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X-ray Structure Analysis Online

Guest Inclusion by *N*,*N*′,*N*″-Trihydroxyisocyanuric Acid: X-Ray Structure of the *N*,*N*-Dimethylformamide Complex

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The inclusion ability of *N*,*N*′,*N*″-trihydroxyisocyanuric acid **1** as a host is reported together with the X-ray crystal structure of a representative inclusion compound with formula **1**·3(*N*,*N*-dimethylformamide). The latter crystallizes in the triclinic space group $P\bar{1}$ with unit-cell parameters $a = 8.7938(1)$Å, $b = 10.5744(2)$Å, $c = 10.8076(2)$Å, $\alpha = 91.731(1)^\circ$, $\beta = 109.910(1)^\circ$, $\gamma = 95.785(1)^\circ$ and $Z = 2$. Each solvent molecule is hydrogen bonded *via* its carbonyl oxygen atom to one of the hydroxyl groups of **1**. Crystal packing was used to rationalise the observed thermal desolvation behavior of the inclusion compound.

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The compound *N*,*N*′,*N*″-trihydroxyisocyanuric acid **1** (Fig.1) has recently been applied as an aerobic oxidation catalyst.[1,2] However, no reports on its ability to act as a host compound have thus far appeared, despite the presence of multiple donor and acceptor functions in the molecule, which suggest this possibility. We recently prepared **1** by a reported method,[1] and obtained several inclusion crystals by slow evaporation of solutions of **1** in neat guests. Using NMR spectroscopy and thermogravimetric analysis (TGA), inclusion crystals (obtained as needles or prisms) with the following compositions were identified: **1**·3(*N*,*N*-dimethylformamide), **1**·*N*,*N*-dimethylacetamide, **1**·1.5(4-methylpyridine), **1**·1.5(2-hydroxypyridine)·1.5(MeOH) and **1**·2H$_2$O.

The 1:3 host-guest stoichiometry for **1**·3(*N*,*N*-dimethylformamide) was deduced from the NMR spectrum of a solution of freshly prepared crystals. However, the TGA trace of the compound showed a total percentage mass loss of only 45.6%, attributable to an included solvent upon heating between ambient temperature and ~150°C, corresponding to a composition **1**·2(*N*,*N*-dimethylformamide) (calcd. 45.2%). Evidently, unusually high lability of one-third of the included *N*,*N*-dimethylformamide (DMF) molecules had led to its loss from the crystal sample during handling prior to themogravimetric analysis. In an attempt to explain the non-uniform desolvation behavior, a single-crystal X-ray analysis of the complex reported here was undertaken. To date, no crystal structures containing **1** have been documented.[3]

A fresh single crystal of **1**·3(*N*,*N*-dimethylformamide) with dimensions of 0.20 × 0.15 × 0.15 mm was coated with Paratone N oil to prevent guest loss. Intensity data were collected with graphite-monochromated Mo K_α radiation on a Nonius Kappa CCD four-circle diffractometer, with the crystal cooled in a stream of nitrogen at 113 ± 2 K. From Laue symmetry $\bar{1}$, the triclinic system was deduced and the centrosymmetric space group $P\bar{1}$ was chosen on the basis of intensity statistics ($|E^2 - 1| = 1.013$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97. All hydrogen atoms were located in difference Fourier maps, and were generally added at idealized positions with U_{iso} equal to 1.2-times those of their parent atoms. Hydroxyl group H atoms were included using the rotating group strategy in SHELXL-97, which reproduced the positions found in the difference Fourier map. Details of the crystal data and refinement appear in Table 1. Final coordinates and equivalent thermal parameters for non-hydrogen atoms are listed in Table 2.

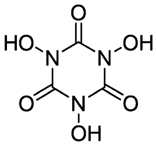

Fig. 1 Chemical structure of host molecule **1**.

