

METAL-ORGANIC COMPOUNDS

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Four interpenetrating three-dimensional frameworks in the hydrogen-bonded structure of 5-hydroxyisophthalic acid–4,4'-trimethylenedipyridine (1/1)

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Abstract

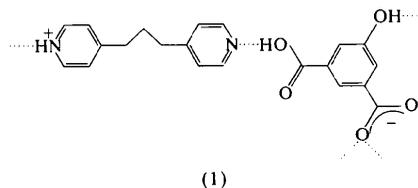
The 1:1 adduct of 5-hydroxyisophthalic acid and 4,4'-trimethylenedipyridine is a salt, $[\text{HNC}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4\text{N}]^+ \cdot [\text{HOC}_6\text{H}_3(\text{COOH})\text{COO}]^- (\text{C}_{13}\text{H}_{15}\text{N}_2^+ \cdot \text{C}_8\text{H}_5\text{O}_5^-)$. The anions are linked into *C*(7) chains by means of $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds [$\text{O} \cdots \text{O}$ 2.734 (2) Å and $\text{O} \cdots \text{H} \cdots \text{O}$ 176°], and these chains are linked by the cations *via* $\text{O} \cdots \text{H} \cdots \text{N}$ and $\text{N} \cdots \text{H} \cdots \text{O}$ hydrogen bonds [$\text{O} \cdots \text{N}$ 2.620 (2) Å, $\text{O} \cdots \text{H} \cdots \text{N}$ 175°, $\text{N} \cdots \text{O}$ 2.748 (2) Å and $\text{N} \cdots \text{H} \cdots \text{O}$ 176°] into four identical but independent interpenetrating three-dimensional frameworks.

Comment

In the supramolecular structures of hydrogen-bonded adducts formed from simple molecular compounds, the local arrangement of the hydrogen bonds can often be predicted with considerable accuracy. However, despite this local predictability, the overall supramolecular architecture often provides surprises, as even a small structural change in just one of the molecular building blocks can sometimes give rise to major changes in the overall architecture. Thus, for example, the hydrogen-bonded adduct of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane with 3-hydroxybenzoic acid forms molecular ladders, while in the corresponding adduct with 4-hydroxybenzoic acid, continuous two-dimensional nets are formed (Gregson *et al.*, 1999). Similarly, with the bis-phenol $\text{S}(\text{C}_6\text{H}_4\text{OH})_2$, piperazine forms a simple chain structure containing no void space (Coupar *et al.*, 1996a), while with the closely related bis-phenol $\text{O}_2\text{S}(\text{C}_6\text{H}_4\text{OH})_2$, piperazine forms a structure containing open channels (Coupar *et al.*, 1996b).

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The extended dipyridine 4,4'-trimethylenedipyridine, $\text{NC}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4\text{N}$, forms a perforated molecular tape in its adduct with 1,3,5-benzenetricarboxylic acid, $\text{C}_6\text{H}_3(\text{OH})_3$ (trimesic acid, TMA; Ferguson *et al.*, 1998). We have now investigated the behaviour of the same extended dipyridine with a closely related acid, 5-hydroxyisophthalic acid, $\text{HOC}_6\text{H}_3(\text{COOH})_2$, which resembles TMA in having a 1,3,5-arrangement of the three substituents on the aromatic ring, all three of which are potential hydrogen-bond donors. The 1,3,5-arrangement of these substituents precludes any intramolecular hydrogen bonding. Here, we report the synthesis and structure of the 1:1 adduct, (1), formed between 4,4'-trimethylenedipyridine and 5-hydroxyisophthalic acid, which proves to contain four interpenetrating three-dimensional frameworks, in sharp contrast to the one-dimensional structure of the product from TMA (Ferguson *et al.*, 1998) and again illustrating the major change in supramolecular structure which can result from a rather minor change in the constitution of one of the molecular components.



It is noteworthy that the 1:1 salt, (1), and the 1:1 analogue formed by TMA are both formed from solutions in which the molar ratio of acid to amine is 2 to 3, so that the numbers of hydrogen bond donors and acceptors are identical. By contrast, similar molar ratios in mixtures of either TMA (Sharma & Zaworotko, 1996) or the tris-phenol $\text{CH}_3\text{C}(\text{C}_6\text{H}_4\text{OH})_3$ (Bényei *et al.*, 1998) with 4,4'-bipyridine itself gave 2:3 adducts as expected. Compound (1) thus forms preferentially from reaction mixtures which are stoichiometrically biased against its formation.

