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Crystal structure of poly[bis{ μ_2 -5-carboxy-4'-methyl-[1,1'-biphenyl]-3-carboxylato- $\kappa^2 O:O'$ }-{ μ_2 -4,4'-bipyridine- $\kappa^2 N:N'$ }]cobalt(II), $C_{40}H_{30}N_2O_8Co$

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Abstract

$C_{40}H_{30}N_2O_8Co$, triclinic, $P\bar{1}$ (no. 2), $a = 9.8766(6)$ Å, $b = 11.5473(8)$ Å, $c = 14.2194(9)$ Å, $\alpha = 84.534(5)^\circ$, $\beta = 85.582(5)^\circ$, $\gamma = 79.413(5)^\circ$, $V = 1583.90(17)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0650$, $wR_{ref}(F^2) = 0.1109$, $T = 293(2)$ K.

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A part of the polymeric title 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.

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Table 1: Data collection and handling.

Crystal:	Red block
Size:	$0.42 \times 0.38 \times 0.31$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.61 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	25.5° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12944, 5740, 0.053
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3354
$N(\text{param})_{\text{refined}}$:	467
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	1.0000	1.0000	0.5000	0.0170(2)
Co2	0.5000	1.0000	0.5000	0.0179(2)
N1	0.9991(3)	0.8088(3)	0.5057(2)	0.0204(8)
N2	0.5035(3)	0.8079(3)	0.5073(2)	0.0229(9)
O1	0.1449(3)	0.9777(2)	0.38516(18)	0.0236(7)
O2	0.3449(2)	1.0372(2)	0.40291(18)	0.0219(7)
O3	0.6453(2)	0.9747(2)	0.38784(18)	0.0225(7)
O4	0.8338(2)	1.0471(2)	0.41238(18)	0.0222(7)
O5	0.6397(3)	1.0376(3)	0.0993(2)	0.0373(8)
H5	0.7050	1.0525	0.0639	0.056*
O6	0.6645(3)	0.8808(3)	0.0152(2)	0.0365(8)
O7	1.1321(3)	1.0598(3)	0.1028(2)	0.0365(8)
H7	1.1959	1.0771	0.0671	0.055*
O8	1.1632(3)	0.9027(3)	0.0188(2)	0.0368(8)
C1	0.2693(4)	0.9838(3)	0.3620(3)	0.0182(10)
C2	0.3324(4)	0.9208(4)	0.2765(3)	0.0167(10)
C3	0.2951(4)	0.8143(4)	0.2611(3)	0.0227(11)
H3	0.2213	0.7904	0.2975	0.027*
C4	0.3642(4)	0.7418(4)	0.1931(3)	0.0217(10)
C5	0.4656(4)	0.7870(4)	0.1344(3)	0.0269(11)
H5A	0.5107	0.7436	0.0858	0.032*
C6	0.5002(4)	0.8946(4)	0.1469(3)	0.0218(10)
C7	0.4381(4)	0.9603(4)	0.2201(3)	0.0216(10)
H7A	0.4669	1.0298	0.2313	0.026*
C8	0.3351(4)	0.6213(4)	0.1876(3)	0.0254(11)
C9	0.2152(4)	0.5881(4)	0.2286(3)	0.0359(12)
H9	0.1486	0.6437	0.2573	0.043*
C10	0.1925(5)	0.4735(4)	0.2278(4)	0.0458(14)
H10	0.1111	0.4538	0.2567	0.055*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C11	0.2860(5)	0.3883(4)	0.1856(4)	0.0417(14)
C12	0.4055(6)	0.4202(5)	0.1446(4)	0.0608(16)
H12	0.4718	0.3642	0.1162	0.073*
C13	0.4285(5)	0.5356(4)	0.1453(4)	0.0534(15)
H13	0.5097	0.5553	0.1160	0.064*
C14	0.6096(4)	0.9373(4)	0.0810(3)	0.0249(11)
C15	0.2576(6)	0.2643(4)	0.1874(4)	0.0741(19)
H15A	0.3295	0.2176	0.1507	0.111*
H15B	0.1706	0.2662	0.1610	0.111*
H15C	0.2546	0.2299	0.2515	0.111*
C16	0.7690(4)	0.9863(3)	0.3695(3)	0.0157(9)
C17	0.8419(4)	0.9229(3)	0.2882(3)	0.0183(10)
C18	0.8104(4)	0.8148(4)	0.2679(3)	0.0231(11)
H18	0.7443	0.7829	0.3071	0.028*
C19	0.8721(4)	0.7533(4)	0.1932(3)	0.0224(10)
C20	0.9670(4)	0.8038(4)	0.1325(3)	0.0259(11)
H20	1.0077	0.7656	0.0800	0.031*
C21	1.0013(4)	0.9116(4)	0.1501(3)	0.0212(10)
C22	0.9412(4)	0.9696(3)	0.2278(3)	0.0180(10)
H22	0.9668	1.0400	0.2400	0.022*
C23	0.8442(4)	0.6346(4)	0.1783(3)	0.0268(11)
C24	0.8438(5)	0.5950(4)	0.0899(3)	0.0399(13)
H24	0.8576	0.6457	0.0366	0.048*
C25	0.8235(5)	0.4821(5)	0.0784(4)	0.0539(15)
H25	0.8213	0.4590	0.0177	0.065*
C26	0.8064(5)	0.4028(4)	0.1559(4)	0.0463(14)
C27	0.8055(5)	0.4412(4)	0.2446(4)	0.0455(14)
H27	0.7924	0.3900	0.2977	0.055*
C28	0.8236(4)	0.5544(4)	0.2559(3)	0.0389(13)
H28	0.8222	0.5782	0.3167	0.047*
C29	0.7896(6)	0.2781(4)	0.1429(4)	0.090(2)
H29A	0.7522	0.2434	0.2009	0.136*
H29B	0.8779	0.2321	0.1259	0.136*
H29C	0.7282	0.2793	0.0935	0.136*
C30	1.1067(4)	0.9581(4)	0.0842(3)	0.0237(11)
C31	0.5181(4)	0.7560(3)	0.4264(3)	0.0214(10)
H31	0.5297	0.8027	0.3704	0.026*
C32	0.5170(4)	0.6374(4)	0.4202(3)	0.0231(10)
H32	0.5273	0.6066	0.3614	0.028*
C33	0.5004(4)	0.5643(3)	0.5023(3)	0.0174(10)
C34	0.4901(4)	0.6171(4)	0.5869(3)	0.0309(12)
H34	0.4831	0.5720	0.6443	0.037*
C35	0.4904(4)	0.7371(4)	0.5857(3)	0.0308(12)
H35	0.4810	0.7703	0.6434	0.037*
C36	0.8840(4)	0.7637(4)	0.5179(3)	0.0285(11)
H36	0.8010	0.8153	0.5277	0.034*
C37	0.8800(4)	0.6453(4)	0.5170(3)	0.0289(11)
H37	0.7960	0.6192	0.5267	0.035*
H39	1.2047	0.5622	0.4784	0.040*
C38	1.0001(4)	0.5648(3)	0.5016(3)	0.0211(10)
C39	1.1203(4)	0.6116(4)	0.4892(3)	0.0337(12)
C40	1.1152(4)	0.7312(4)	0.4927(3)	0.0257(11)
H40	1.1980	0.7595	0.4855	0.031*

