Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$\cdots$O22^{i}	0.84	1.89	2.734 (2)	176
O12—H12$\cdots$N31	0.84	1.78	2.620 (2)	175
N41—H41$\cdots$O22^{ii}	0.88	1.87	2.748 (2)	176
C46—H46$\cdots$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 Å.

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*, *ORTEP*II (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.

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Linking of $C_4^4(32)[R_4^4(30)]$ 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$\cdots$N hydrogen bonds [O$\cdots$N 2.685 (3)–2.814 (3) Å and O—H$\cdots$N 170–178°] into a $C_4^4(32)[R_4^4(30)]$ 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$\cdots$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

1,3,5-trihydroxybenzene adduct (Coupar et al., 1996) contains a $C_4^4(30)[R_4^4(30)]$ chain of rings (Bernstein et al., 1995). Intrigued by the difference in behaviour with 4,4'-bipyridine shown by these two trigonally symmetric hydrogen-bond donors, we have now investigated the corresponding hydrogen-bonded adduct formed between 4,4'-bipyridine and the hybrid donor 3,5-dihydroxybenzoic acid, 3,5-(HO)$_2$C$_6$H$_3$COOH, and here we report the synthesis and structural characterization of this adduct, (1).

(1)
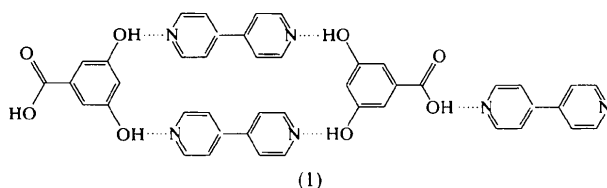
The adduct, (1), has 2:3 stoichiometry, 2C$_7$H$_6$O$_4$·-3C$_{10}$H$_8$N$_2$, and the asymmetric unit (Fig. 1) consists of two molecules of the acid and three of the diamine, all lying in general positions in the space group $P\overline{1}$. Difference maps showed that all the H atoms are fully ordered and there is no transfer of H from the acid to the diamine. Both molecules of the acid act as triple donors of hydrogen bonds and each molecule of the diamine acts as a double acceptor. Within the asymmetric unit, the four independent hydroxyl groups, containing O13, O15, O23 and O25, act as donors to N51, N71, N61 and N81, respectively (Fig. 1 and Table 2), so producing an $R_4^4(30)$ ring from which the two independent carboxyl groups are pendent. The carboxyl hydroxy group O12—H acts as donor to N31 in the third diamine molecule within the asymmetric unit, while the second carboxyl hydroxy group O22—H at (x, y, z) acts as donor to N41 in the unit at $(3 + x, 1 + y, z)$, so generating a $C_4^4(32)[R_4^4(30)]$ chain of rings running parallel to the [310] direction.

Considering other related systems containing triple-donor and double-acceptor building blocks in the molar ratio of 2:3, the 2:3 adduct of the triphenol

CH$_3$C(C$_6$H$_4$OH)$_3$ and 4,4'-bipyridine is built from tenfold interwoven nets of $R_{12}^2(126)$ rings (Bényei et al., 1998), whereas the 2:3 adduct of phloroglucinol and (CH$_2$)$_6$N$_4$ (which generally acts as just a double acceptor) forms a $C_4^3(20)[R_4^4(20)]$ chain of rings (Coupar et al., 1997).

The O—H···N hydrogen bonds within the structure are all nearly linear (Table 2), and the entire chain is virtually linear. Three chains parallel to [310], all lying within the domain $0 < z < \frac{1}{2}$, run through each unit cell, and three further chains antiparallel to the first set and related to them by centres of inversion lie within the domain $\frac{1}{2} < z < 1$, so making a total of six chains running through each unit cell. Within each domain of z defined above, every chain is connected to its two neighbouring chains by means of aromatic $\pi \cdots \pi$ stacking interactions. Each of the two rings of the bridging bipyridine unit overlaps an aryl ring in the acid components in two other chains: the N31,C32–C36 ring at (x, y, z) overlaps the C11–C16 ring at $(-1 + x, y, z)$, with a perpendicular separation of 3.53 (1) Å and a centroid offset of 1.47 (1) Å, and the N41,C42–C46 ring in the same diamine at (x, y, z) overlaps the C21–C26 ring at $(-2 + x, -1 + y, z)$, with perpendicular separations and a centroid offset of 3.50 (1) and 1.66 (1) Å, respectively. These values are close to the ideal for aromatic $\pi \cdots \pi$ stacking interactions (Hunter, 1994). The asymmetric unit at $(-2 + x, -1 + y, z)$ is in the same [310] chain as that at $(1 + x, y, z)$. Hence, the chain containing the asymmetric unit at (x, y, z) is linked by the $\pi \cdots \pi$ stacking interactions to its neighbours containing units at $(-1 + x, y, z)$ and $(1 + x, y, z)$. Thus, all the chains in a given domain are linked in this manner. Between the chains in different domains there are no contacts shorter than the sum of the van der Waals radii.

