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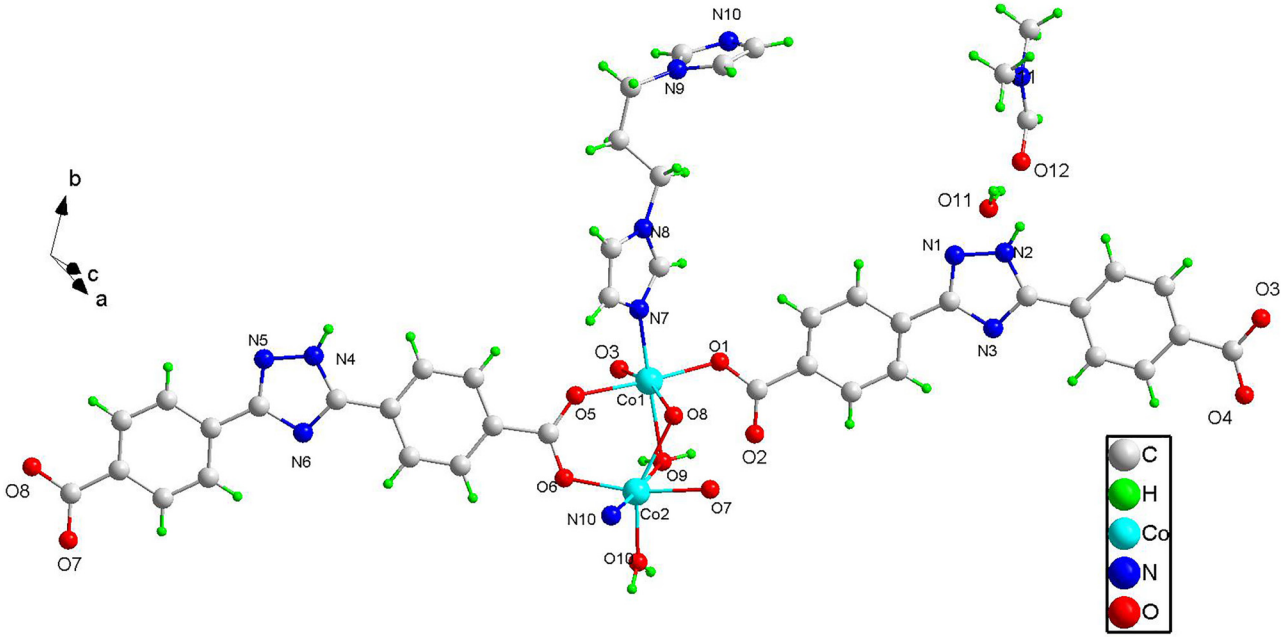
Crystal structure of poly[μ_2-aqua-aqua-(μ_2-1,3-di(1*H*-imidazol-1-yl)propane-κ^2*N:N′*)-(μ_2-4,4′-(1*H*-1,2,4-triazole-3,5-diyl)dibenzoato-κ^2*O:O′*)-(μ_4-4,4′-(1*H*-1,2,4-triazole-3,5-diyl)dibenzoato-κ^5*O, O′:O″:O‴:O‴*)dicobalt(II)] – water – dimethylformamide (1/1/1) $C_{44}H_{43}N_{11}O_{12}Co_2$



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Abstract

$C_{44}H_{43}N_{11}O_{12}Co_2$, triclinic, $P\bar{1}$ (no. 2), a = 10.7333(11) Å, b = 13.6796(11) Å, c = 16.751(2) Å, α = 113.982(2)°, β = 90.578(2)°, γ = 105.7310(10)°, V = 2142.7(4) Å^3, Z = 2, $R_{gt}(F)$ = 0.0460, w$R_{ref}(F^2)$ = 0.1015, T = 296(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.

Table 1: Data collection and handling.

