

2,6-Bis(5,6-dicyclohexyl-1,2,4-triazin-3-yl)-pyridine–dichloromethane–water (1/1/0.625)

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Key indicators

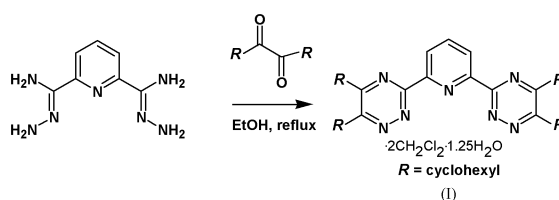
Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C–C}) = 0.005 \text{ \AA}$
 Disorder in solvent or counterion
 R factor = 0.058
 wR factor = 0.155
 Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, 2,6-bis(5,6-dicyclohexyl-1,2,4-triazin-3-yl)pyridine, $\text{C}_{35}\text{H}_{57}\text{N}_7 \cdot \text{CH}_2\text{Cl}_2 \cdot 0.625\text{H}_2\text{O}$, crystallizes with two molecules in the asymmetric unit, along with 1.25 molecules of water and two molecules of dichloromethane. The water molecules are involved in hydrogen-bond interactions with some N atoms of the triazine rings.

Comment

In the context of nuclear waste reprocessing, several possible chelating agents have been tested in liquid–liquid extraction experiments to separate the trivalent minor actinides from the trivalent lanthanides. Various aza-aromatic bases are among the most extensively studied chelating agents since they have shown unique capabilities to extract americium over europium from acidic solutions into an organic phase. Some metal complexes with aza-aromatic bases containing triazine fragments have recently been reported (Drew, Hudson, Iveson & Madic, 2000; Drew, Hudson, Iveson, Madic & Russell, 2000; Drew, Guillaneux, Hudson, Iveson, Russell & Madic, 2001; Drew, Guillaneux, Hudson, Iveson & Madic, 2001; Iveson *et al.*, 2001), but no structure of a free pyridyltriazine ligand has appeared so far in the literature. During the synthesis of a series of polyaza-heterocycles, we isolated and characterized 2,6-bis(5,6-dicyclohexyl-1,2,4-triazin-3-yl)pyridine as a mixed dichloromethane and water solvate, (I).



The asymmetric unit of (I) contains two independent molecules (A and B), two dichloromethane solvent molecules and 1.25 water molecules. A view of molecule A, showing its interaction with a water molecule, is given in Fig. 1. Selected bond lengths are given in Table 1. The two independent molecules are roughly identical, differing only in the relative conformation of the cyclohexyl groups and by their interaction with the water molecules. Indeed, as shown in Table 2, the O–H···N interactions differ in the two molecules. Atom O1 interacts symmetrically with N12 and N23, whereas O2 is involved in a much stronger hydrogen-bond interaction with N72 than with N62. These two molecules are roughly parallel in a head-to-tail arrangement (Fig. 2). All the cyclohexyl groups have a chair conformation, but they are twisted

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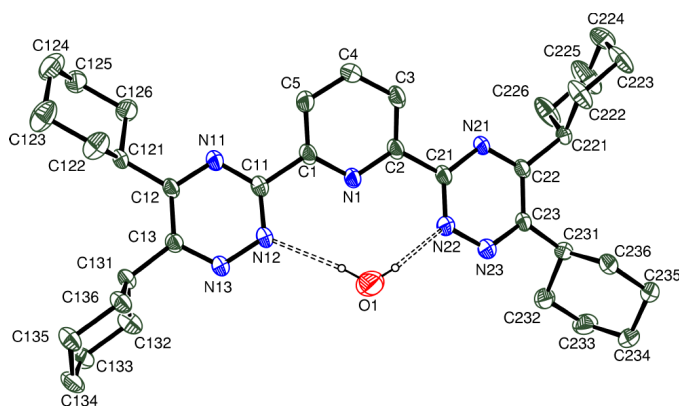


Figure 1
ORTEP (Burnett & Johnson, 1996) view of molecule *A* with the hydrogen-bonded water molecule. H atoms attached to carbon have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

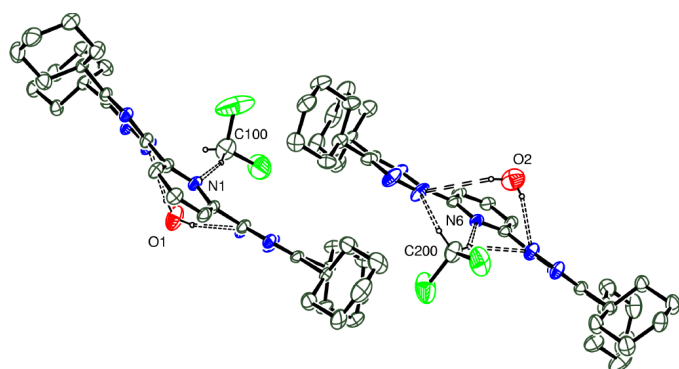


Figure 2
View showing the head-to-tail packing of molecules *A* and *B*.

differently with respect to the triazine rings in the two molecules. The bond lengths and angles within the pyridine and triazine rings are as expected (Allen, 2002).

