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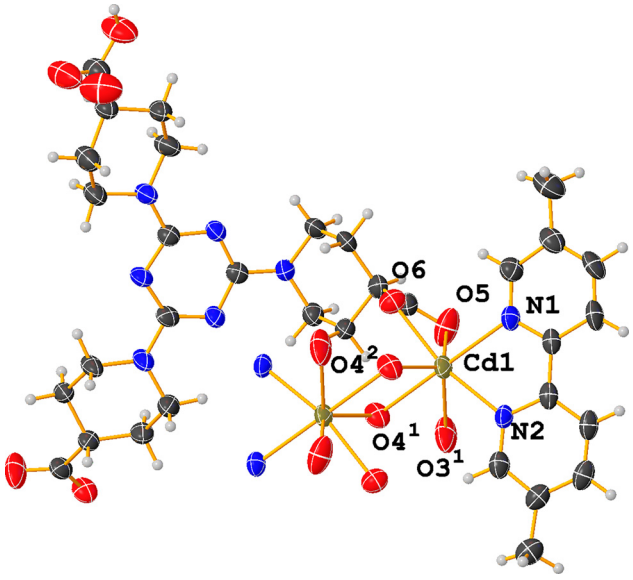
Crystal structure of *catena*-poly[(5,5′-dimethyl-2,2′-bipyridine-κ^2N,N')-(μ_3-hydrogen-1,1′,1″-(1,3,5-triazine-2,4,6-triyl)tris(piperidine-4-carboxylato)- $\kappa^5O:O,O':O'',O'''$)-cadmium(II)], $C_{33}H_{40}CdN_8O_6$



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Abstract

$C_{33}H_{40}CdN_8O_6$, triclinic, $P\bar{1}$ (no. 2), a = 10.6468(11) Å, b = 11.6739(9) Å, c = 14.5312(9) Å, α = 93.976(5)°, β = 102.005(7)°, γ = 111.827(8)°, V = 1618.4(2) Å^3, Z = 2, $R_{gt}(F)$ = 0.0480, $wR_{ref}(F^2)$ = 0.1102, T = 293(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.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.10 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.73 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Advance, φ and ω
θ_{max}, completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10151, 5699, 0.046
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4293
$N(param)_{refined}$:	449
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

The raw materials were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. For the reaction $Cd(NO_3)_2 \cdot 4H_2O$ (0.0308 g, 0.1 mmol), 1,1′,1″-(1,3,5-triazine-2,4,6-triyl) tris(piperidine-4-carboxylic acid) (H_3L, 0.0139 g, 0.03 mmol), 5,5′-dimethyl-2,2′-bipyridine (DMBPY, 0.0092 g, 0.05 mmol), DMF (8 mL) and two drops of concentrated hydrochloric acid were mixed in a 20 mL capped vial and transferred to an 100 °C oven for 72 h, After the system cooled to room temperature, clear light colourless block crystals were obtained, yielding 37%, based on the metal-salt.

Experimental details

The following steps are operated via the OLEX2 software. The initial structure of the complex was solved by SHELXT. Refinement process was performed by SHELXL program. The hydrogen atoms were placed in their idealized positions with isotropic thermal parameters. Note that the oxygen atom belonging to C=O of the undeprotonated carboxylic group is disordered.

Comment

As a tridentate carboxylic acid cotaining triazine centre, 1,1′,1″-(1,3,5-triazine-2,4,6-triyl)tris(piperidine-4-carboxylic

