

4,4'-Methylenediphenol–4,4'-bipyridine (2/3): decarboxylation of 5,5'-methylenedisalicylic acid under hydrothermal conditions

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Received 1 June 2009

Accepted 3 August 2009

Online 15 August 2009

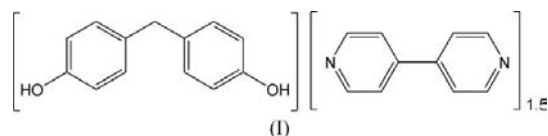
Reaction of 5,5'-methylenedisalicylic acid (5,5'-H₄mdsa) with 4,4'-bipyridine (4,4'-bipy) and manganese(II) acetate under hydrothermal conditions led to the unexpected 2:3 binary cocrystal 4,4'-methylenediphenol–4,4'-bipyridine (2/3), C₁₃H₁₂O₂·1.5C₁₀H₈N₂ or (4,4'-H₂dhdp)(4,4'-bipy)_{1.5}, which is formed with a concomitant decarboxylation. The asymmetric unit contains one and a half 4,4'-bipy molecules, one of which straddles a centre of inversion, and one 4,4'-H₂dhdp molecule. O—H···N interactions between the hydroxy and pyridyl groups lead to a discrete ribbon motif with an unusual 2:3 stoichiometric ratio of strong hydrogen-bonding donors and acceptors. One of the pyridyl N-atom donors is not involved in hydrogen-bond formation. Additional weak C—H···O interactions between 4,4'-bipy and 4,4'-H₂dhdp molecules complete a two-dimensional bilayer supramolecular structure.

Comment

Hydrothermal syntheses have been widely used in crystal engineering to produce functional metal–organic coordinate networks such as zeolites, nanomaterials and metal–oxide hydrogen-storage materials (Rowell & Yaghi, 2005). Many unprecedented *in situ* metal/organic reactions, including ligand oxidative coupling, hydrolysis and substitution, have been detected during the hydrothermal process (Chen & Tong, 2007). Among these cases, hydrothermal decarboxylations have frequently been reported in the process of discovering novel metal–organic frameworks (Yigit *et al.*, 2006; Sun *et al.*, 2006).

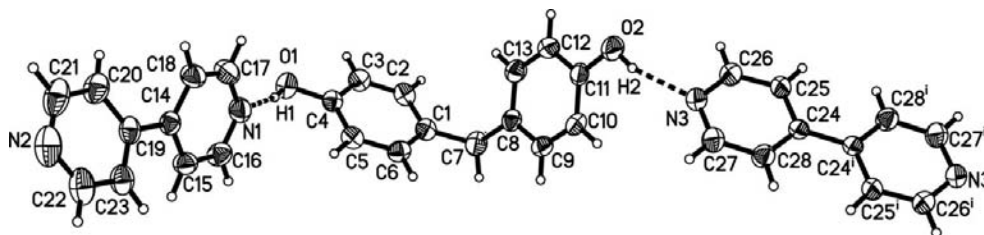
In this work, we chose 5,5'-methylenedisalicylic acid (5,5'-H₄mdsa), bearing both carboxyl and hydroxy groups, along with 4,4'-bipyridine (4,4'-bipy) and manganese(II) acetate, in an attempt to create a novel inorganic–organic hybrid complex under hydrothermal conditions. Unexpectedly, hydrothermal reaction at 413 K led ultimately to the forma-

tion of the title 2:3 binary cocrystal (4,4'-H₂dhdp)(4,4'-bipy)_{1.5}, (I), in which 4,4'-methylenediphenol (4,4'-H₂dhdp) is generated by concomitant *in situ* decarboxylation of 5,5'-H₄mdsa. Notably, combination of 5,5'-H₄mdsa and 4,4'-bipy without Mn^{II} ions under the same synthetic conditions did not lead to decarboxylation, rather resulting in an unidentified white precipitate. Due to one of the pyridyl N-atom donors of 4,4'-bipy not forming any hydrogen bonds, this composition is not consistent with the hydrogen-bond donating/accepting ability of the two subunits (equivalent hydroxy and pyridyl groups). In compound (I), both classical O—H···N and weak C—H···O interactions are involved in constructing an unusual two-dimensional hydrogen-bonded bilayer with a simple mononodal **hcb** network (Delgado-Friedrichs *et al.*, 2005). Significantly, the decarboxylation of 5,5'-H₄mdsa under hydrothermal conditions has not been documented thus far, although incomplete decarboxylation catalyzed by Mn^{II} ions of other polycarboxylic acids containing N-atom donors has been detected recently (Wu *et al.*, 2007).

