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Bis[*N*,*N*′-*o*-phenylenebis(pyridine-2,6-dicarboxamide)] dimethylformamide solvate

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In the title macrocyclic compound, 3,10,18,25,31,32-hexaazapentacyclo[25.3.1.$1^{12,16}$.$0^{4,9}$.$0^{19,24}$]dotriconta-1(30),4,6,8,12,14,16(32),19,21,23,27(31),28-dodecaene-2,11,17,26-tetrone dimethylformamide solvate, $C_{26}H_{18}N_6O_4 \cdot C_3H_7NO$, the two pyridine rings are approximately perpendicular to each other, the dihedral angle between them being 82.1 (1)°. The macrocycle possesses mirror symmetry. The dihedral angle between the two benzene rings is 119.6 (1)°.

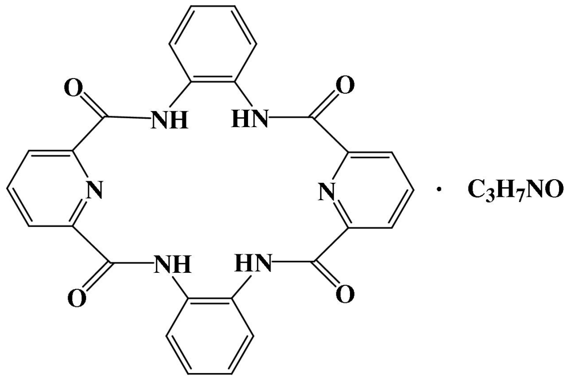
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.047
wR factor = 0.098
Data-to-parameter ratio = 12.9

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

Comment

Functional mimics of manganese superoxide dismutase (Mn-SOD) are of great potential as therapeutic agents (Riley, 1999). N-containing macrocyclic manganese complexes have high catalytic SOD activity and are chemically and biologically stable *in vivo* (Salvemini *et al.*, 1999). *N*,*N*′-(1,2-Phenylene)bis(pyridine-2-carboxamide) and an Mn^{III} complex have been synthesized and reported previously (Lin *et al.*, 2003). The Mn^{III} complex proved itself a relatively effective superoxide scavenger and provided an interesting example of very low-molecular-weight Mn-SOD mimics. In this work, we report the crystal structure of the title compound, (I), whose structure is very similar to that of *N*,*N*′-(1,2-phenylene)bis(pyridine-2-carboxamide).



(I)

The molecular structure of (I) is shown in Fig. 1. The macrocyclic molecule is symmetrical about a mirror plane (symmetry code: $x, \frac{1}{2} - y, z$) which passes through the mid-points of the bonds C7—C7*A* and C11—C11*A*. The X-ray crystallographic study shows that the bond lengths and angles are within expected ranges (Allen *et al.*, 1987). The mean C—N length in the pyridine rings is 1.331 (2) Å. The N2—C6, N2—C7, N3—C10 and N3—C11 bond distances are comparable to those in *N*,*N*′-(1,2-phenylene)bis(pyridine-2-carboxamide) [1.356 (3), 1.406 (3), 1.343 (3) and 1.432 (3) Å; Lin *et*

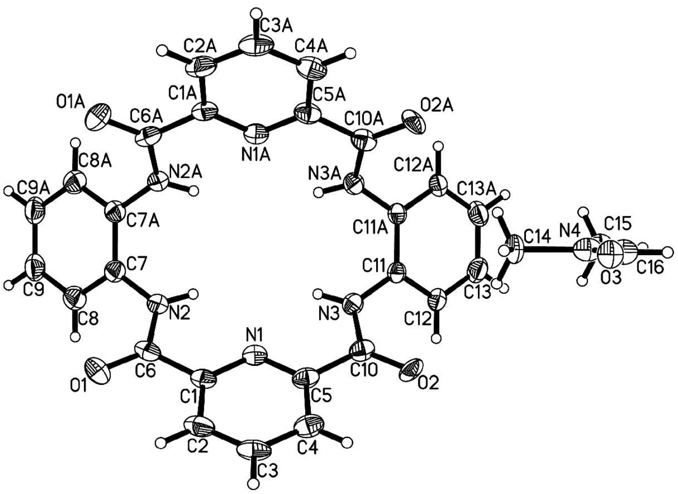


Figure 1
The structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. Only one of the two disordered components of the solvent molecule is shown. The suffix A corresponds to the symmetry position $x, \frac{1}{2}-y, z$.