Table 1 Crystal and experimental data

CCDC deposition number 295054	
Formula	$C_3H_3N_3O_6\cdot(C_3H_7NO)_3$
Formula weight	396.36
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
a	8.7938(1)Å
b	10.5744(2)Å
c	10.8076(2)Å
α	91.731(1)°
β	109.910(1)°
γ	95.785(1)°
V	937.87(3)Å^3
D_x	1.403 g cm^{-3}
No. of reflections used	4477
$2\theta_{\max}$	55.8° with Mo K_α
R	0.040
$(\Delta/\sigma)_{\max}$ final cycle	< 0.001
$(\Delta\rho)_{\max}$	0.210 eÅ^{-3}
$(\Delta\rho)_{\min}$	–0.330 eÅ^{-3}
Measurement	Nonius Kappa CCD
Program system	DENZO-SMN
Structure determination	SHELXS-97
Refinement	full-matrix: SHELXL-97

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Table 2 Atomic coordinates and equivalent thermal parameters (Å^2)

Atom	x	y	z	U_{eq}
N1	0.26721(14)	0.30309(11)	0.61130(11)	0.0181(3)
C2	0.13019(17)	0.31091(14)	0.50154(14)	0.0184(4)
N3	0.13568(14)	0.42578(11)	0.44459(11)	0.0195(4)
C4	0.25767(18)	0.52751(14)	0.48552(14)	0.0208(5)
N5	0.38571(14)	0.50354(11)	0.59624(12)	0.0197(4)
C6	0.40109(17)	0.39431(13)	0.66378(14)	0.0172(4)
O7	0.25999(12)	0.19921(9)	0.68492(10)	0.0227(3)
O8	0.01988(12)	0.22640(10)	0.45908(10)	0.0268(3)
O9	-0.00360(12)	0.44544(11)	0.34145(10)	0.0276(3)
O10	0.25334(14)	0.62542(10)	0.43112(11)	0.0319(4)
O11	0.52040(12)	0.59501(10)	0.63576(11)	0.0264(4)
O12	0.51777(12)	0.37864(10)	0.75844(10)	0.0254(3)
O13	0.46915(12)	0.05076(9)	0.67360(10)	0.0231(3)
C14	0.58985(17)	0.09100(14)	0.64350(14)	0.0198(4)
N15	0.70852(14)	0.02284(11)	0.64699(12)	0.0197(4)
C16	0.7042(2)	-0.10763(14)	0.68654(17)	0.0296(5)
C17	0.83774(18)	0.07102(14)	0.59829(16)	0.0242(5)
O18	0.02870(12)	0.34718(10)	0.13303(10)	0.0264(3)
C19	0.13449(18)	0.40626(14)	0.09644(14)	0.0218(5)
N20	0.14845(14)	0.38594(12)	-0.01990(12)	0.0214(4)
C21	0.0387(2)	0.29062(16)	-0.11793(16)	0.0330(6)
C22	0.27792(18)	0.45637(16)	-0.05502(16)	0.0269(5)
O23	0.47223(13)	0.70988(10)	0.82787(10)	0.0269(3)
C24	0.36197(18)	0.78069(14)	0.79515(15)	0.0228(5)
N25	0.31731(14)	0.84680(11)	0.87963(12)	0.0215(4)
C26	0.18722(19)	0.92754(15)	0.83423(17)	0.0308(5)
C27	0.3911(2)	0.83891(17)	1.02104(15)	0.0311(5)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

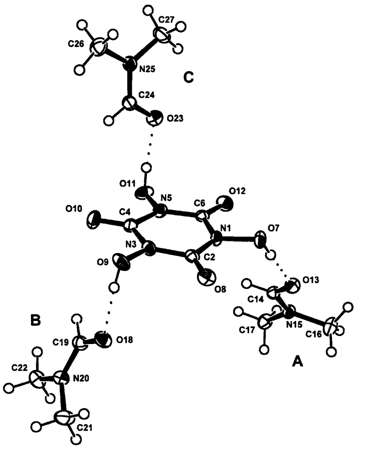

Fig. 2 ORTEP drawing of **1**·3(DMF) at the 50% probability level.