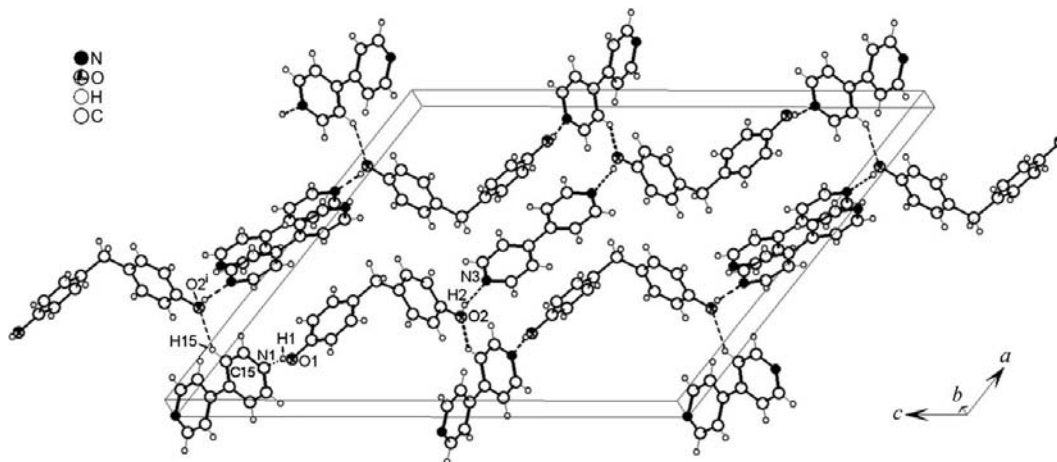


The asymmetric unit of (I) contains one and a half 4,4'-bipy molecules and one 4,4'-H₂dhdp molecule (Fig. 1). In the 4,4'-H₂dhdp component, the dihedral angle between the two benzene rings is 76.2 (3)°, while the two pyridyl ring planes in one of the 4,4'-bipy molecules which occupies a general position make a dihedral angle of 27.9 (4)° with each other. The centrosymmetric 4,4'-bipy molecule is connected to two 4,4'-H₂dhdp components *via* O2—H2···N3 interactions between a pyridyl N atom and a hydroxy H atom, and the other hydroxy group of the 4,4'-H₂dhdp molecule is linked to the other 4,4'-bipy molecule through O1—H1···N1 hydrogen bonds (Fig. 2 and Table 1). Such hydrogen bonds lead to a discrete ribbon-like motif with a repeat length of *ca* 40 Å, which is further extended to a two-dimensional supramolecular architecture *via* weak C15—H15···O2¹ interactions [symmetry code: (i) *x*, *-y* + $\frac{5}{2}$, *z* + $\frac{1}{2}$]. Further topological analysis using the *TOPOS* package indicates that (I) is an **hcb** (6³) bilayer net (Blatov, 2004, 2006). Additionally, neighbouring two-dimensional arrays stack somewhat offset along the [010] direction, and they are further joined into a three-dimensional supramolecular motif by aromatic π – π interactions between the non-hydrogen-bonded pyridyl groups from adjacent layers, with centroid–centroid and centroid–ring distances of 3.806 (2) and 3.423 (1) Å, respectively.

Thermogravimetric analysis shows that three consecutive weight losses occur in the range 318–598 K, corresponding to the complete decomposition of the hydrogen-bonding network. The first weight loss occurs in the range 318–373 K, corresponding to the removal of the centrosymmetric 4,4'-bipy molecule (calculated 18.0%; observed 17.9%). The second weight loss of 35.8% at 396–476 K corresponds to the loss of


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x + 1, -y + 3, -z + 1$.]