Crystal:	Purple block
Size:	0.18 × 0.15 × 0.12 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.86 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.0°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10,985, 7503, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 5201
$N(param)_{refined}$:	648
Programs:	Bruker [1], SHELX [2, 3]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3879 (4)	0.1110 (3)	0.3604 (3)	0.0274 (9)
C2	0.4536 (4)	0.2238 (3)	0.4345 (2)	0.0252 (9)
C3	0.5784 (4)	0.2481 (3)	0.4761 (3)	0.0308 (10)
H3	0.623960	0.195684	0.455387	0.037*
C4	0.6354 (4)	0.3499 (3)	0.5479 (3)	0.0303 (10)
H4	0.719467	0.365467	0.574119	0.036*
C5	0.5692 (4)	0.4285 (3)	0.5812 (3)	0.0282 (10)
C6	0.4446 (4)	0.4046 (3)	0.5394 (3)	0.0387 (12)
H6	0.398785	0.456715	0.560308	0.046*
C7	0.3888 (4)	0.3034 (3)	0.4668 (3)	0.0379 (11)
H7	0.305956	0.288977	0.439237	0.046*
C8	0.6243 (4)	0.5326 (3)	0.6615 (3)	0.0267 (9)
C9	0.7500 (4)	0.6526 (3)	0.7785 (3)	0.0249 (9)
C10	0.8560 (4)	0.7113 (3)	0.8530 (3)	0.0257 (9)
C11	0.9415 (4)	0.6544 (3)	0.8603 (3)	0.0361 (11)
H11	0.931307	0.581923	0.818010	0.043*
C12	1.0409 (4)	0.7041 (3)	0.9294 (3)	0.0356 (11)
H12	1.098930	0.665642	0.932324	0.043*
C13	1.0560 (4)	0.8096 (3)	0.9944 (3)	0.0262 (9)
C14	0.9697 (4)	0.8660 (3)	0.9887 (3)	0.0352 (11)
H14	0.977279	0.936575	1.033182	0.042*
C15	0.8711 (4)	0.8183 (3)	0.9170 (3)	0.0365 (11)
H15	0.816005	0.858311	0.912341	0.044*
C16	1.1592 (4)	0.8599 (3)	1.0734 (3)	0.0268 (9)
C17	−0.0552 (4)	−0.2869 (3)	0.1583 (2)	0.0238 (9)
C18	−0.1650 (3)	−0.3556 (3)	0.0828 (2)	0.0212 (9)
C19	−0.1792 (4)	−0.4673 (3)	0.0276 (3)	0.0276 (10)
H19	−0.121121	−0.501797	0.037775	0.033*
C20	−0.2794 (4)	−0.5275 (3)	−0.0426 (2)	0.0264 (9)
H20	−0.287924	−0.602121	−0.079108	0.032*
C21	−0.3674 (3)	−0.4768 (3)	−0.0587 (2)	0.0220 (9)
C22	−0.3541 (4)	−0.3658 (3)	−0.0033 (3)	0.0284 (10)
H22	−0.413149	−0.331431	−0.012582	0.034*
C23	−0.2521 (4)	−0.3057 (3)	0.0665 (3)	0.0276 (10)
H23	−0.242519	−0.230722	0.102591	0.033*
C24	−0.4723 (3)	−0.5406 (3)	−0.1342 (2)	0.0212 (9)
C25	−0.5955 (3)	−0.6628 (3)	−0.2525 (2)	0.0217 (9)
C26	−0.6481 (3)	−0.7666 (3)	−0.3331 (2)	0.0214 (9)
C27	−0.5836 (4)	−0.8472 (3)	−0.3611 (2)	0.0255 (9)
H27	−0.505495	−0.834942	−0.328760	0.031*
C28	−0.6339 (3)	−0.9460 (3)	−0.4369 (2)	0.0243 (9)
H28	−0.589998	−0.999828	−0.454519	0.029*
C29	−0.7503 (3)	−0.9650 (3)	−0.4867 (2)	0.0220 (9)
C30	−0.8144 (4)	−0.8840 (3)	−0.4591 (3)	0.0276 (10)
H30	−0.891362	−0.895400	−0.492235	0.033*
C31	−0.7653 (4)	−0.7863 (3)	−0.3828 (3)	0.0288 (10)
H31	−0.810492	−0.733410	−0.364307	0.035*
C32	−0.8017 (4)	−1.0718 (3)	−0.5680 (2)	0.0245 (9)
C33	0.0147 (4)	0.1560 (3)	0.3035 (3)	0.0358 (11)
H33	0.093369	0.202487	0.299681	0.043*
C34	−0.1301 (4)	0.0159 (4)	0.3037 (3)	0.0382 (11)
H34	−0.171273	−0.055442	0.299786	0.046*
