)	−0.1593(2)	0.048(3)	0.033(2)	0.065(3)	0.005(2)	0.015(2)	0.004(2)
C(37)	2*i*	−0.2860(4)	0.1685(3)	−0.1823(2)	0.037(2)	0.040(2)	0.037(2)	0.009(2)	0.002(2)	0.001(2)
C(38)	2*i*	−0.2652(5)	0.2880(4)	−0.1835(2)	0.044(2)	0.046(3)	0.062(3)	0.007(2)	0.020(2)	0.012(2)
C(39)	2*i*	−0.3670(5)	0.3502(4)	−0.1622(2)	0.056(3)	0.033(2)	0.066(3)	0.009(2)	0.022(2)	0.014(2)
C(40)	2*i*	−0.1817(5)	0.1022(4)	−0.2086(2)	0.040(2)	0.058(3)	0.042(3)	0.015(2)	0.001(2)	−0.004(2)
C(41)	2*i*	−0.3276(4)	−0.0563(4)	0.3051(2)	0.040(2)	0.032(2)	0.052(3)	0.002(2)	0.013(2)	0.009(2)
C(42)	2*i*	−0.2583(5)	−0.2202(4)	0.3053(2)	0.060(3)	0.035(2)	0.062(3)	0.013(2)	0.020(2)	0.012(2)
C(43)	2*i*	−0.3842(5)	−0.2307(4)	0.3304(2)	0.065(3)	0.030(2)	0.074(3)	−0.002(2)	0.023(3)	0.014(2)
C(44)	2*i*	−0.5559(4)	−0.0933(4)	0.3566(2)	0.034(2)	0.063(3)	0.046(3)	0.001(2)	0.010(2)	0.007(2)
C(45)	2*i*	−0.5242(4)	−0.0456(4)	0.4311(2)	0.029(2)	0.051(3)	0.041(2)	0.006(2)	0.007(2)	0.010(2)
C(46)	2*i*	−0.4653(5)	−0.1047(4)	0.4824(2)	0.077(3)	0.052(3)	0.052(3)	0.025(3)	0.007(3)	0.002(2)
C(47)	2*i*	−0.4432(5)	−0.0614(4)	0.5505(2)	0.067(3)	0.067(3)	0.047(3)	0.032(3)	0.005(2)	0.018(2)
N(1)	2*i*	−0.2224(3)	−0.1101(3)	0.2888(2)	0.032(2)	0.037(2)	0.049(2)	0.002(2)	0.008(2)	0.006(2)
N(2)	2*i*	−0.4271(3)	−0.1262(3)	0.3308(2)	0.035(2)	0.042(2)	0.039(2)	0.002(2)	0.008(2)	0.005(2)
O(1)	2*i*	0.3936(3)	0.2891(2)	0.2252(1)	0.035(2)	0.044(2)	0.059(2)	0.003(1)	0.007(1)	0.013(1)
O(2)	2*i*	0.4851(3)	0.1702(3)	0.2921(2)	0.044(2)	0.045(2)	0.083(2)	0.001(2)	0.008(2)	0.024(2)
O(3)	2*i*	1.0536(3)	0.5351(2)	0.2709(1)	0.043(2)	0.042(2)	0.047(2)	−0.008(1)	0.011(1)	0.002(1)
O(4)	2*i*	1.0260(3)	0.6567(3)	0.3843(2)	0.055(2)	0.081(2)	0.045(2)	0.030(2)	0.001(2)	−0.007(2)
O(5)	2*i*	0.8005(3)	0.7940(3)	0.6594(1)	0.050(2)	0.049(2)	0.048(2)	−0.000(2)	0.014(2)	0.003(1)
O(6)	2*i*	0.9498(4)	0.9555(3)	0.6497(2)	0.082(2)	0.041(2)	0.047(2)	−0.005(2)	0.012(2)	−0.003(1)
O(7)	2*i*	0.0647(3)	0.2121(3)	0.1904(2)	0.036(2)	0.058(2)	0.058(2)	0.011(2)	−0.000(1)	0.017(2)
O(8)	2*i*	−0.1162(3)	0.0676(3)	0.1964(2)	0.042(2)	0.068(2)	0.074(2)	0.014(2)	0.006(2)	0.033(2)
O(9)	2*i*	−0.4570(3)	0.3739(3)	0.0051(2)	0.053(2)	0.060(2)	0.071(2)	0.017(2)	−0.012(2)	0.021(2)
O(10)	2*i*	−0.5921(3)	0.3590(3)	−0.1253(2)	0.057(2)	0.054(2)	0.054(2)	0.031(2)	0.023(2)	0.020(2)
O(11)	2*i*	−0.2088(4)	−0.0065(3)	−0.2127(2)	0.075(2)	0.040(2)	0.078(2)	0.022(2)	0.009(2)	−0.007(2)
O(12)	2*i*	−0.0677(3)	0.1534(3)	−0.2276(2)	0.043(2)	0.063(2)	0.060(2)	0.016(2)	0.015(2)	−0.002(2)
Co(1)	2*i*	−0.03781(6)	−0.03350(5)	0.26000(3)	0.0341(3)	0.0384(3)	0.0448(3)	0.0063(3)	0.0104(2)	0.0063(3)
Co(2)	2*i*	0.23801(6)	0.17003(5)	0.24628(3)	0.0328(3)	0.0368(3)	0.0453(3)	0.0058(2)	0.0071(2)	0.0096(2)