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cd1	0.64004 (3)	0.49225 (3)	0.44780 (2)	0.03877 (13)
O1[a]	−0.5068 (12)	0.4547 (9)	−0.1090 (6)	0.089 (3)
O2	−0.3998 (5)	0.4152 (4)	−0.2100 (3)	0.0797 (14)
O3	−0.6320 (4)	−0.3048 (3)	0.4685 (3)	0.0791 (12)
O4	−0.4601 (4)	−0.3669 (3)	0.4867 (2)	0.0476 (9)
O5	0.5792 (4)	0.3139 (3)	0.3246 (3)	0.0738 (11)
O6	0.4547 (4)	0.4251 (3)	0.3060 (2)	0.0484 (8)
N1	0.8190 (4)	0.6012 (3)	0.3773 (3)	0.0383 (9)
N2	0.8491 (4)	0.5829 (3)	0.5641 (3)	0.0382 (9)
N3	0.0576 (4)	0.0522 (3)	0.1551 (2)	0.0396 (9)
N4	−0.1285 (4)	0.1031 (3)	0.0958 (2)	0.0367 (9)
N5	−0.3050 (4)	0.0740 (3)	0.1817 (3)	0.0397 (9)
N6	−0.1071 (4)	0.0244 (3)	0.2428 (3)	0.0391 (9)
N7	−0.2763 (4)	0.0005 (4)	0.3245 (3)	0.0498 (11)
N8	−0.3137 (4)	0.1587 (3)	0.0422 (3)	0.0452 (10)
C1	−0.4422 (6)	0.3979 (5)	−0.1335 (4)	0.0543 (14)
C2	−0.4270 (5)	0.2884 (4)	−0.0901 (3)	0.0445 (12)
H2A	−0.500564	0.212431	−0.130104	0.053*
C3	−0.2878 (5)	0.2790 (4)	−0.0893 (3)	0.0465 (12)
H3A	−0.275475	0.275950	−0.153577	0.056*
H3B	−0.211998	0.352537	−0.049915	0.056*
C4	−0.2828 (6)	0.1644 (5)	−0.0514 (3)	0.0518 (13)
H4A	−0.350216	0.090770	−0.095707	0.062*
H4B	−0.190628	0.164143	−0.046250	0.062*
C5	−0.4427 (6)	0.1717 (5)	0.0479 (4)	0.0521 (14)
H5A	−0.448220	0.177364	0.113783	0.063*
H5B	−0.522120	0.098430	0.011402	0.063*
C6	−0.4488 (6)	0.2871 (5)	0.0097 (4)	0.0571 (15)
H6A	−0.377239	0.360903	0.051711	0.068*
H6B	−0.539012	0.289763	0.008864	0.068*
C7	−0.2472 (5)	0.1091 (4)	0.1086 (3)	0.0356 (11)
C8	−0.2270 (5)	0.0344 (4)	0.2470 (3)	0.0380 (11)
C9	−0.4044 (5)	0.0072 (4)	0.3407 (3)	0.0453 (12)
H9A	−0.453706	0.028008	0.284689	0.054*
H9B	−0.381430	0.072203	0.394128	0.054*
C10	−0.4980 (5)	−0.1186 (4)	0.3615 (3)	0.0400 (11)
H10A	−0.578307	−0.111009	0.378497	0.048*
H10B	−0.532048	−0.180763	0.304413	0.048*
C11	−0.4196 (5)	−0.1624 (4)	0.4425 (3)	0.0371 (11)
H11	−0.394831	−0.100645	0.499555	0.045*
C12	−0.5114 (5)	−0.2884 (4)	0.4653 (3)	0.0431 (12)
C13	−0.2844 (5)	−0.1590 (4)	0.4257 (3)	0.0479 (13)
H13A	−0.304093	−0.224299	0.373268	0.057*