Within the molecular components, the three independent diamine units are all twisted about the central C—C bonds. The dihedral angles between the aryl rings are 20.1 (2), 21.4 (2) and 19.5 (2)°, respectively, for the diamines containing N31, N51 and N71. In the two carboxylic acid units, the carboxyl groups are twisted away
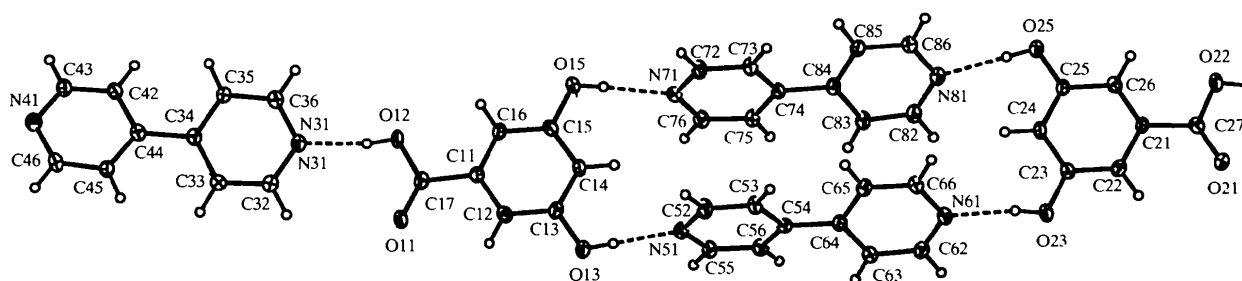

Fig. 1. The asymmetric unit of (1) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as circles of an arbitrary radius.

from the planes of the aryl rings by 7.5 (2) and 4.5 (2)°, respectively, for the units containing C11 and C21. The C—O distances (Table 1) are in accord with the location of the acidic H atoms; other bond lengths and angles are typical of their types.
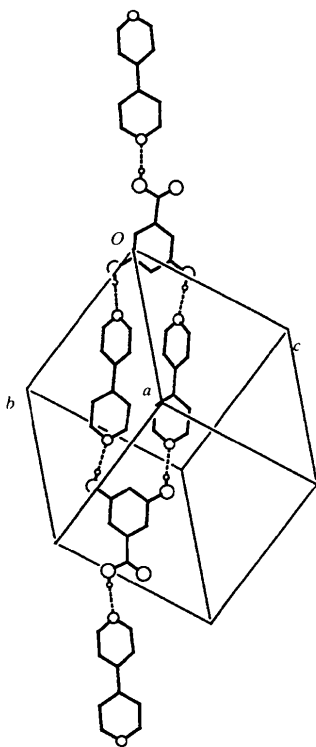

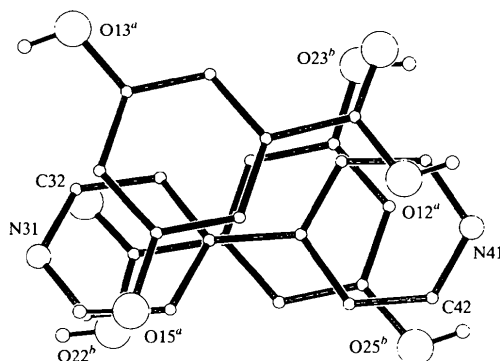Fig. 2. Part of the crystal structure of (1) showing one of the [310] chains.

Fig. 3. Part of the crystal structure of (1) showing the overlap of the rings in neighbouring chains. The diamine component is at (x, y, z); atoms marked a are in the unit at (− 1 + x, y, z), and atoms marked b are in the unit at (− 2 + x, − 1 + y, z).

Experimental

Stoichiometric quantities of the two components were separately dissolved in dry methanol. The solutions were mixed and the mixture was set aside to crystallize, yielding analytically pure (1). Analysis: found C 67.8, H 4.8, N 10.8%; $C_{44}H_{36}N_6O_8$ requires C 68.0, H 4.7, N 10.8%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$2C_7H_6O_4 \cdot 3C_{10}H_8N_2$	Mo $K\alpha$ radiation
$M_r = 776.79$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 6384
$P\bar{1}$	reflections
$a = 9.6826\,(11)$ Å	$\theta = 4.08{-}25.10°$
$b = 14.378\,(3)$ Å	$\mu = 0.100$ mm^{-1}
$c = 14.797\,(3)$ Å	$T = 100.0\,(1)$ K
$\alpha = 63.17\,(6)°$	Needle
$\beta = 83.25\,(11)°$	$0.27 \times 0.10 \times 0.10$ mm
$\gamma = 80.17\,(10)°$	Colourless
$V = 1809.4\,(5)$ Å^3	
$Z = 2$	
$D_x = 1.426$ Mg m^{-3}	
D_m not measured	

