

A New Clathrate: Synthesis and Crystal Structure of the [36]ene-O₆N₈/THF (1 : 2) Clathrate

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Abstract. A new clathrate inclusion compound of 2,3:11,12:20,21:29,30-tetrabenzotetraaza-1,13,16,19,31,34-hexaaza-5,6,8,9,23,24,26,27-octaaza-7,25-dithioketone-2,3:4,5:9,10:11,12:22,23:27,28:29,30-cyclo-[36]ene([36]eneO₆N₈), which contains THF, has been prepared and crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.829(5)\text{Å}$, $b = 24.23(1)\text{Å}$, $c = 10.181(9)\text{Å}$, $\beta = 92.93(5)^\circ$. Each unit cell contains two [36]ene-O₆N₈ molecules and four THF molecules. The [36]ene-O₆N₈ molecule lies on the crystallographic centre of symmetry and a pair of the THF molecules with half-chair conformation are located within rectangular channels formed by the macrocycle molecules.

Key words: THF clathrate, Schiff base macrocycle, crystal structure.

Supplementary data relevant to this publication have been deposited with the British Library as Supplementary Publication No. SUP 82225 (22 pages).

1. Introduction

Clathrate inclusion compounds have attracted considerable interest since, unlike ordinary compounds, the clathrates consist of two different molecular species, host and guest, which associate together to form a crystal, and there are no covalent or ionic bonds linking the two dissimilar species. The important aspect of clathrate structures is the specific microenvironment created by the complete enclosure of the guest by the host. Such a microenvironment leads to a variety of applications [1–3].

The architectural study of clathrates has shown that in a large number of them, the host–host bonding forces are primarily strong H-bonds, however the tri-*o*-thymotide clathrate has a greater flexibility, where only van der Waals forces are involved [4]. The ability of lanthanide metal ions to promote the Schiff base condensation of the appropriate diamine and dicarboxyl precursors is well established [5, 6]. Recently we have synthesized a new clathrate inclusion compound with a [36]ene-O₆N₈ host framework, which is actually a new macrocycle, as a relatively rigid entity in the presence of La(NO₃)₃, and we report its crystal structure.

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Table I. Crystal data, summary of data collection and refinement results.

Formula	$C_{38}H_{40}N_8O_6S_2 \cdot 2C_4H_8O$
Mol. wt.	968
Space group	$P2_1/n$
a (Å)	9.829(5)
b (Å)	24.23(1)
c (Å)	10.181(9)
β (°)	92.93(5)
Cell vol. (Å ³)	2422(3)
Z	2
D_c (g cm ⁻³)	1.25
λ (Mo K_α , Å)	0.71069
μ (Mo K_α , cm ⁻¹)	16.0
Crystal size (mm)	0.30 × 0.25 × 0.20
Crystal color	Light yellow
Scan mode	$\omega/2\theta$
Scan range (°)	2–50
h, k, l range	0–11, 0–28, –12–11
Reflections measured	4658
Independent reflections	4387
Reflections observed, $I > 3\sigma(I)$	1743
R	0.056
R_w	0.069
w	$1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\max}$	0.01
$\Delta\rho_{\max}$ ($e \text{ \AA}^{-3}$)	0.36
S	1.54

2. Experimental

A solution of 1 mmol of thiocarbonhydrazide in hot water (30 mL) was slowly added to a solution of 1 mmol of 2,2'-bis(*o*-formylphenoxy)ethyl ether in hot ethanol (50 mL). The mixture was stirred for 4 ~ 5 h and the precipitated yellow powder was separated. The solid was dissolved with 1 mmol of La(NO₃)₃ and (C₂H₅)₃N (2 ~ 3 mL) in THF (40 mL) and heated to boiling for several hours and allowed to stand at room temperature for one week. Yellow crystals of sufficient quality for structure determination were obtained.

The intensity data were collected on a Rigaku AFC5R diffractometer with graphite monochromatized Mo K_α radiation. The crystal data and a summary of data collection and refinement results are presented in Table I. The intensities were corrected for LP factor and empirical absorption. Most of the non-hydrogen atoms were located by direct methods using program MITHRILL. The atoms of the guest and the remaining non-hydrogen atoms of the macrocycle were found

Table II. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2).