In compound (1), one unit of each component lies in a general position in space group $P2_1/c$. Difference maps clearly showed the complete transfer of an H atom from one carboxyl group to one of the N atoms of the diamine, so that (1) is the salt $[\text{HNC}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4\text{N}]^+ \cdot [\text{HOC}_6\text{H}_3(\text{COOH})\text{COO}]^-$. Within the selected asymmetric unit (Fig. 1), O12 acts as a donor to N31 in a short, almost linear, $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen bond (Table 2). Just two further types of hydrogen bond (Table 2) between these molecular aggregates then serve to generate the entire supramolecular structure.

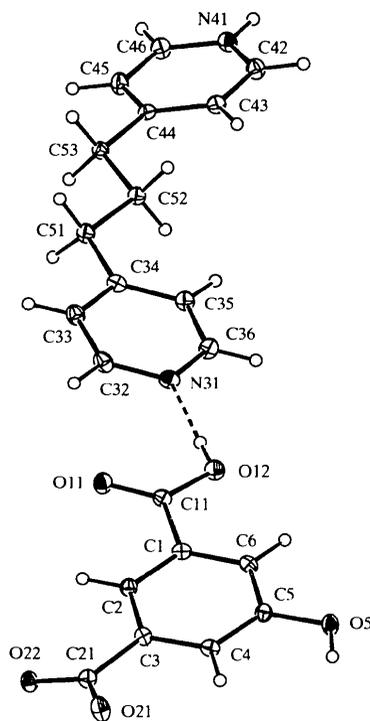


Fig. 1. The asymmetric unit of (1) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of an arbitrary radius.

The 5-hydroxyisophthalate anions are linked into chains by means of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, and the diamine cations link these chains into a continuous three-dimensional framework. The hydroxyl group $\text{O5}-\text{H5}$ at (x, y, z) acts as a donor to the carboxylate-O atom O22 at $(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$, and $\text{O5}-\text{H5}$ at $(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$ acts in turn as donor to O22 at $(x, y, -1+z)$, so producing a $C(7)$ chain running parallel to the $[001]$ direction. This chain, generated by the glide plane at $y = -\frac{1}{4}$, lies along a line at approximately $(\frac{1}{4}, -\frac{1}{4}, z)$. There is a second chain generated by the glide plane at $y = \frac{1}{4}$, running in the opposite direction approximately along the line $(\frac{3}{4}, \frac{1}{4}, z)$, and related to the first chain by the action of centres of inversion. Hence, two antiparallel $C(7)$ chains run through each unit cell.

The connections between the $C(7)$ chains involve the diamine cations acting as donors of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and acceptors of $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds. The $\text{O12}-\text{H12}$ hydroxyl group acts as donor to N31 within the asymmetric unit at (x, y, z) , and the protonated nitrogen N41 in the same molecular aggregate at (x, y, z) acts as donor to the carboxylate-O atom O22 at $(-1+x, 1+y, z)$, so producing a $C_2^2(20)$ chain running parallel to the $[\bar{1}10]$ direction. In the other component of the $C(7)$ chain, at $(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$, N41 acts as hydrogen-bond donor to O22 at $(-1+x, -\frac{3}{2}-y, -\frac{1}{2}+z)$, so

producing a second $C_2^2(20)$ chain running parallel to the $[110]$ direction. The anions at $(-1+x, 1+y, z)$ and $(-1+x, -\frac{3}{2}-y, -\frac{1}{2}+z)$ are themselves components of $C(7)$ chains running approximately along the lines $(\frac{3}{4}, \frac{3}{4}, z)$ and $(-\frac{3}{4}, -\frac{5}{4}, z)$ respectively. There are thus two families of $C_2^2(20)$ chains, related by the action of the glide planes, and it is the interaction of these $C_2^2(20)$ chains with the $C(7)$ chains they share in common which generates the three-dimensional framework.

The combination of $C(7)$ and $C_2^2(20)$ chains running parallel to the $[001]$ and $[\bar{1}10]$ directions, respectively, generates a two-dimensional net parallel to the (110) plane built from $R_8^7(62)$ rings (Fig. 2), while the corresponding combination of $[001]$ and $[110]$ chains generates a similar net parallel to $(\bar{1}\bar{1}0)$. The stacks of these nets generated by translation thus repeatedly intersect at the $C(7)$ chains which serve to connect the (110) and $(\bar{1}\bar{1}0)$ sheets. However, within each stack only the alternate members are linked by members of the other stack: thus, for example, the 5-hydroxyisophthalate anion at (x, y, z) is directly connected, *via* a series of hydrogen bonds and covalent bonds, to the corresponding anions at $(1+x, 1+y, z)$ and $(1+x, -1+y, z)$, but no such connection can be traced to the anion at $(1+x, y, z)$. There are thus two independent but fully interpenetrating three-dimensional frameworks resulting from these