H13B	−0.232046	−0.176360	0.482115	0.057*
C14	−0.1958 (5)	−0.0349 (5)	0.4031 (3)	0.0513 (13)
H14A	−0.162918	0.028831	0.459002	0.062*
H14B	−0.114781	−0.040634	0.385846	0.062*
C15	−0.0628 (5)	0.0607 (3)	0.1654 (3)	0.0346 (11)
C16	0.1336 (5)	0.1210 (4)	0.0902 (3)	0.0433 (12)
H16A	0.070481	0.141107	0.042088	0.052*
H16B	0.170054	0.069292	0.058285	0.052*
C17	0.2538 (5)	0.2411 (4)	0.1447 (3)	0.0408 (11)
H17A	0.305529	0.284166	0.101142	0.049*
H17B	0.216796	0.295672	0.172444	0.049*
C18	0.3514 (5)	0.2122 (4)	0.2233 (3)	0.0394 (11)
H18	0.391479	0.160894	0.193482	0.047*
C19	0.2680 (5)	0.1366 (4)	0.2881 (3)	0.0402 (11)
H19A	0.328897	0.112295	0.334667	0.048*
H19B	0.233947	0.188519	0.322241	0.048*
C20	0.1453 (5)	0.0208 (4)	0.2320 (3)	0.0428 (12)
H20A	0.179660	−0.036786	0.205260	0.051*
H20B	0.089899	−0.020562	0.274335	0.051*
C21	0.4707 (5)	0.3263 (5)	0.2854 (3)	0.0427 (12)
C22	0.7981 (5)	0.6121 (4)	0.2853 (3)	0.0454 (12)
H22	0.706795	0.576738	0.247542	0.055*
C23	0.9046 (6)	0.6730 (4)	0.2417 (4)	0.0505 (13)
C24	1.0380 (6)	0.7162 (4)	0.2993 (4)	0.0523 (14)
H24	1.113099	0.754193	0.273224	0.063*
C25	1.0640 (5)	0.7051 (4)	0.3940 (4)	0.0488 (13)
H25	1.155146	0.735037	0.431710	0.059*
C26	0.9504 (5)	0.6478 (4)	0.4327 (3)	0.0368 (11)
C27	0.9676 (5)	0.6339 (4)	0.5344 (3)	0.0377 (11)
C28	1.0966 (5)	0.6671 (4)	0.5977 (4)	0.0456 (12)
H28	1.177928	0.701554	0.577237	0.055*
C29	1.1047 (5)	0.6492 (4)	0.6910 (4)	0.0486 (13)
H29	1.191658	0.670596	0.733090	0.058*
C30	0.9837 (5)	0.5993 (4)	0.7228 (3)	0.0436 (12)
C31	0.8587 (5)	0.5676 (4)	0.6547 (4)	0.0464 (12)
H31	0.776055	0.533387	0.673696	0.056*
C32	0.9851 (6)	0.5761 (5)	0.8236 (3)	0.0570 (14)
H32A	0.899858	0.508176	0.824102	0.085*
H32B	0.993239	0.650120	0.861918	0.085*
H32C	1.063218	0.555311	0.849041	0.085*
C33	0.8719 (7)	0.6877 (5)	0.1391 (4)	0.0772 (19)
H33A	0.875462	0.770473	0.134698	0.116*
H33B	0.779943	0.627442	0.107205	0.116*
H33C	0.939190	0.674579	0.109607	0.116*
H2	−0.408 (12)	0.477 (6)	−0.233 (7)	0.22 (5)*
O1A[b]	−0.393 (6)	0.500 (3)	−0.073 (2)	0.096 (10)

