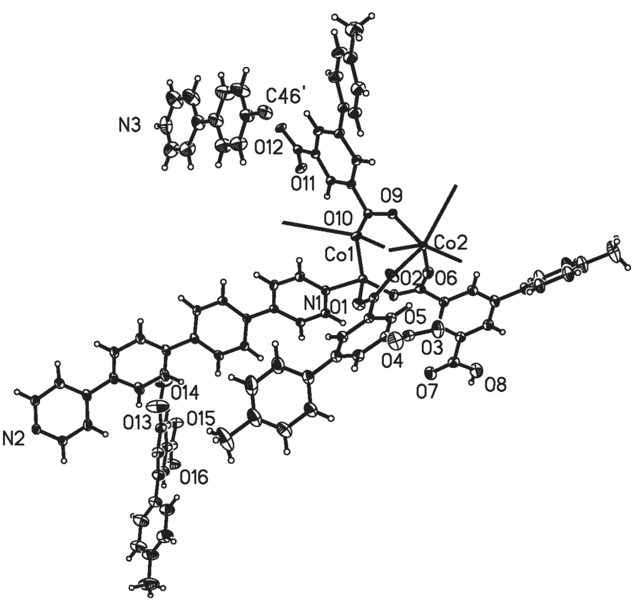
Qian-Qian Tang*, Shi-Hui Li and Zhan-Quan Cheng

Crystal structure of 4,4′-bis(pyridin-1-ium-4-yl)biphenyl poly[bis(μ_2-4,4′-bis(pyrid-4-yl)biphenyl-$\kappa^2N:N'$)-tetrakis(μ_4-4′-methyl-[1,1′-biphenyl]-3,5-dicarboxylato-$\kappa^4O,O':O'':O'''$)-bis[[μ_2-1,1′-biphenyl]-3-carboxyl-5-carboxylato-$\kappa^2O:O'$]tetracobalt(II)]— [1,1′-biphenyl]-3,5-dicarboxylic acid (1/2), $C_{93}H_{68}N_3O_{16}Co_2$



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Abstract

$C_{93}H_{68}N_3O_{16}Co_2$, triclinic, $P\bar{1}$ (no. 2), $a = 9.9281(4)$ Å, $b = 19.1304(8)$ Å, $c = 22.0724(10)$ Å, $\alpha = 66.036(4)°$, $\beta = 87.374(4)°$, $\gamma = 85.610(3)°$, $V = 3819.1(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0580$, $wR_{ref}(F^2) = 0.1276$, $T = 293(2)$ K.

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The molecular 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.

Table 1: Data collection and handling.

Crystal:	Red block
Size:	$0.42 \times 0.32 \times 0.21$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.51 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	41860, 14116, 0.065
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 10371
$N(param)_{refined}$:	1034
Programs:	Crysalis^{PRO} [1], SHELX [2, 3]

Source of material

A mixture of $Co(OAc)_2 \cdot 6H_2O$ (0.1 mmol, 29.1 mg), 4′-methyl-[1,1′-biphenyl]-3,5-dicarboxylic acid (0.1 mmol, 0.0256 g) (H2mbdc), 4,4′-bis(pyrid-4-yl)biphenyl (0.1 mmol, 0.0308 g) and distilled water (10 mL) was heated in a 25 mL stainless steel reactor with a Teflon liner at 423 K for 30 h, followed by slow cooling to room temperature. Red crystals of the compound formed.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. There is some evidence that the uncoordinated cation is disordered over two positions but disorder was not modelled for this ambient-temperature structure.

