

Bis[2,2'-ethylenedioxydibenzaldehyde bis(thiocarbohydrazide)] tris(pyridine) solvate¹

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The title compound, a novel 30-membered 2:2 macrocyclic thiocarbohydrazone, $C_{34}H_{32}N_8O_4S_2 \cdot 3C_5H_5N$, has been prepared and crystallographically characterized. The molecule of the compound is twisted. One dioxabutane group is boat-like in shape, whereas the other is highly disordered. The crystal structure is stabilized by inter- and intramolecular hydrogen bonds.

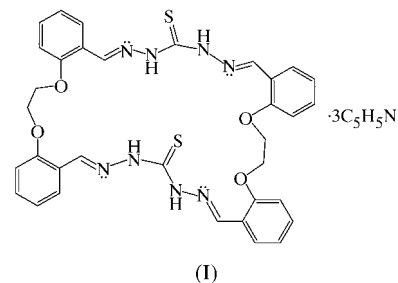
Comment

Thiocarbohydrazide, $H_2NHC(S)NHNH_2$, and its Schiff base derivatives are interesting ligand systems because of the availability of several different kinds of potential donor sites (Bustos *et al.*, 1990; Bacchi *et al.*, 1996; Souza *et al.*, 1994). Recently, many open-chain ligands of thiocarbohydrazone have been rapidly developed and studied in detail. The aim of the present research is the design of a new macrocyclic ligand involving mixed N-, S- and O-donor atoms, and we describe here the synthesis and characterization of a novel 30-membered 2:2 macrocyclic thiocarbohydrazone, (I), obtained by the condensation of thiocarbohydrazone with 1,4-bis(2-formylphenyl)-1,4-dioxabutane.

As shown in Fig. 1, the molecule of (I) is twisted. The S1—C1 [1.666 (3) Å] and S2—C18 [1.657 (3) Å] distances indicate that they are double bonds (Bustos *et al.*, 1990; Bacchi *et al.*, 1996). This suggests the presence of a thioketo form in the solid state. The torsion angle along the O1—C9—C10—O2 dioxabutane moiety is 64.8 (4)°. This dioxabutane group is boat-like in shape, whereas the other is highly disordered (atoms O4, C26 and C27 are disordered).

¹ Systematic name: 2,5,25,28-tetraoxa-13,14,16,17,36,37,39,40-octaazapentacyclo[40.4.0.0^{6,11}.0^{19,24}.0^{29,34}]hexatetraconta-6,8,10,12,17,19,21,23,29,31,33,35,-40,42,44,46-hexadecaene-15,38-dithione tris(pyridine) solvate.

Each unit of the macrocyclic ring, consisting of the thiocarbohydrazone and the axially substituted phenyl rings, adopts a planar conformation. The dihedral angles are 15.4 (2)° between rings C3—C8 and C28—C33, and 12.6 (2)° between rings C11—C16 and C20—C25. The twist is introduced by the dioxabutane bridges connecting the two units. The dihedral angle between the two thiocarbohydrazone groups is 30.98 (8)°.



The three molecules of pyridine present as solvate in (I) help to stabilize the structure by forming intra- and intermolecular hydrogen bonds with the macrocyclic ring; details are given in Table 2. The C—H...Cg(π -ring) interactions [Cg1 = C20—C25, Cg2 = C28—C33, Cg3 = N10 and C40—C44 (one of the three pyridine molecules), and Cg4 = C11—C16], *i.e.* the interaction between a phenyl H atom and a centre of gravity of a pyridine ring, and between the H atoms of the pyridine rings and the centres of gravity of the phenyl rings, play a major role in the packing and molecular arrangement in the crystal (Table 2).