[a]Occupancy: 0.815 (18), [b]Occupancy: 0.185 (18).

acid) (H_3L) has been used to build complexes with metal salts [5–9]. However, almost all of the reported structures are based on only the H_3L ligand which greatly limited the quantity of the H_3L-complexes. Mixed-ligand strategy has been proved to be a effective way for preparation of valuable functional complexes with diversiform structures [10–12]. With this in mind, we introduced 5,5′-dimethyl-2,2′-bipyridine (DMBPY) as an auxiliary ligand, combined with cadmium salt to build metal complexes. As a result, the title complex was synthesized through one-pot synthesis method.

The complex crystallizes in the triclinic system within the space group $P\bar{1}$. The asymmetric unit contains one partial deprotonated H_3L ligand (two of the three carboxylic groups are deprotonated), one DMBPY ligand and one Cd(II) ion. The Cd(II) ion is seven-coordinated with five oxygen atoms (O3^1,

$O4^1$, $O4^2$, O5, O6) derived from three different H_3L ligands and two DMBPY nitrogen atoms (N1, N2). The distances of Cd–N and Cd–O bonds are within the range of 2.316(4)–2.559(4) Å, parallel to the reported Cd(II)-based complexes with similar environment [13–15]. Two Cd(II) ions, two H_3L and two DMBPY ligands formed a $Cd_2(H_3L)_2(DMBPY)_2$ binuclear unit. These units are bridged by carboxylic oxygen atoms with the Cd(II) ions to generate a infinite one-dimensional (1D) structure. As a result, the 1D structures are further expended by hydrogen bonding (O2–H2—$O6^3$) and π-π stacking interactions between the ligand rings, centroid-centroid distance: 3.748(3) Å, to form a three-dimensional (3D) supramolecular network (symmetry code: #1: $-x$, $-y$, $1-z$; #2: $1+x$, $1+y$, z; #3: $-x$, $1-y$, $-z$).

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References

1. Bruker. SAINT and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2000.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
5. Jiao W.-N., Wang C., Xing Y.-H., Bai F.-Y., Sun L.-X., Shi Z. Triazine crystalline framework complexes with flexible arms bearing carboxylate coordinating moieties: synthesis, structure, spectroscopy and photocatalytic property. *Polyhedron* 2021, *205*, 115314.
6. Lin X. M., Niu J. L., Lin J., Wei L. M., Hu L., Zhang G., Cai Y. P. Lithium-ion-battery anode materials with improved capacity from a metal-organic framework. *Inorg. Chem.* 2016, *55*, 8244–8247.
7. Tang Q., Liu S., Liu Y., Miao J., Li S., Zhang L., Shi Z., Zheng Z. Cation sensing by a luminescent metal-organic framework with multiple lewis basic sites. *Inorg. Chem.* 2013, *52*, 2799–2801.
8. Yu S., Zhang K. Y., Li J. X., Xiao Y., Sun L. X., Bai F. Y., Xing Y. H. Three $Pb_x(COO)_y$ cluster frameworks based on a flexible triazinetricarboxylic acid ligand: syntheses, structures, and fluorescent sensing application for nitrophenols. *Inorg. Chem.* 2021, *60*, 7887–7899.
9. Zeng L. W., Hu K. Q., Huang Z. W., Mei L., Kong X. H., Liu K., Zhang X. L., Zhang Z. H., Chai Z. F., Shi W. Q. Controlling the secondary assembly of porous anionic uranyl-organic polyhedra through organic cationic templates. *Dalton Trans.* 2021, *50*, 4499–4503.
10. Gu J. Z., Cai Y., Wen M., Shi Z. F., Kirillov A. M. A new series of Cd(II) metal-organic architectures driven by soft ether-bridged tricarboxylate spacers: synthesis, structural and topological versatility, and photocatalytic properties. *Dalton Trans.* 2018, *47*, 14327–14339.
11. Du D.-D., Ren N., Zhang J.-J. Construction of lanthanide ternary complexes based on 2,4-difluorobenzoic acid and 5,5′-dimethyl-2,2′-bipyridine: crystal structures, thermoanalysis and luminescence properties. *Thermochim. Acta* 2021, *696*, 178839.
12. Mazurier A., Billy I., Lemoine P., Viossat B., Tomas A. Crystal structure of bis(salicylato)(1,10-phenanthroline)(dimethylformamide)cadmium(II), $C_{27}H_{25}CdN_3O_7$. *Z. Kristallogr. N. Cryst. Struct.* 2000, *215*, 113–114.
13. Wu W. P., Wang J., Lu L., Xie B., Wu Y., Kumar A. Syntheses, hirshfeld surface analyses, and luminescence of four new complexes. *Russ. J. Coord. Chem.* 2016, *42*, 71–80.
14. Wang H., Wang K., Sun D., Ni Z.-H., Jiang J. Synthesis, crystal structures, and luminescent properties of Cd(II) coordination polymers assembled from asymmetric semi-rigid V-shaped multicarboxylate ligands. *CrystEngComm* 2011, *13*, 279–286.
15. Tai X., Jiang J. Synthesis, crystal structure and luminescent property of Cd (II) complex with N-benzenesulphonyl-L-leucine. *Materials* 2012, *5*, 1626–1634.