Comment

In the last two decades, a large number of mixed ligands metal-organic frameworks (MOFs) have been reported in the literature. Mixed ligands-MOFs can be constructed from metal ions and carboxylic acid and nitrogen-containing ligands. In most situations, N-containing ligands are electrically

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.91716(4)	0.57489(2)	0.58513(2)	0.02341(12)
Co2	1.11133(4)	0.68709(2)	0.63519(2)	0.02289(12)
N1	0.7788(3)	0.51376(14)	0.56577(12)	0.0259(6)
N2	0.1081(3)	−0.19044(15)	0.60012(13)	0.0316(7)
N3	−0.1488(4)	0.4747(2)	0.82217(17)	0.0652(12)
H3	−0.2204	0.4721	0.8028	0.078*
O1	1.0543(2)	0.49457(13)	0.63187(11)	0.0389(6)
O2	1.1428(2)	0.56670(14)	0.67464(13)	0.0501(7)
O3	1.6211(2)	0.46766(16)	0.77252(13)	0.0533(8)
O4	1.6026(3)	0.35067(16)	0.85050(13)	0.0586(8)
O5	0.9822(2)	0.63692(13)	0.49588(11)	0.0331(6)
O6	1.0970(2)	0.70045(14)	0.53856(11)	0.0396(6)
O7	1.1258(3)	0.66494(16)	0.26412(13)	0.0578(8)
O8	1.2307(3)	0.77027(17)	0.20173(12)	0.0646(9)
H8	1.2187	0.7560	0.1721	0.097*
O9	0.9276(2)	0.68500(13)	0.67523(11)	0.0328(6)
O10	0.8048(2)	0.61980(14)	0.63585(11)	0.0358(6)
O11	0.3208(2)	0.68052(14)	0.63836(11)	0.0359(6)
O12	0.2154(2)	0.67942(14)	0.72764(11)	0.0344(6)
O13	0.0073(4)	0.1995(2)	0.23041(16)	0.1048(14)
O14	−0.1499(3)	0.2849(2)	0.17257(14)	0.0681(9)
H14A	−0.1598	0.2920	0.2067	0.102*
O15	−0.2447(3)	0.32085(17)	−0.05447(13)	0.0548(8)
H15	−0.2900	0.3345	−0.0880	0.082*
O16	−0.1473(4)	0.2398(2)	−0.09362(14)	0.0855(12)
C1	0.6832(3)	0.48056(19)	0.61067(17)	0.0334(8)
H1	0.6763	0.4897	0.6490	0.040*
C2	0.5940(3)	0.43309(19)	0.60238(17)	0.0340(8)
H2	0.5289	0.4113	0.6350	0.041*
C3	0.6005(3)	0.41765(17)	0.54609(15)	0.0241(7)
C4	0.6989(3)	0.45377(18)	0.49950(16)	0.0273(7)
H4	0.7068	0.4465	0.4603	0.033*
C5	0.7850(3)	0.50014(18)	0.51058(16)	0.0291(7)
H5	0.8504	0.5231	0.4785	0.035*
C6	0.5092(3)	0.36465(17)	0.53786(15)	0.0256(7)
C7	0.3922(3)	0.34447(19)	0.57578(17)	0.0326(8)
H7	0.3671	0.3677	0.6047	0.039*
C8	0.3117(3)	0.29076(19)	0.57186(17)	0.0340(8)
H8A	0.2330	0.2791	0.5976	0.041*
C9	0.3461(3)	0.25367(18)	0.53000(16)	0.0310(7)
C10	0.4599(3)	0.27602(18)	0.49058(16)	0.0326(8)
H10	0.4833	0.2539	0.4607	0.039*
C11	0.5408(3)	0.33024(18)	0.49386(16)	0.0311(7)
H11	0.6168	0.3438	0.4664	0.037*
C12	0.2721(3)	0.18751(19)	0.53292(17)	0.0347(8)
C13	0.1979(4)	0.1448(2)	0.58876(19)	0.0429(9)
H13	0.1814	0.1628	0.6219	0.052*
C14	0.1477(4)	0.0760(2)	0.5964(2)	0.0442(9)
H14	0.0974	0.0490	0.6342	0.053*
C15	0.1715(4)	0.0471(2)	0.54840(18)	0.0379(8)