The triazine rings *Tr1* (C11/N11/C12/C13/N13/N12) and *Tr2* (C21/N21/C22/C23/N23/N22) are slightly twisted with respect to the central pyridine ring *py1* (N1/C2–C5), making dihedral angles of 23.36 (7) and 22.30 (9)°, respectively. The distortion is less symmetrical in molecule *B*, where the related dihedral angles *Tr3/py2* and *Tr4/py2* are 9.40 (11) and 18.90 (9)°, respectively.

There are weak C–H···N interactions (Table 2) between the dichloromethane molecules and some of the N atoms of the triazine or pyridine rings (Fig. 2).

Experimental

A solution of 0.65 g (3.3 mmol) of 2,6-dicarboxamidehydrazinopyridine and 1.89 g (6.7 mmol) of dicyclohexylethanedione in absolute ethanol was refluxed overnight. After evaporating off the solvent, the crude product was chromatographed on silica gel with 30% AcOEt in pentane. The chromatographed product was further purified by recrystallization from pentane and gave 1.25 g (66%) of a yellow powder (m.p. = 397 K). Mass spectrometry (DCI/NH₃): *m/z* 566 (MH⁺). ¹H NMR (CDCl₃, 200 MHz): δ 8.65 [*d*, *J* = 7.8 Hz, 2H, H(3,5)], 8.04 [*t*, *J* = 7.9 Hz, 1H, H(4)], 2.98 (*m*, 4H, H cyclohexyl), 1.87 (*m*, 32H, H cyclohexyl), 1.40 (*m*, 8H, H cyclohexyl).

Crystal data

C₃₅H₅₇N₇·CH₂Cl₂·0.625H₂O
M_r = 661.98
 Triclinic, *P* $\bar{1}$
a = 12.167 (5) Å
b = 15.961 (5) Å
c = 19.293 (5) Å
 α = 81.750 (5)°
 β = 76.040 (5)°
 γ = 76.840 (5)°
V = 3525 (2) Å³

Z = 4
D_x = 1.247 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 8000 reflections
 θ = 2.2–26.1°
 μ = 0.22 mm⁻¹
T = 293 (2) K
 Block, yellow
 0.60 × 0.45 × 0.25 mm

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: none
 25502 measured reflections
 11727 independent reflections
 6377 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.055
 θ_{\max} = 25.0°
h = −14 → 14
k = −18 → 18
l = −22 → 22

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.058
wR (*F*²) = 0.155
S = 0.89
 11727 reflections
 841 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0856P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.73 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.69 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å).

N1–C1	1.342 (4)	N6–C7	1.336 (4)
N1–C2	1.343 (4)	N6–C6	1.350 (4)
N11–C12	1.330 (3)	N61–C62	1.323 (4)
N11–C11	1.338 (4)	N61–C61	1.346 (4)
N12–C11	1.324 (4)	N62–C61	1.314 (4)
N12–N13	1.348 (3)	N62–N63	1.347 (4)
N13–C13	1.328 (4)	N63–C63	1.331 (4)
N21–C22	1.323 (4)	N71–C72	1.326 (4)
N21–C21	1.345 (3)	N71–C71	1.347 (4)
N22–C21	1.328 (4)	N72–C71	1.320 (4)
N22–N23	1.341 (4)	N72–N73	1.352 (3)
N23–C23	1.330 (3)	N73–C73	1.327 (4)
C1–C11	1.496 (4)	C6–C61	1.487 (4)
C2–C21	1.479 (4)	C7–C71	1.493 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O2–H1O2···N62	0.8 (1)	2.9 (2)	3.698 (12)	161 (14)
O2–H2O2···N72	0.8 (1)	2.2 (1)	2.946 (12)	156 (20)
O1–H1O1···N22	0.83 (1)	2.22 (3)	3.032 (4)	165 (4)
O1–H2O1···N12	0.83 (1)	2.29 (3)	3.108 (3)	170 (5)
C100–H10A···N1	0.97	2.57	3.503 (5)	162
C200–H20A···N6	0.97	2.57	3.440 (5)	150

Carbon-bound H atoms were introduced at calculated positions as riding atoms, with C–H distances of 0.93 (CH) and 0.97 Å (CH₂) and an isotropic displacement parameter equal to 1.2 times *U*_{eq} of the parent atom. The H atoms of the water molecules were refined with O–H distances restrained to 0.84 (1) Å and H···H distances restrained to 1.37 (1) Å, with displacement parameters fixed at 1.5 times *U*_{eq} of the parent O atoms. These restraints ensured a reasonable geometry for the water molecules. The occupation factor of O2 was deduced from the refinement of the site occupancy for both

the O atoms of water molecules with a common isotropic displacement parameter in the early stages of refinement.

Data collection: *IPDS Software* (Stoe & Cie, 1996); cell refinement: *IPDS Software*; data reduction: *XRED* (Stoe & Cie, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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