C35	−0.1872 (4)	0.0979 (4)	0.3230 (3)	0.0423 (12)
H35	−0.272753	0.093985	0.334042	0.051*
C36	−0.1073 (5)	0.2999 (4)	0.3462 (4)	0.0531 (14)
H36A	−0.024813	0.349647	0.344180	0.064*
H36B	−0.127010	0.329331	0.406262	0.064*
C37	−0.2116 (4)	0.3000 (4)	0.2870 (3)	0.0478 (13)
H37A	−0.286519	0.235094	0.275246	0.057*
H37B	−0.179958	0.291345	0.231172	0.057*
C38	−0.2558 (4)	0.4021 (3)	0.3214 (3)	0.0431 (12)
H38A	−0.314243	0.398790	0.275192	0.052*
H38B	−0.304809	0.402445	0.369836	0.052*
C39	−0.0844 (4)	0.5516 (3)	0.3011 (3)	0.0284 (10)
H39	−0.104639	0.520312	0.240085	0.034*
C40	−0.0913 (4)	0.5771 (4)	0.4375 (3)	0.0439 (12)
H40	−0.114927	0.568785	0.488157	0.053*
C41	0.0054 (4)	0.6610 (4)	0.4329 (3)	0.0388 (11)
H41	0.060557	0.720810	0.481298	0.047*
C42	0.5167 (4)	0.9317 (4)	0.8532 (3)	0.0417 (12)
H42	0.583760	0.957964	0.825472	0.050*
C43	0.3216 (5)	0.9538 (5)	0.9212 (4)	0.0633 (16)
H43A	0.325772	0.888710	0.928576	0.095*
H43B	0.240335	0.936662	0.886481	0.095*
H43C	0.327428	1.014132	0.977922	0.095*
C44	0.4384 (5)	1.0850 (4)	0.8610 (4)	0.0562 (15)
H44A	0.507387	1.094781	0.826336	0.084*
H44B	0.456681	1.150016	0.916436	0.084*
H44C	0.357138	1.075325	0.829959	0.084*
Co1	0.12432 (5)	−0.04372 (4)	0.26195 (3)	0.02256 (15)
Co2	0.13780 (5)	−0.25823 (4)	0.29449 (3)	0.02151 (15)
N1	0.5670 (3)	0.6119 (3)	0.6928 (2)	0.0344 (9)
N2	0.6491 (3)	0.6885 (3)	0.7679 (2)	0.0331 (9)
H2	0.637801	0.750821	0.803415	0.040*
N3	0.7377 (3)	0.5538 (3)	0.7122 (2)	0.0281 (8)
N4	−0.5693 (3)	−0.5042 (3)	−0.1497 (2)	0.0265 (8)
H4A	−0.579942	−0.440714	−0.116252	0.032*
N5	−0.6492 (3)	−0.5808 (2)	−0.2254 (2)	0.0259 (8)
N6	−0.4845 (3)	−0.6411 (2)	−0.1984 (2)	0.0227 (7)
N7	−0.0034 (3)	0.0520 (3)	0.2907 (2)	0.0280 (8)
N8	−0.0929 (3)	0.1883 (3)	0.3228 (2)	0.0369 (9)
N9	−0.1475 (3)	0.5069 (3)	0.3523 (2)	0.0321 (9)
N10	0.0108 (3)	0.6458 (3)	0.3474 (2)	0.0262 (8)
N11	0.4295 (3)	0.9870 (3)	0.8766 (2)	0.0402 (10)
O1	0.2751 (2)	0.0990 (2)	0.32642 (18)	0.0321 (7)
O2	0.4434 (3)	0.0372 (2)	0.33751 (19)	0.0382 (8)
O3	1.1577 (3)	0.9508 (2)	1.13595 (17)	0.0326 (7)
O4	1.2389 (3)	0.8072 (2)	1.07241 (18)	0.0362 (7)
O5	−0.0371 (2)	−0.1834 (2)	0.19469 (18)	0.0306 (7)
O6	0.0105 (2)	−0.3381 (2)	0.18025 (17)	0.0300 (7)
O7	−0.7561 (3)	−1.1515 (2)	−0.58065 (18)	0.0331 (7)
O8	−0.8919 (2)	−1.0835 (2)	−0.62484 (17)	0.0294 (7)
O9	0.2604 (3)	−0.1510 (2)	0.24192 (18)	0.0263 (6)
O10	0.2457 (3)	−0.3655 (2)	0.25684 (19)	0.0286 (7)
O11	0.3705 (3)	0.6984 (3)	0.9298 (2)	0.0488 (9)
O12	0.5167 (3)	0.8481 (3)	0.8651 (2)	0.0487 (9)
H11A	0.411 (3)	0.7516 (13)	0.9170 (15)	0.026 (12)*
H11B	0.326 (2)	0.7269 (19)	0.9698 (14)	0.063 (18)*
H10A	0.3189 (14)	−0.355 (2)	0.2376 (18)	0.050 (15)*
H10B	0.236 (3)	−0.4229 (13)	0.2671 (16)	0.042 (14)*
H9B	0.326 (2)	−0.0922 (19)	0.2647 (18)	0.068 (17)*
H9A	0.258 (4)	−0.172 (3)	0.1865 (3)	0.073 (18)*

