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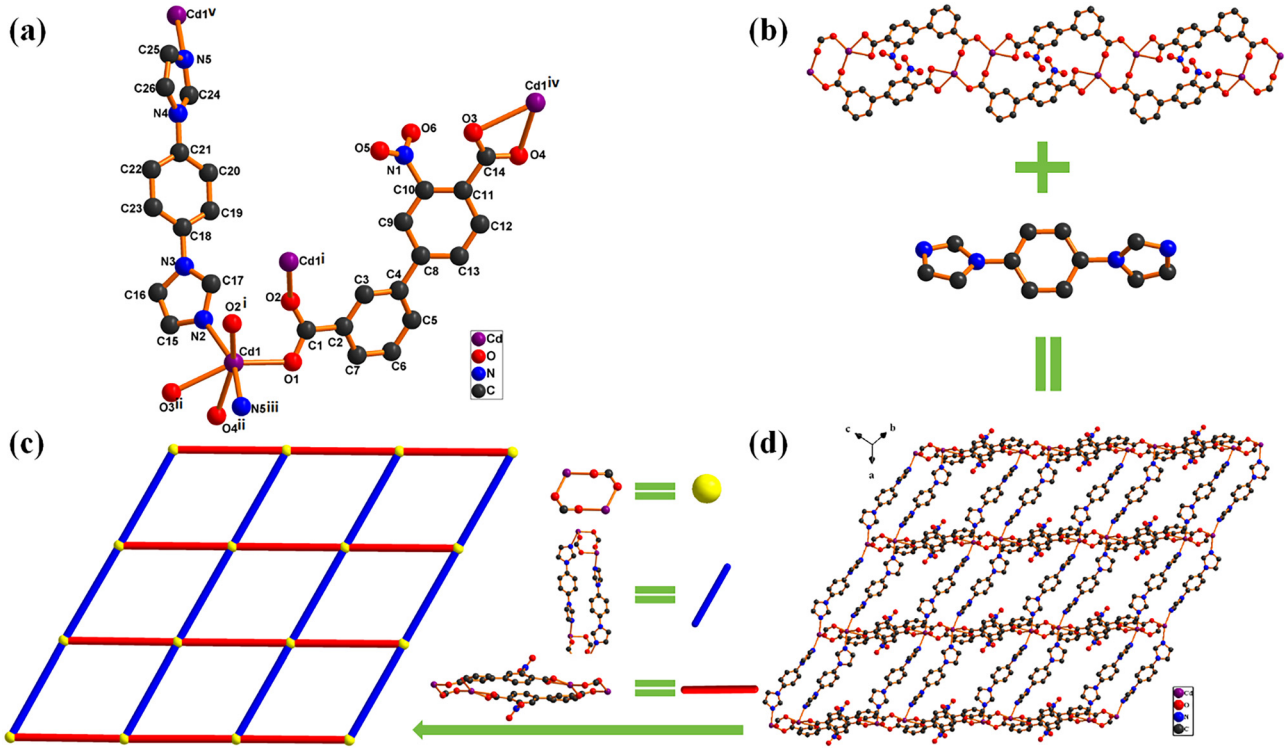
The crystal structure of poly((μ2-3-(3-nitro-4-carboxylphenyl)benzoate-κ3O, O′:O″)-μ2-1,4-bis(1-imidazolyl)benzene-κ2N:N′-cadmium(II)), $C_{26}H_{17}N_5O_6Cd$



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Abstract

$C_{26}H_{17}N_5O_6Cd$, triclinic, $P\bar{1}$ (no. 2), a = 8.9027(7) Å, b = 11.2670(5) Å, c = 11.6794(6) Å, α = 77.630(4)°, β = 87.620(5)°, γ = 87.138(5)°, V = 1142.33(12) Å^3, Z = 2, $R_{gt}(F)$ = 0.0335, $wR_{ref}(F^2)$ = 0.0753, T = 298 K.

CCDC no.: 2045767

Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.15 × 0.10 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.01 mm^{-1}
Diffractometer, scan mode:	Oxford Xcalibur, ω scan
θ_{max}, completeness:	25.1°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6,314, 4,068, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3491
$N(param)_{refined}$:	343
Programs:	Oxford,[1] Olex2,[2] SHELX[3,4]

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parameters can be found in the cif-file attached to this article.