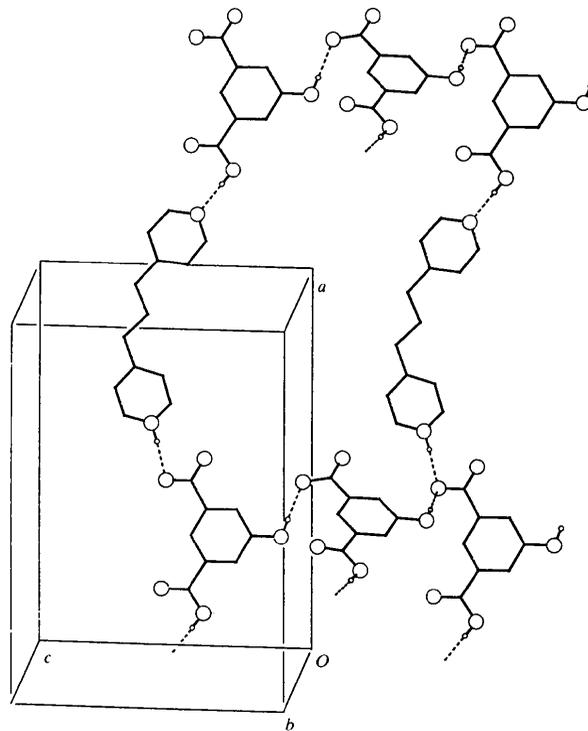


Fig. 2. Part of the crystal structure of (1), showing one of the framework-forming $R_8^7(62)$ rings.

two stacks of nets. These two frameworks are generated by means of the glide plane and translation operations only. There is, in addition, an entirely similar pair of frameworks resulting from the action of the inversion centres on the first pair. Hence, the entire supramolecular structure consists of four identical hydrogen-bonded frameworks, each fully interwoven with the other three. The sole connection between these frameworks is provided by the aromatic $\pi \cdots \pi$ stacking interactions between unprotonated pyridine rings in pairs of aggregates related by centres of inversion. Thus, the N31/C32–C36 rings in the units at (x, y, z) and $(-x, 1-y, 1-z)$ are parallel, with a perpendicular distance between their planes of 3.41 (1) Å and with their centroids offset by 1.22 (1) Å, almost optimum for $\pi \cdots \pi$ stacking (Hunter, 1994).

In addition to the hard hydrogen bonds of the O—H \cdots O, O—H \cdots N and N—H \cdots O types, there is a single type of soft C—H \cdots O hydrogen bond within the structure (Table 2). The C46—H46 aromatic group at (x, y, z) acts as a donor to the O21 carboxylate group at $(-1+x, \frac{1}{2}-y, \frac{1}{2}+z)$: this interaction occurs within a single framework and so has no significant effect on the overall structure description. In this respect, the structure of (1) may be contrasted with that of the corresponding salt formed from TMA (Ferguson *et al.*, 1998), where the local hydrogen bonding is very different from that in (1). In the TMA salt, [C₆H₃(COOH)₂COO]⁻ mono-anions are linked into centrosymmetric R₂²(16) rings by means of paired O—H \cdots O⁻ hydrogen bonds [cf. the C(7) chain of anions in (1)], and these dimer units are then linked by the cations into a molecular tape. There are, however, four different types of strong short C—H \cdots O hydrogen bonds which serve to link these tapes. By contrast, the C—H \cdots O hydrogen bond in (1), although very short (Table 2) because of the anionic nature of the acceptor and the cationic N adjacent to the donor (Gilli *et al.*, 1994), does not significantly influence the overall structure.

Within the molecular building blocks in (1), the C—O distances in the anions (Table 1) are all in accord with the location of the H atoms. In the cations, there is no significant difference between the C—N distances involving the protonated and unprotonated N atoms, but the C—N—C angles at these N atoms are very different (Table 1), consistent with the greater effective electronegativity of the protonated-N atom (Domenicano & Murray-Rust, 1979). The carboxyl groups containing C11 and C12 are rotated out of the plane of the carboxylic acid ring by 7.2 (1) and 18.8 (1)°, respectively. The trimethylene spacer group adopts the extended chain conformation (Table 1), and the neutral and protonated pyridine rings are twisted out of the plane of the trimethylene skeleton by 7.5 (1) and 18.0 (1)°, respectively. Examination of the structure with PLATON (Spek, 1999) showed that there were no solvent accessible voids in the crystal lattice.