Source of material

A mixture of 4,4′-(1,2-phenylenebis(oxy))dibenzoic acid (0.2 mmol, 0.086 g), 1-(4-((1*H*-imidazol-1-yl)methyl)-benzyl)-1*H*-imidazole (0.2 mmol, 0.040 g), $CoCl_2 \cdot 6H_2O$, (0.2 mmol, 0.050 g), and H_2O (20 mL) was stirred for ten minutes. The mixtures were transfered in a 25 mL stainless steel reactor with a Teflon liner and heated from 293 to 443 K in 3 h and a constant temperature was maintained at 443 K for 72 h. After cooling to room temperature, pink block-shaped crystals were collected in 58% yield based on the added amounts of $CoCl_2 \cdot 6H_2O$.

Experimental details

All H atoms were refined using a riding model, with C—H distances of 0.93 Å and U_{iso}(H) values of 1.2U_{eq}(C) for aromatic and imidazole rings and 0.97 Å and U_{iso}(H) values of 1.2U_{eq}(C) for methylene groups.

Results and discussion

The assembly of mixed-ligand coordination polymers attracted greatly attention due to their intriguingly complicated architecture and potential applications in adsorption, separation and magnetism [1–5]. Molecular building blocks associated with polydentate carboxylic acid are widely used in chiral catalysis, optoelectronic materials, hematopathology, and medicine [6–8]. In our laboratory, we synthesized a novel cobalt coordination polymer constructed by polydentate carboxylic acid in combination with 1-(4-((1*H*-imidazol-1-yl)methyl)benzyl)-1*H*-imidazole as ancillary ligand.

In the asymmetric unit of the title structure, there are two crystallographically independent cobalt(II) ions, two 4,4′-(1,2-phenylenebis(oxy))dibenzoate, and one half of 1-(4-((1*H*-imidazol-1-yl)methyl)benzyl)-1*H*-imidazole molecule. One of the cobalt(II) ions is five-coordinated by five O atoms of four 4,4′-(1,2-phenylenebis(oxy))dibenzoate ligands. and one N atom from amide molecule. The other cobalt(II) ion is four-coordinated by three O atoms of two 4,4′-(1,2-phenylenebis(oxy))dibenzoate ligands and one N atom from 1-(4-((1*H*-imidazol-1-yl)methyl)benzyl)-1*H*-imidazole ligand. The distances between Co and coordination atoms are the following: d(Co1—N1) = 2.001(3) Å, d(Col—O6) = 1.954(3) Å, d(Co1—O8) = 1.942(3) Å, d(Co1—O12) = 1.968(3) Å, d(Co2—O1) = 1.973(3) Å, d(Co2—O2) = 2.358(3) Å, d(Co2—O5) = 1.982(3) Å, d(Co2—O7) = 1.978(3) Å, and d(Co2—O11) = 1.957(3) 2 Å, respectively. The Co(II) coordination angles are in the normal range from 59.80(11) Å to 159.87(12) Å. The polydentate carboxylate ligands link the cobalt ions into one-dimensional chains. The ancillary ligand lies on a center of inversion and bridges two chains into a two-dimensional structure.

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