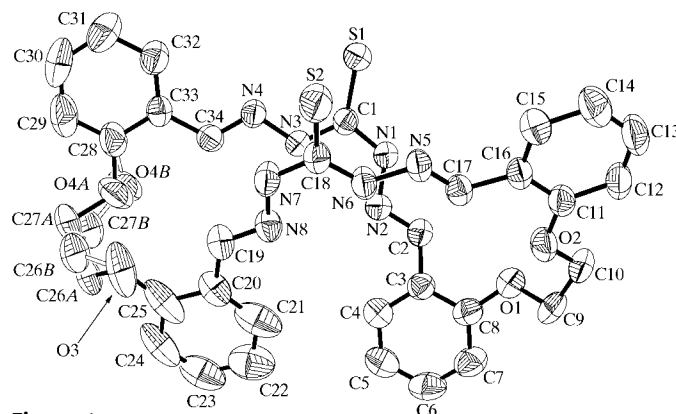


Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms and the pyridine solvate molecules have been omitted for clarity.

Experimental

A solution of 1,4-bis(2-formylphenyl)-1,4-dioxabutane (10 mmol) in ethanol (150 ml) was dripped slowly into a refluxing solution of thiocarbohydrazide (10 mmol) in aqueous ethanol (100 ml), followed by the addition of concentrated hydrochloric acid (0.25 ml). The reaction mixture was refluxed for 10 h with stirring and cooled to room temperature. The yellow precipitated powder of (I) was filtered and washed thoroughly with water and ethanol, and then air dried. A crystal suitable for X-ray diffraction was obtained by evaporation from a benzene–pyridine (1:1) solution.

Crystal data

C₃₄H₃₂N₈O₄S₂·3C₅H₅N
M_r = 918.10
 Monoclinic, *P*2₁/*c*
a = 12.1752 (2) Å
b = 22.2029 (1) Å
c = 19.8479 (4) Å
 β = 117.168 (1)°
V = 4773.42 (13) Å³
Z = 4

D_x = 1.278 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5918 reflections
 θ = 2.77–33.11°
 μ = 0.168 mm⁻¹
T = 293 (2) K
 Block, yellow
 0.37 × 0.33 × 0.28 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.941, *T_{max}* = 0.955
 30 445 measured reflections

10 907 independent reflections
 5918 reflections with *I* > 2σ(*I*)
R_{int} = 0.043
 θ_{max} = 27.5°
h = -14 → 15
k = -28 → 23
l = -25 → 23

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.068
wR (*F*²) = 0.166
S = 1.051
 10 907 reflections
 593 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0460P)^2 + 2.8579P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S1—C1	1.666 (3)	S2—C18	1.657 (3)
N1—C1—N3	114.6 (2)	N6—C18—N7	113.2 (2)
N1—C1—S1	119.5 (2)	N6—C18—S2	126.3 (2)
N3—C1—S1	125.9 (2)	N7—C18—S2	120.5 (2)
O1—C9—C10—O2	64.8 (4)		

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on the atoms to which they were attached, with *U*_{iso} = 1.2*U*_{eq} of the parent atoms, and with C—H = 0.93–0.97 Å and N—H = 0.86 Å. The ratio of the major to the minor component of the disordered dioxabutane group is 0.56:0.44. The bond lengths of the disordered group were restrained to be the same as those of the non-disordered dioxabutane group.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve

Table 2

Hydrogen-bonding geometry (Å, °).

Cg1 is the centroid of the C20–C25 ring, Cg2 is the centroid of the C28–C33 ring, Cg3 is the centroid of the N10/C40–C44 ring (pyridine solvate) and Cg4 is the centroid of the C11–C16 ring.

<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>
N1—H1A···N9 ⁱ	0.86	2.135	2.990 (4)	173
N3—H3A···N10	0.86	2.321	3.061 (4)	144
N7—H7A···N11	0.86	2.173	3.008 (4)	164
C40—H40A···Cg1	0.93	2.757	3.453 (5)	132
C45—H45A···Cg2	0.93	2.868	3.673 (5)	146
C13—H13A···Cg3 ⁱⁱ	0.93	2.752	3.522 (4)	141
C36—H36A···Cg2 ⁱⁱⁱ	0.93	2.942	3.746 (5)	146
C46—H46A···Cg4 ^{iv}	0.93	2.941	3.769 (5)	149

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) -*x*, *y* - ½, ½ - *z*; (iii) 1 - *x*, *y* - ½, ½ - *z*; (iv) 1 - *x*, ½ + *y*, ½ - *z*.

structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1435). Services for accessing these data are described at the back of the journal.

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