Experimental

The two components were dissolved separately in dry methanol. Aliquots of these solutions were mixed to give a stoichiometric ratio, acid to amine, of 2:3, and the mixture was set aside to crystallize, yielding analytically pure (1). Analysis: found C 65.8, H 5.5, N 7.4%; C₂₁H₂₀N₂O₅ requires C 66.3, H 5.3, N 7.4%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

C₁₃H₁₅N₂·C₈H₅O₅⁻

M_r = 380.39

Monoclinic

*P*2₁/*c*

a = 19.2490 (6) Å

b = 7.3915 (4) Å

c = 12.6587 (6) Å

β = 92.554 (3)°

V = 1799.28 (14) Å³

Z = 4

D_x = 1.404 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 4073

reflections

θ = 4.21–27.48°

μ = 0.101 mm⁻¹

T = 100.0 (1) K

Block

0.28 × 0.25 × 0.20 mm

Colourless

Data collection

Nonius KappaCCD diffractometer

φ and ω scans with κ offsets

Absorption correction:

multi-scan (DENZO-SMN;

Otwinowski & Minor,

1997)

T_{min} = 0.972, *T_{max}* = 0.980

11 920 measured reflections

4073 independent reflections

2707 reflections with

I > 2σ(*I*)

R_{int} = 0.056

θ_{\max} = 27.48°

h = -24 → 24

k = -9 → 0

l = 0 → 16

Intensity decay: negligible

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.046

wR(*F*²) = 0.116

S = 1.025

4073 reflections

255 parameters

H atoms constrained

w = 1/[σ²(*F_o*²) + (0.0569*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.232 e Å⁻³

Δρ_{min} = -0.293 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O11—C11	1.220 (2)	N31—C32	1.341 (2)
O12—C11	1.317 (2)	N31—C36	1.335 (2)
O21—C21	1.242 (2)	N41—C42	1.337 (2)
O22—C21	1.281 (2)	N41—C46	1.337 (2)
O5—C5	1.361 (2)		
O5—C5—C4	121.98 (14)	O21—C21—O22	123.71 (15)
O5—C5—C6	118.62 (14)	C32—N31—C36	116.93 (13)
O11—C11—O12	124.22 (14)	C42—N41—C46	121.48 (14)
C33—C34—C51—C52	173.6 (2)	C45—C44—C53—C52	164.0 (2)
C34—C51—C52—C53	175.4 (2)	C51—C52—C53—C44	-179.2 (2)

Table 2. *Hydrogen-bonding geometry* (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O5—H5...O22 ⁱ	0.84	1.89	2.734 (2)	176
O12—H12...N31	0.84	1.78	2.620 (2)	175
N41—H41...O22 ⁱⁱ	0.88	1.87	2.748 (2)	176
C46—H46...O21 ⁱⁱⁱ	0.95	2.12	3.023 (2)	158

Symmetry codes: (i) $x, -\frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x - 1, 1 + y, z$; (iii) $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$.

Compound (1) crystallized in the monoclinic system; space group $P2_1/c$ was deduced from the systematic absences. H atoms were treated as riding, with C—H 0.95 and 0.97, N—H 0.88 and O—H 0.84 \AA .

Data collection: *Kappa-CCD Server Software* (Nonius, 1997). Cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997). Data reduction: *DENZO-SMN*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *NRCVAX96* (Gabe *et al.*, 1989) and *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1999). Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC, Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1297). Services for accessing these data are described at the back of the journal.

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Linking of $C_4^1(32)[R_4^1(30)]$ chains of rings in the hydrogen-bonded adduct 3,5-dihydroxybenzoic acid–4,4'-bipyridine (2/3) by means of $\pi \cdots \pi$ stacking interactions

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Abstract

In the 2:3 adduct of 3,5-dihydroxybenzoic acid and 4,4'-bipyridine, $2C_7H_6O_4 \cdot 3C_{10}H_8N_2$, the two components are linked by six independent O—H...N hydrogen bonds [O...N 2.685 (3)–2.814 (3) \AA and O—H...N 170–178 $^\circ$] into a $C_4^1(32)[R_4^1(30)]$ chain of rings. Each chain is linked to two neighbouring chains by means of aromatic $\pi \cdots \pi$ stacking interactions.

Comment

Both trimesic acid (1,3,5-benzenetricarboxylic acid, TMA) and phloroglucinol (1,3,5-trihydroxybenzene) form hydrogen-bonded adducts with 4,4'-bipyridine (Sharma & Zaworotko, 1996; Coupar *et al.*, 1996). In each case, the amine acts as a double acceptor of hydrogen bonds and the hydroxylic component acts as a triple donor, and the observed 2:3 stoichiometric ratio of donor molecules to acceptors means that the numbers of carboxyl or hydroxyl hydrogen-bond donor sites and amine acceptor sites are precisely matched. However, despite the similar stoichiometries of these two adducts, and the similar local arrangement of the O—H...N hydrogen bonds, the overall supramolecular architectures are entirely different. The TMA adduct (Sharma & Zaworotko, 1996) contains two-dimensional nets built from a single type of $R_2^2(102)$ ring (Bernstein *et al.*, 1995), while the

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