Table 3 Selected bond distances (Å) and angles (°)

N1 - C2	1.385(2)	C2 - O8	1.203(2)
C2 - N3	1.382(2)	C4 - O10	1.204(2)
N3 - C4	1.385(2)	C6 - O12	1.207(2)
C4 - N5	1.386(2)	N1 - O7	1.385(2)
N5 - C6	1.379(2)	N3 - O9	1.386 (2)
C6 - N1	1.386(2)	N5 - O11	1.386(2)
O7 - N1 - C2	115.7(1)	O10 - C4 - N3	123.9(4)
O7 - N1 - C6	116.5(1)	O10 - C4 - N5	123.8(1)
C2 - N1 - C6	127.3(1)	N3 - C4 - N5	112.3(1)
O8 - C2 - N1	123.8(1)	O11 - N5 - C4	116.0(1)
O8 - C2 - N3	123.7(1)	O11 - N5 - C6	116.1(1)
N1 - C2 - N3	112.5(1)	C4 - N5 - C6	127.6(1)
O9 - N3 - C2	115.8(1)	O12 - C6 - N1	123.1(1)
O9 - N3 - C4	116.2(1)	O12 - C6 - N5	124.2(1)
C2 - N3 - C4	127.7(1)	N1 - C6 - N5	112.7(1)

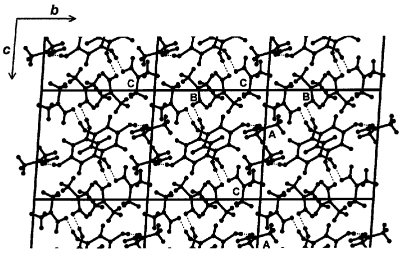

Fig. 3 [100] projection of the crystal structure showing the location of DMF molecules in two distinct layers of different composition.

The asymmetric unit of the structure (Fig. 2) comprises one molecule of host **1** and three independent molecules of DMF, with each of the three hydroxyl groups of **1** hydrogen bonded to a guest carbonyl oxygen atom. Two of the guest molecules are located on one side of the host plane, while the third is on the opposite side.

In view of the structural novelty of host **1**, a discussion of its geometry is warranted. The six C–N bonds in the host ring are equivalent (bond length range 1.379(2) – 1.386(2)Å, Table 3) but the hexagon is irregular as a result of an alternation of C and N atoms. Thus, the C–N–C angles are in the range 127.3(1) – 127.7(1)°, while the N–C–N angles are in the range 112.3(1) – 112.7(1)°. The hexagon is planar (max. deviation from the least-squares plane = 0.009(2)Å, for C6) with the carbonyl oxygen atoms deviating from this plane by no more than 0.033(1)Å, but the hydroxyl oxygen atoms deviating to a greater extent (max 0.214(1)Å, for O7). The directions of the latter deviations correlate with the hydrogen bonding shown in Fig. 2, being above the six-membered ring for atoms O7 and O9, and below the ring for O11. All of the DMF molecules have normal bond lengths and angles and adopt planar conformations with no C–N–C–O torsion angle deviating by more than 2.2(1)° from 0 or 180°.

The unusual lability of one of the three independent guest molecules cannot be attributed to differences in the host-guest hydrogen bonding, since the three hydrogen bonds are of uniform strength (O···O range 2.553(2) – 2.566(2)Å, H···O range 1.727(1) – 1.730(1)Å and angle O–H···O 165.6(1) – 178.3(1)°). It was therefore necessary to consider the influence of the crystal packing, and thus a detailed analysis of this aspect, including the topology of guest inclusion, was performed. This revealed that the host molecules (located in the center of the unit cell and stacked along the crystal *a*-axis) are bounded by two distinct sets of layers (Fig. 3), one containing DMF molecules B, C (001 planes) and one containing DMF molecules A, C (010 planes). Desolvation upon heating must involve the diffusion of DMF molecules out of these layers. The observed non-uniformity in the desolvation behavior is thus attributed to the differences in the composition of these guest layers and their consequently different host-guest interactions.

Acknowledgements

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