Data collection

Nonius KappaCCD diffractometer	6384 independent reflections
	3132 reflections with
φ and ω scans with κ offsets	$I > 2\sigma(I)$
Absorption correction:	$R_{int} = 0.083$
multi-scan (DENZO-SMN;	$\theta_{max} = 25.10°$
Otwinowski & Minor,	$h = 0 \rightarrow 11$
1997)	$k = -16 \rightarrow 17$
$T_{min} = 0.974$, $T_{max} = 0.990$	$l = -17 \rightarrow 17$
13 753 measured reflections	Intensity decay: negligible

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.232$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.056$	$\Delta\rho_{min} = -0.235$ e Å^{-3}
$wR(F^2) = 0.134$	Extinction correction:
$S = 0.932$	SHELXL97 (Sheldrick,
6384 reflections	1997a)
530 parameters	Extinction coefficient:
H-atom parameters	0.0044 (8)
constrained	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2]$	International Tables for
where $P = (F_o^2 + 2F_c^2)/3$	Crystallography (Vol. C)
$(\Delta/\sigma)_{max} < 0.001$	

Table 1. Selected geometric parameters (Å, °)

O11—C17	1.215 (4)	O21—C27	1.216 (4)
O12—C17	1.334 (4)	O22—C27	1.332 (4)
O13—C13	1.375 (4)	O23—C23	1.358 (4)
O15—C15	1.371 (4)	O25—C25	1.362 (4)
O13—C13—C14	121.1 (3)	O11—C17—O12	123.2 (3)
O13—C13—C12	117.7 (3)	O11—C17—C11	123.5 (3)
O15—C15—C16	119.0 (3)	O12—C17—C11	113.3 (3)
O15—C15—C14	120.4 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O12—H12⋯N31	0.84	1.85	2.685 (3)	171
O13—H13⋯N51	0.84	1.89	2.720 (3)	172
O15—H15⋯N71	0.84	1.98	2.814 (3)	176
O22—H22⋯N41^i	0.84	1.88	2.721 (3)	177
O23—H23⋯N61	0.84	1.92	2.750 (3)	170
O25—H25⋯N81	0.84	1.92	2.756 (3)	178

Symmetry code: (i) $3 + x, 1 + y, z$.

The *DENZO-SMN* program uses a scaling algorithm (Fox & Holmes, 1966) which effectively corrects for absorption effects. Compound (1) crystallized in the triclinic system and space group $P\bar{1}$ was assumed. Examination of the structure using *PLATON* (Spek, 1999) confirmed the absence of any symmetry beyond that required by space group $P\bar{1}$. H atoms were treated as riding, with C—H 0.95 and O—H 0.84 Å.

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, 1997*b*). Program(s) used to refine structure: *NRCVAX96* (Gabe *et al.*, 1989) and *SHELXL97* (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX96*, *ORTEP*II (Johnson, 1976) and *PLATON*. Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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2,2'-Bi-2-imidazoline

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Abstract

The title compound, $C_6H_{10}N_4$, forms hydrogen-bonded ribbons which are packed in a herring-bone pattern controlled by CH⋯N(imine) interactions.

Comment

2,2'-Bi-2-imidazoline is a versatile ligand for transition metals; it has the potential to act as a bidentate α-diimine, a diamine or, if deprotonated, as a dianionic bridge between two metal ions. The infrared spectrum of the compound shows some unusual features; the imine stretching frequency ($\nu_{C=N}$, 1571 cm^{-1}) is very low, much closer to that expected for a complex with a metal ion bound to the imine than for the free imine. In comparison, the equivalent band in the infrared spectrum of the closely related 2,2'-bi-2-oxazoline appears at 1625 cm^{-1} (Burnett *et al.*, 1981). Wang & Bauman (1965) have noted the low frequency of the ν_{NH} stretch, at 3179 cm^{-1} and observed that this band shifted to 3450 cm^{-1} in chloroform solution, suggesting that this might indicate intermolecular association in the solid state. A structure determination of 2,2'-bi-2-imidazoline, (I), was undertaken to investigate the origin of these effects and to provide a basis for the interpretation of spectral data for metal complexes of this ligand.

(I)
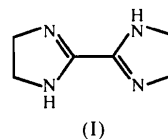
The 2,2'-bi-2-imidazoline molecule sits on a centre of symmetry, so that the asymmetric unit consists of one five-membered ring. The non-H atoms of the molecule are close to planar (r.m.s. deviation 0.008 Å) and the α-diimine is in the *trans* configuration. The amine-H atom, located from difference maps, lies within 0.01 (2) Å of the mean plane of the imidazoline ring. This observation, together with the slightly elongated C1—N(imine) and shortened C1—N(amine) distances of 1.285 (2) and 1.344 (2) Å, respectively, suggests a partial delocalization of the π system over the section comprising of N1, C1 and N2 of both rings.