1 Source of materials

All chemicals were purchased from commercial sources and used as received. A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.0492 g, 0.2 mmol), 3-(3-nitro-4-carboxylphenyl)benzoate (H_2nba) (0.0281 g, 0.1 mmol), 1,4-bis(1-imidazolyl)benzene (bib) (0.0213 g, 0.1 mmol), H_2O (6 mL), and C_2H_5OH (3 mL) were placed in a Teflon-lined stainless-steel vessel (25 mL), which was sealed and heated at 140° for 4 days. After cooling to room temperature, light yellow crystals of I were collected by filtration, washed with distilled water, and then dried in air (yield: 68 % based on Cd). IR data (cm^{-1}): 3062 (w), 1584 (m), 1518 (s), 1405 (w), 1341 (m), 1146 (w), 1106 (w), 844 (m), 784 (m), 724 (s), 646 (w). Elemental analysis calc. for $C_{26}H_{17}N_5O_6Cd$, *Mr* = 607.84: C, 51.41; H, 2.80; N, 11.51. Found: C, 51.34; H, 2.67; N, 11.47 (CCDC number 2045767).

2 Experimental details

CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018) empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was used.[1] Using Olex2,[2] the structure was solved with the ShelXT[3] structure solution program and refined with the ShelXL[4] refinement package. Carbon-bound hydrogen atoms were placed in calculated positions (d = 0.93 Å for CH and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq}(C) for –CH). The structure was examined using the ADDSYM subroutine of PLATON[5] to ensure that no additional symmetry could be applied to the models.

3 Comment

The crystal engineering based on metal-organic frameworks (MOFs) or coordination polymers (CPs) obtains great interest for appealing structures and potential applications in gas storage, microelectronics, ion exchange, chemical separations, nonlinear optics, heterogeneous catalysis, and so on.[6] Generally, structures of such materials are dependent on many factors, such as metal ion, template, metal-ligand ratio, pH, counteranion, and number of coordination sites provided by organic ligands.[7] In assembly of MOFs or CPs, the use of ligands is very important in obtaining the desired MOFs.[8] Compared to other biphenyl carboxylic acids, such as 4,4′-biphenyl-dicarboxyli acid, 2,4′-biphenyl-tetracarboxylic acid, 3,3′,5,5′-biphenyl-dicarboxylic acid, and 3,3′,4,4′-biphenyl-tetracarboxylic acid, biphenyl-3,4′-dicarboxylic acid (H_2bpda) is less common, and the angle between carboxyl groups makes large porous coordination polymers possible.[9–12] Among this kind of ligands, biphenyl-based tetra-, tri-, and bicarboxylates are especially interesting because the free rotation of two phenyl rings can afford different coordination conformations depending on the dihedral angle between them.[13] As indicated by a CSD (Cambridge Structure Database) survey with the help of CSD version 5.46 (November 2024) only 38 H_2bpba-based coordination complexes have been sporadically characterized and reported until now.[14–22]

H_2nba features two biphenyl rings and a nitro group in the 3-position. H_2nba was selected as a ligand, which has the following characteristics: (i) the two carboxyl groups have four O-donor atoms with the dihedral angle 180°, are able to establish bridges between several metal nodes through variety of coordination modes and conjugated aromatic ring allows them to become rigid linkers. (ii) The nitro group in H_2nba provides more hydrogen bonding donor or acceptor sites for supramolecular interactions. In particular, the two nitro O donors play a key role in the formation of potential hydrogen bonded or N–O$\cdots\pi$ interactions. (iii) The ditopic linear rod-like topology introduces low steric hindrance, thus, allowing formation of a porous and stabilized framework. (iv) Biphenyl ring functions as a big space mediator for transmitting exchange interaction between metal centers. (v) Moreover, the two aromatic rings of H_2nba may take part in π–π and C–H$\cdots\pi$ stacking interactions. Despite that numerous MOFs or CPs have been synthesized based on 2,4′-, 4,4′-, and 3,4′-biphenyldicarboxylate acid, little attention has been focused on its derivatives, such as H_2nba. To the best of our knowledge and in a search of the Cambridge Crystal Database (CSD), however, there is only one crystal structure report of H_2nba as ligand for the construction of MOFs or CPs by our research group to date.[23,24] In addition, it is known that a strategy to increase the chemical stability of CPs/MOFs is to strengthen the metal-ligand bond using linkers such as inflexible neutral nitrogen-containing pyridine, pyrazolates or imidazolates instead of carboxylates. In this work, we used H_2nba and bib as organic ligands for Cd(II) centers.