C16	0.2380(4)	0.0918(2)	0.49062(18)	0.0429(9)
H16	0.2507	0.0751	0.4566	0.051*
C17	0.2857(4)	0.1611(2)	0.48281(18)	0.0435(9)
H17	0.3280	0.1906	0.4431	0.052*
C18	0.1405(4)	−0.0331(2)	0.56263(18)	0.0374(8)
C19	0.0356(4)	−0.0700(2)	0.60351(18)	0.0396(9)
H19	−0.0267	−0.0426	0.6196	0.047*
C20	0.0218(3)	−0.1474(2)	0.62082(17)	0.0349(8)
H20	−0.0506	−0.1703	0.6480	0.042*
C21	0.2077(4)	−0.1549(2)	0.55893(17)	0.0383(8)
H21	0.2670	−0.1834	0.5426	0.046*
C22	0.2269(4)	−0.0780(2)	0.53932(18)	0.0427(9)
H22	0.2978	−0.0561	0.5104	0.051*
C23	0.8205(3)	0.65734(18)	0.67039(15)	0.0256(7)
C24	0.7001(3)	0.66955(18)	0.70870(15)	0.0253(7)
C25	0.7137(3)	0.68874(19)	0.76243(16)	0.0300(7)
H25	0.7987	0.6978	0.7726	0.036*
C26	0.6022(3)	0.6947(2)	0.80132(16)	0.0315(7)
C27	0.4751(3)	0.68693(19)	0.78104(16)	0.0310(7)
H27	0.3991	0.6905	0.8061	0.037*
C28	0.4593(3)	0.67406(18)	0.72438(16)	0.0271(7)
C29	0.5726(3)	0.66196(18)	0.68999(16)	0.0266(7)
H29	0.5630	0.6487	0.6543	0.032*
C30	0.6186(3)	0.7101(2)	0.86147(17)	0.0363(8)
C31	0.7373(4)	0.6905(2)	0.89584(18)	0.0460(9)
H31	0.8097	0.6686	0.8801	0.055*
C32	0.7532(4)	0.7020(2)	0.95273(19)	0.0523(10)
H32	0.8351	0.6872	0.9747	0.063*
C33	0.6497(4)	0.7351(3)	0.9772(2)	0.0540(10)
C34	0.5297(4)	0.7568(3)	0.9426(2)	0.0582(10)
H34	0.4586	0.7802	0.9579	0.070*
C35	0.5135(4)	0.7442(2)	0.8859(2)	0.0510(9)
H35	0.4316	0.7587	0.8639	0.061*
C36	0.3233(3)	0.67744(19)	0.69643(17)	0.0291(8)
C37	0.6662(5)	0.7488(3)	1.0397(2)	0.0818(15)
H37A	0.7490	0.7231	1.0608	0.123*
H37B	0.5916	0.7292	1.0696	0.123*
H37C	0.6685	0.8028	1.0282	0.123*
C38	−0.0357(5)	0.4368(3)	0.8171(2)	0.0737(13)
H38	−0.0347	0.4055	0.7940	0.088*
C39	0.0815(4)	0.4427(3)	0.8456(2)	0.0712(12)
H39	0.1598	0.4148	0.8415	0.085*
C40	0.0856(4)	0.4884(3)	0.8796(2)	0.0576(10)
C41	−0.0353(5)	0.5250(3)	0.8851(3)	0.0819(13)
H41	−0.0397	0.5563	0.9082	0.098*
C42	−0.1514(5)	0.5163(3)	0.8569(3)	0.0851(14)
H42	−0.2326	0.5405	0.8628	0.102*
C43	0.2084(4)	0.4954(3)	0.9118(2)	0.0572(10)
C44	0.3294(4)	0.4593(3)	0.9071(2)	0.0694(11)
H44	0.3365	0.4323	0.8802	0.083*
C45	0.4427(4)	0.4613(3)	0.9409(2)	0.0700(11)
H45	0.5228	0.4352	0.9362	0.084*
C46	0.4400(4)	0.5002(2)	0.9807(2)	0.0499(10)
C47	0.3222(5)	0.5383(3)	0.9836(3)	0.0777(12)
H47	0.3162	0.5670	1.0091	0.093*
C48	0.2078(5)	0.5362(3)	0.9494(2)	0.0779(12)
H48	0.1289	0.5640	0.9526	0.094*
C49	1.1388(3)	0.50591(19)	0.66769(15)	0.0280(7)
C50	1.2386(3)	0.44104(18)	0.70418(15)	0.0270(7)
C51	1.2135(3)	0.36653(19)	0.71453(16)	0.0323(8)
H51	1.1357	0.3577	0.6975	0.039*