Source of material

A mixture of Co(OAc)₂ · 6 H₂O (0.1 mmol, 29.1 mg), 4,4'-bipyridine (0.1 mmol, 15.6 mg), and 3',5'-dicarboxyl-4-methyl biphenyl (H₂dmb) (0.1 mmol, 25.6 mg), was dissolved in 9 mL H₂O. The solution was heated in a 23 mL Teflon-lined autoclave under autogenous pressure at 383 K for four days. After cooling to room temperature crystals formed.

Experimental details

Coordinates of hydrogen atoms were positioned using geometrical considerations. Their *U*_{iso} values were set to 1.2*U*_{eq} of the parent atoms.

Comment

In the last two decades, a large number of mixed ligands MOFs have been reported. Mixed ligands MOFs can be constructed from metal ions and carboxylic acid and nitrogen-containing ligands [4, 5]. In most situations, *N*-containing ligands are electrically neutral, while carboxylate ligands are negatively charged. Among organic aromatic multicarboxylates like the 3',5'-dicarboxyl-4-methyl biphenyl can yield networks and have been widely utilized to construct MOFs [6, 7]. On the other hand, 4,4'-bipyridine serves as bridging ligand to coordinate two metal ions [8, 9].

In the title complex, there are two half Co(II) ions, two monoanionic Hdmb ligands, and two half of the 4,4'-bipyridine ligand in the asymmetric unit. The atom Co1 is six-coordinated with a distorted octahedral geometry by four O atoms from the Hdmb ligands, and two N atoms from two 4,4'-bipyridine ligands from the axial positions (see the figure). The Co—N bond length is 2.204(3) Å; and the Co—O ones are in the range of 2.089(3) to 2.098(2) Å. The bond angles of O—Co—O are in the range of 87.13(10)° to 180°. The Co2 is six-coordinated with a distorted octahedral geometry by four O atoms from the Hdmb ligands, and two N atoms from two 4,4'-bipyridine ligands from the axial positions. The Co—N bond length is 2.204(3) Å; and the Co—O ones are in the range of 2.066(3) to 2.100(2) Å. The bond angles of O—Co—O are in the range of 88.94(10)° to 180°. All geometric parameters are comparable to related ones [10]. Co(II) ions are linked by 4,4'-bipyridine ligands and Hdmb ligands to form a 2-D layer. The lengths of bipy and the methy-biphenyl groups are almost the same. In the packing scheme of the title coordination polymers these moieties are arranged in a parallel fashion which is known as dimensional caging [11] in particular bipyridine and its derivatives is a prominent class of compounds to be used for dimensional caging [12]. This arrangement seems to further contribute to the structure formation.

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