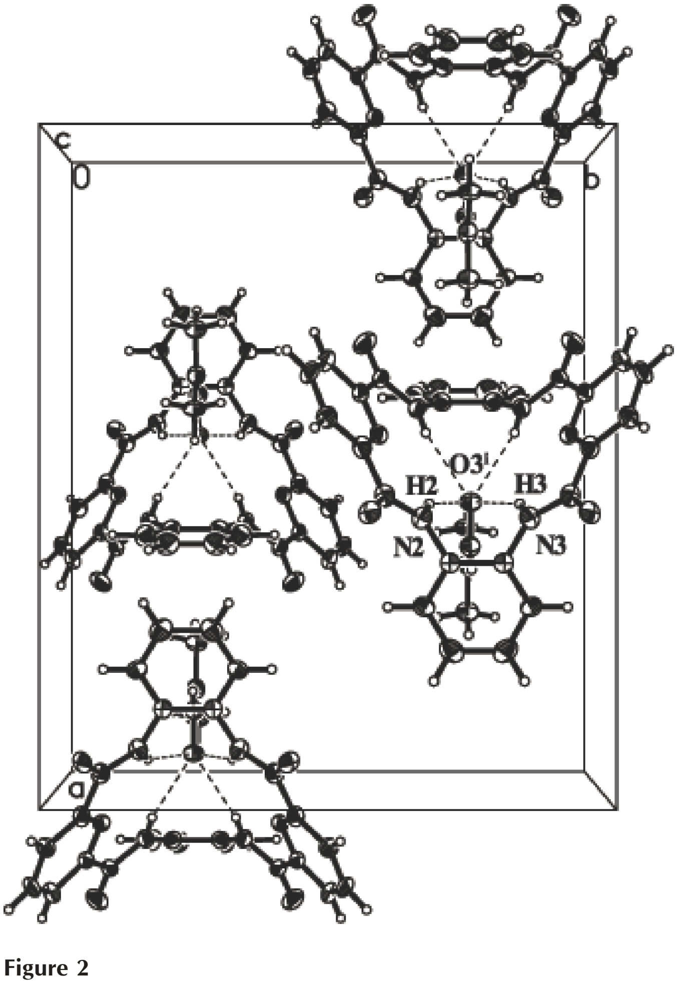


Figure 2
The packing in the crystal structure. Dashed lines indicate hydrogen bonds.

al., 2001]. The amide N—C distances towards the bridging ring [N2—C7 and N3—C11] are longer than those to the pyridine rings [N2—C6 and N3—C10].

In the title compound, the two pyridine rings are approximately perpendicular to each other, and the dihedral angle between them being 82.1 (1)°. The dihedral angle between the planes of the two benzene rings is 119.6 (1) Å. The orientation of the dicarboxamide-2,6-pyridine substituents with respect to the benzene planes is defined by C6—N2—C7—C8 and C10—N3—C11—C12 torsion angles of −51.6 (3) and 51.0 (3)°, respectively. Compound (I) contains a molecule of dimethylformamide, disordered over two sites in a 0.5 occupancy ratio. The crystal packing of compound (I) is shown in Fig. 2. There are four intramolecular hydrogen bonds (Table 2) in the crystal structure.

Experimental

The title compound was synthesized by the reaction of pyridine-2,6-dicarboxylic acid (2 mmol) and 2-phenylenediamine (2 mmol) in the presence of triphenyl phosphate (1 ml) in pyridine (17 ml) at 373 K for 2 h (Leung *et al.*, 1991). Crystals suitable for X-ray structure analysis were obtained by slow evaporation of a dimethylformamide solution at room temperature.

Crystal data

$C_{26}H_{18}N_6O_4 \cdot C_6H_{14}N_2O_2$
$M_r = 624.06$
Orthorhombic, *Pnma*
$a = 18.2331$ (17) Å
$b = 15.3467$ (14) Å
$c = 9.5134$ (9) Å
$V = 2662.0$ (4) Å^3
$Z = 4$
$D_x = 1.376$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1146 reflections
$\theta = 2.4$–18.7°
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.32 × 0.28 × 0.26 mm

Data collection

Bruker Smart Apex CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.966$, $T_{\max} = 0.972$
13 689 measured reflections
2725 independent reflections
1708 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.051$
$\theta_{\max} = 26.0°$
$h = -22 \rightarrow 22$
$k = -18 \rightarrow 18$
$l = -6 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.098$
$S = 0.96$
2725 reflections
211 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.329 (2)	N3—C10	1.347 (2)
N1—C5	1.333 (2)	N3—C11	1.416 (2)
N2—C6	1.343 (2)	C6—O1	1.224 (2)
N2—C7	1.414 (2)	C10—O2	1.219 (2)
C1—N1—C5	117.69 (16)	O1—C6—C1	121.88 (18)
C6—N2—C7	125.22 (16)	O2—C10—N3	124.14 (19)
C10—N3—C11	123.97 (16)	O2—C10—C5	121.51 (17)
O1—C6—N2	124.1 (2)		

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Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O3^{i}	0.86	2.23	3.010 (2)	150
N3—H3···O3'^{i}	0.86	2.25	3.034 (2)	152

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

All H atoms were placed in geometrically calculated positions (C—H = 0.93 Å for CH, C—H = 0.96 Å for CH_3 and N—H = 0.86 Å), assigned fixed U_{eq}(H) equal to 1.2 times U_{eq} of the atoms to which they are attached (1.5 times for the methyl groups) and allowed to ride on their respective parent atoms. The dimethylformamide solvate is disordered over two sites with occupancy factors of 0.5.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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