Table 2 (continued)

Atom	*x*	*y*	*z*	$U_{iso}*/U_{eq}$
C52	1.3027(3)	0.30460(19)	0.75001(17)	0.0347(8)
C53	1.4170(3)	0.32009(19)	0.77570(17)	0.0352(8)
H53	1.4769	0.2796	0.8002	0.042*
C54	1.4441(3)	0.39424(19)	0.76573(16)	0.0304(7)
C55	1.3552(3)	0.45459(19)	0.72965(15)	0.0291(7)
H55	1.3732	0.5044	0.7223	0.035*
C56	1.2789(4)	0.2252(2)	0.75975(19)	0.0453(9)
C57	1.1584(4)	0.1929(2)	0.7869(2)	0.0691(12)
H57	1.0902	0.2216	0.7985	0.083*
C58	1.1389(6)	0.1168(3)	0.7971(3)	0.0885(15)
H58	1.0573	0.0959	0.8151	0.106*
C59	1.2379(6)	0.0729(3)	0.7810(3)	0.0783(14)
C60	1.3564(5)	0.1045(2)	0.7537(2)	0.0689(12)
H60	1.4237	0.0758	0.7417	0.083*
C61	1.3767(4)	0.1797(2)	0.7438(2)	0.0560(10)
H61	1.4588	0.1999	0.7260	0.067*
C62	1.2149(7)	−0.0098(3)	0.7932(3)	0.129(2)
H62A	1.1208	−0.0145	0.7885	0.194*
H62B	1.2424	−0.0432	0.8373	0.194*
H62C	1.2670	−0.0237	0.7616	0.194*
C63	1.5661(3)	0.4055(2)	0.79842(17)	0.0337(8)
C64	1.0623(3)	0.68736(18)	0.49058(16)	0.0273(7)
C65	1.1188(3)	0.73360(18)	0.42351(15)	0.0285(7)
C66	1.1791(3)	0.80106(19)	0.41258(16)	0.0335(8)
H66	1.1829	0.8163	0.4474	0.040*
C67	1.2334(4)	0.84605(19)	0.35170(17)	0.0359(8)
C68	1.2299(3)	0.8212(2)	0.30045(17)	0.0366(8)
H68	1.2654	0.8506	0.2589	0.044*
C69	1.1736(3)	0.75237(19)	0.31116(16)	0.0325(8)
C70	1.1167(3)	0.70899(19)	0.37216(15)	0.0292(7)
H70	1.0775	0.6638	0.3788	0.035*
C71	1.3005(4)	0.9169(2)	0.34262(17)	0.0393(8)
C72	1.3990(4)	0.9134(2)	0.38644(19)	0.0490(10)
H72	1.4226	0.8667	0.4210	0.059*
C73	1.4627(4)	0.9777(2)	0.3798(2)	0.0541(10)
H73	1.5298	0.9731	0.4095	0.065*
C74	1.4299(5)	1.0474(2)	0.3312(2)	0.0624(12)
C75	1.3310(5)	1.0517(3)	0.2874(2)	0.0799(14)
H75	1.3066	1.0987	0.2535	0.096*
C76	1.2675(5)	0.9868(2)	0.2934(2)	0.0658(12)
H76	1.2013	0.9912	0.2634	0.079*
C77	1.1736(4)	0.7235(2)	0.25749(17)	0.0391(9)
C78	1.5013(6)	1.1174(3)	0.3241(3)	0.104(2)
H78A	1.4421	1.1625	0.3037	0.156*
H78B	1.5812	1.1213	0.2970	0.156*
H78C	1.5260	1.1130	0.3671	0.156*
C79	−0.0601(4)	0.2281(3)	0.18183(19)	0.0508(10)
C80	−0.0416(4)	0.2069(2)	0.12410(17)	0.0405(8)
C81	0.0533(4)	0.1482(2)	0.12877(19)	0.0468(9)
H81	0.1021	0.1236	0.1675	0.056*
C82	0.0775(4)	0.1250(2)	0.07689(19)	0.0483(9)
C83	0.0034(4)	0.1644(2)	0.01907(18)	0.0472(9)
H83	0.0180	0.1505	−0.0166	0.057*
C84	−0.0905(4)	0.2234(2)	0.01366(17)	0.0408(8)
C85	−0.1144(4)	0.2447(2)	0.06654(17)	0.0406(9)
H85	−0.1788	0.2840	0.0633	0.049*
C86	0.1804(5)	0.0636(2)	0.0811(2)	0.0569(10)
C87	0.3040(5)	0.0572(3)	0.1082(2)	0.0661(11)
H87	0.3233	0.0912	0.1266	0.079*
C88	0.4017(6)	0.0007(3)	0.1089(2)	0.0827(14)
H88	0.4857	−0.0020	0.1271	0.099*
C89	0.3755(6)	−0.0513(3)	0.0830(3)	0.0838(15)
C90	0.2540(6)	−0.0460(3)	0.0571(3)	0.0929(14)
H90	0.2346	−0.0808	0.0397	0.111*
C91	0.1566(6)	0.0105(3)	0.0557(3)	0.0810(13)
H91	0.0732	0.0127	0.0373	0.097*
C92	−0.1635(4)	0.2622(2)	−0.05001(19)	0.0455(9)
C93	0.4835(7)	−0.1111(3)	0.0813(3)	0.133(3)
H93A	0.4815	−0.1153	0.0395	0.199*
H93B	0.4667	−0.1597	0.1165	0.199*
H93C	0.5706	−0.0961	0.0868	0.199*