Source of material

The mixture of 3,5-bis(4′-carboxy-phenyl)-1,2,4-triazole 15.45 mg (0.05 mmol), cobalt nitrate hexahydrate 43.65 mg (0.075 mmol), 1,3-di(1*H*-imidazol-1-yl)propane 17.6 mg (0.05 mmol), NaOH 12 mg (0.15 mmol) and *N*,*N*-dimethylformamide (6 mL) were placed in the autoclave lined with PTFE and heated at 120 °C for 24 h, then cooled down to room temperature over 24 h. The light pink crystals after cooling to room temperature were collected.

Experimental details

The structure was solved by direct methods and refined with the SHELX crystallographic software package [1]. The hydrogen atoms were placed at calculated positions and refined as riding atoms.

Comment

Coordination polymers (CPs) have raised special interest as a class of organic-inorganic hybrid materials due to their unique infinite structures, rich structural diversities formed by the combination of metal ions with organic ligands and important potential applications. Mixed ligands-CPs are often constructed from metal ions, carboxylates and nitrogen-containing ligands. In most situations, N containing ligands are electrically neutral, while carboxylate ligands are negatively charged in such coordination polymers. Multicarboxylates like the 3,5-bis(4′-carboxy-phenyl)-1,2,4-triazole have been widely utilized in such networks [4–7]. On the other hand, 1,3-di(1*H*-imidazol-1-yl)propane (diim) is known to serve as bridging ligand [8–10]. Meanwhile, similar coordination polymer has been reported [11] which is constructed by same metal ion and ligands, the title compound exhibts a totally different structure by changing the synthesis conditions.

The asymmetric unit of title structure contains two independent Co(II) cations (Co1, Co2), two deprotonated 3,5-bis(4′-carboxy-phenyl)-1,2,4-triazole ligands, one 1,3-di(1*H*-imidazol-1-yl)propane ligand, one bridging water molecule, one unidentate coordinated water molecule, one free DMF and one free water. As shown in the figure, the two Co(II) exhibit similar coordination modes which exhibit distorted octahedral geometry. The six atoms that coordinate with Co1 come from one nitrogen atom (N7) of 1,3-di(1*H*-imidazol-1-yl)propane, one oxygen atom (O9) of bridged water, three unidentate coordinated oxygen atoms (O1,O3,O5) of three 4,4′-(1*H*-1,2,4-triazole-3,5-diyl) dibenzoate ligands, one bridged carboxyl oxygen atom (O8) of one 4,4′-(1*H*-1,2,4-triazole-3,5-diyl)dibenzoate ligand. Meanwhile, Co2 exhibits another distorted octahedral geometry with one nitrogen atom (N10) of 1,3-di(1*H*-imidazol-1-yl)propane, one oxygen atom (O9) of bridging coordinated water molecule, one oxygen atom (O10) of one unidentate water, three atoms (O6,O7,O8) of three 4,4′-(1*H*-1,2,4-triazole-3,5-diyl)dibenzoate ligands. An interesting two dimensional double layer framework is formed.

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