Single-crystal X-ray diffraction analysis shows that I crystallizes in the triclinic crystal system with space group $P\bar{1}$ (no. 2). The asymmetric unit of I contains one Cd(II) cation, one nba^{2-} dianion and one bib ligand. The environment around Cd(II) can be described as a slightly distorted octahedral geometry, defined by four carboxylate oxygen atoms (O1, $O2^{i}$, $O3^{ii}$, $O4^{ii}$; symmetry codes seen in figures or tables) from three independent nba^{2-} dianions

and two nitrogen atoms (N2, N5^{iii}) from two different bib ligands. Each nba^{2-} dianion connects two Cd(II) ions, which are located at its two ends, The Cd–O and Cd–N bond lengths are in the ranges of 2.232(2)–2.351(3) and 2.323(3)–2.491(3) Å, respectively. The Cd(II) cations are connected by nba^{2-} dianions to construct a $[Cd(nba)]_n$ chain (Figure b). The range of distances between Cd(II) and Cd(II) within the $[Cd(nba)]_n$ chain were 4.374(4)–14.387(3) Å. The $[Cd(nba)]_n$ chains are connected by bib ligands to form a 2D network structure (Figure d). In the two-dimensional frame diagram, the structure shown in Figure 1c is simplified into yellow nodes and red and blue connectors. Topologically, the 2D structure of polymer I can be simplified as a 4-c unimodal *sql* topology with a Schläfli symbol $\{4^4.6^2\}$. In the packing, it obviously exist either offset face-to-face $\pi\cdots\pi$ or edge-to-face C–H$\cdots\pi$ and N–O$\cdots\pi$ stacking interactions calculated by PLATON software. The offset face-to-face $\pi\cdots\pi$ interactions between benzene rings (Cg1: C2–C3–C4–C5–C6–C7) of two nba^{2-} ligands (Cg1–Cg1^{iv}, symmetry code: iv 2 – *x*, –*y*, 1 – *z*), and the spacing is 3.738(2) Å (Cg1–Cg1^{iv}), and the dihedral angle between planes Cg1 and Cg1^{iv} is 0°. It is worth mentioning that the adjacent two-dimensional depend not only by C–H$\cdots$O, and $\pi\cdots\pi$, but also by 3 edge-to-face C–H$\cdots\pi$ and 2 N–O$\cdots\pi$ stacking interactions, i.e. between the Cg2^{v} and C5–H5 (C5–H5$\cdots$Cg2^{v}, symmetry code: v *x*, *y*, –1 + *z*), between the Cg3^{vi} and C7–H7 (C7–H7$\cdots$Cg3^{vi}, symmetry code: vi 1 – *x*, –*y*, 2 – *z*), between the Cg1^{vi} and C16–H16 (C16–H16$\cdots$Cg1^{vi}), and between the Cg4^{vii} and N1–O5 (N1–O5$\cdots$Cg4^{vii}, symmetry code: vii 1 – *x*, 1 – *y*, 2 – *z*), between the Cg5^{viii} and N1–O5 (N1–O5$\cdots$Cg5^{viii}, symmetry code: viii 2 – *x*, 1 – *y*, 1 – *z*) (Cg2: N2–C15–C16–N3–C17, Cg3: C18–C19–C20–C21–C22–C23, Cg4: N4–C24–N5–C25–C26, Cg5: C8–C9–C10–C11–C12–C13). The C–H$\cdots$Cg, N1–O5$\cdots$Cg (Y–X$\cdots$Cg) dihedral angles range from 118 to 155°, and with H$\cdots$Cg, O5$\cdots$Cg (X$\cdots$Cg) distances of 2.86–2.97 and 3.266(4)–3.717(4) Å, and C$\cdots$Cg, N1$\cdots$Cg (Y$\cdots$Cg) distances of 3.512(4)–3.837(4) and 4.180(4)–4.428(4) Å, respectively. However, their contribution to the overall lattice energy must be very small. Thus a supramolecular 3D network fragment is formed by C–H$\cdots$O and $\pi\cdots\pi$, C–H$\cdots\pi$, N–O$\cdots\pi$ interactions stabilizing the coordination polymer. Furthermore, PLATON analysis shows that the unit cell contains no residual solvent accessible void.

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