neutral, while carboxylate ligands are negatively charged. Among organic aromatic multicarboxylates like the 4′-methyl-[1,1′-biphenyl]-3,5-dicarboxylato can yield predetermined networks and have been widely utilized to construct MOFs [4–8]. On the other hand, 4,4′-bis(pyrid-4-yl)biphenyl serves as bridging ligand to coordinate to two metal ions [9–13].

In the title complex, there are two Co(II) ions, three H2mbdc ligands, one half of the 4,4′-bis(pyrid-4-yl)biphenyl ligand, one free H2mbdc, one free 4,4′-bis(pyrid-4-yl)biphenyl in the asymmetric unit. The cobalt atom Co1 is four-coordinated with a distorted tetrahedron geometry by three O atoms from the H2mbdc ligands, and one N atom from the 4,4′-bis(pyrid-4-yl)biphenyl ligand at the axial positions (see the figure). The Co—N bond length is 2.034(2) Å; and the Co—O ones are in the range of 1.9389(19) to 1.9517(19) Å. The bond angles of O—Co—O are in the range of 109.89(9)° to 121.55(9)°. Co2 is six-coordinated with a distorted octahedral geometry by five O atoms from the H2mbdc ligands, and one N atom from the 4,4′-bis(pyrid-4-yl)biphenyl ligand at the axial positions. The Co—N bond length is 2.146(2) Å; and the Co—O ones are in the range of 1.9858(19) to 2.2758(18) Å. The bond angles of O—Co—O are in the range of 82.03(8)° to 153.25(8)°. All geometric parameters are comparable to the ones found in related structures mentioned above. Co(II) ions are linked by 4,4′-bis(pyrid-4-yl)biphenyl ligands and H2mbdc ligands to form a 2-D layer. In the title complex, there are hydrogen bonds between carboxylic and carboxylate O atoms. So an extended three-dimensional network of hydrogen bonds contributes to the stability of the structure.

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