Figure 2

A view of the two-dimensional hydrogen-bonded bilayer of (I). Hydrogen bonds are indicated by dashed lines. [Symmetry code: (i) $x, -y + \frac{5}{2}, z + \frac{1}{2}$.]

the other 4,4'-bipy component (calculated 36.0%). A sharp weight loss of all residual samples then begins at 488 K and stops at 598 K, indicating the decomposition of the 4,4'-H₂dhdp molecules.

The 4,4'-H₂dhdp molecule has seldom been utilized in the construction of coordination complexes (Son *et al.*, 2005) or molecular cocrystals (Vangala *et al.*, 2005). There are only two examples of its cocrystals, which arise from complementary O—H···N and N—H···O recognition with dianilines. Both cases reveal that the formation of 1:1 diphenol–diamine molecular cocrystals is the usual propensity, since the resulting N—H···O hydrogen bonds are stronger than the O—H···O and N—H···N bonds in the crystal structures of the respective individual components (Vangala *et al.*, 2005). By contrast, in this work, an unexpected 2:3 molecular cocrystal of diphenol–diamine is afforded, connected by strong O—H···N hydrogen bonds. It is unusual that one of the pyridyl N-atom donors is 'free' and this phenomenon plays a dominant role in controlling the discrete hydrogen-bonding ribbon array with the 2:3 ratio of hydroxy and pyridyl subunits. This result presents a new challenge in the seemingly predictable crystal engineering of complementary diphenol–diamine systems, and further investigation is warranted.

Experimental

An aqueous solution (10 ml) of 4,4'-bipy (7.8 mg, 0.05 mmol), 5,5'-H₄mdsa (14.4 mg, 0.05 mmol) and Mn(OAc)₂·4H₂O (12.3 mg,

0.05 mmol) was placed in a Parr Teflon-lined stainless steel vessel (20 ml), which was sealed and heated to 413 K for 72 h and then subsequently cooled to room temperature at a rate of 5 K h⁻¹. Colourless block-shaped crystals of (I) were obtained in 45% yield (9.8 mg, based on 4,4'-bipy). Analysis calculated for C₂₈H₂₄N₃O₂: C 77.40, H 5.57, N 9.67%; found: C 77.44, H 5.69, N 9.71%. Thermogravimetric analysis (TGA) was recorded with a Dupont thermal analyser in the temperature range 298–1073 K under a nitrogen atmosphere at a heating rate of 10 K min⁻¹.

Crystal data

C ₁₃ H ₁₂ O ₂ ·1.5C ₁₀ H ₈ N ₂	$V = 2261.0 (4) \text{ \AA}^3$
$M_r = 434.50$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 19.606 (2) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$b = 5.7354 (6) \text{ \AA}$	$T = 294 \text{ K}$
$c = 25.4316 (18) \text{ \AA}$	$0.25 \times 0.16 \times 0.14 \text{ mm}$
$\beta = 127.755 (5)^\circ$	

Data collection

Bruker APEXII CCD area-detector diffractometer	11614 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	3976 independent reflections
$T_{\min} = 0.981, T_{\max} = 0.988$	2727 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	299 parameters
$wR(F^2) = 0.120$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
3976 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots N1	0.82	1.91	2.712 (2)	167
O2—H2 \cdots N3	0.82	1.98	2.770 (2)	161
C15—H15 \cdots O2 ⁱ	0.93	2.59	3.414 (2)	149

Symmetry code: (i) $x, -y + \frac{5}{2}, z + \frac{1}{2}$.

All H atoms were visible in difference maps. C-bound H atoms were placed at calculated positions, with C—H = 0.93 (for Csp^2 atoms) or 0.97 Å (for Csp^3 atoms) and refined as riding atoms. Hydroxy H atoms were refined as rigid groups that were allowed to rotate but not tip, with O—H = 0.82 Å. For all H atoms, $U_{iso}(H)$ values were set at $1.2U_{eq}(C)$ or $1.5U_{eq}(O)$.

Data collection: *APEX2* (Bruker, 2003); cell refinement: *APEX2* and *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

This work was supported financially by Jiangsu Polytechnic University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3200). Services for accessing these data are described at the back of the journal.

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