Atom	x	y	z	B_{eq}
S(1)	0.6358(2)	0.42776(7)	0.0513(1)	6.6(1)
O(1)	0.9023(4)	0.2509(2)	-0.3999(5)	6.4(2)
O(2)	0.9579(5)	0.3354(2)	-0.5672(5)	7.1(3)
O(3)	0.7789(4)	0.4290(2)	-0.5485(4)	5.0(2)
O(4)	0.8895(9)	0.5739(4)	-0.789(1)	17.8(8)
N(1)	0.6329(4)	0.3804(2)	-0.1851(4)	4.2(2)
N(2)	0.7209(4)	0.3406(2)	-0.1355(4)	4.2(2)
N(3)	0.5004(4)	0.4557(2)	-0.1679(4)	4.3(2)
N(4)	0.4592(4)	0.4480(2)	-0.2975(4)	4.0(2)
C(1)	0.5897(5)	0.4208(2)	-0.1055(5)	4.0(3)
C(2)	0.7759(5)	0.3110(2)	-0.2216(5)	4.2(3)
C(3)	0.8696(5)	0.2665(2)	-0.1791(6)	4.5(3)
C(4)	0.8966(6)	0.2542(3)	-0.0489(7)	6.0(4)
C(5)	0.9897(8)	0.2141(3)	-0.0099(8)	7.8(4)
C(6)	1.0573(7)	0.1864(3)	-0.105(1)	7.2(4)
C(7)	1.0323(6)	0.1971(3)	-0.2352(8)	6.4(4)
C(8)	0.9370(6)	0.2377(2)	-0.2734(7)	5.1(3)
C(9)	1.0029(7)	0.2454(3)	-0.4953(7)	7.2(4)
C(10)	0.9615(7)	0.2798(3)	-0.6094(7)	7.5(4)
C(11)	0.9276(7)	0.3735(3)	-0.6694(7)	6.9(4)
C(12)	0.9062(7)	0.4290(3)	-0.6091(6)	6.5(4)
C(13)	0.7570(6)	0.4742(2)	-0.4706(5)	4.2(3)
C(14)	0.8102(5)	0.4756(2)	-0.3427(5)	4.1(3)
C(15)	0.7823(6)	0.5194(2)	-0.2629(6)	5.5(3)
C(16)	0.7009(7)	0.5615(3)	-0.3101(7)	6.8(4)
C(17)	0.6488(7)	0.5604(4)	-0.4370(6)	6.9(4)
C(18)	0.6744(6)	0.5166(3)	-0.5201(7)	5.8(4)
C(19)	0.6195(5)	0.5144(2)	-0.6540(6)	4.4(3)
C(20)	0.899(2)	0.5826(9)	-0.924(1)	21(2)
C(21)	0.807(2)	0.6254(8)	-0.975(2)	21(1)
C(22)	0.784(1)	0.6524(4)	-0.843(2)	12.3(7)
C(23)	0.866(1)	0.6233(5)	-0.742(1)	12.0(7)

in the succeeding difference Fourier syntheses. Four hydrogen atoms (H(25) ~ H(28) attached to C(1), C(19), N(1), N(3), respectively) also were located from the difference Fourier map, and the remaining hydrogen atoms were introduced by the HYDROGEN program. The structure was refined by the full-matrix least squares method. Calculations were performed on a Vax 785 computer. The fairly large B factor of the guest may be due to its slight disorder. The fractional coordinates

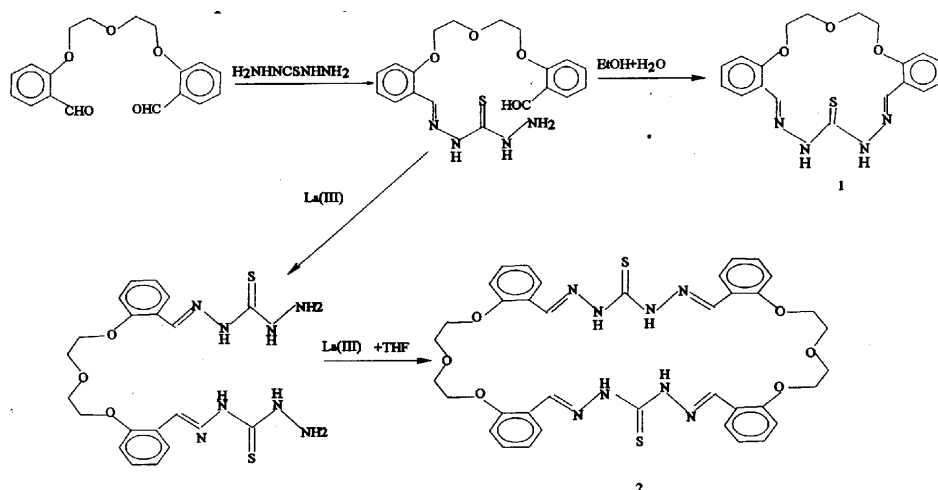
Table III. Selected interatomic distances (Å) and bond angles (°).

S(1)—C(1)	1.646(5)	N(3)—C(1)	1.354(6)	C(11)—C(12)	1.497(8)
O(1)—C(8)	1.354(7)	N(3)—N(4)	1.373(5)	C(14)—C(13)	1.379(8)
O(1)—C(9)	1.427(7)	N(4)—C(19)	1.278(6)	C(15)—C(14)	1.373(9)
O(2)—C(11)	1.413(8)	C(2)—C(3)	1.470(7)	C(16)—C(15)	1.368(9)
O(2)—C(10)	1.415(7)	C(3)—C(4)	1.372(7)	C(17)—C(16)	1.366(8)
O(3)—C(13)	1.376(6)	C(3)—C(8)	1.383(7)	C(18)—C(13)	1.388(7)
O(3)—C(12)	1.423(7)	C(4)—C(5)	1.377(8)	C(18)—C(17)	1.389(7)
O(4)—C(23)	1.31(1)	C(5)—C(6)	1.37(1)	C(19)—C(18)	1.441(7)
O(4)—C(20)	1.40(1)	C(6)—C(7)	1.365(9)	C(20)—C(21)	1.46(2)
N(1)—C(1)	1.351(6)	C(7)—C(8)	1.400(8)	C(21)—C(22)	1.52(2)
N(1)—N(2)	1.376(5)	C(9)—C(10)	1.470(9)	C(22)—C(23)	1.46(1)
N(2)—C(2)	1.274(6)				
C(1)—N(1)—N(2)	119.9(4)	O(4)—C(20)—C(21)	113(2)		
C(2)—N(2)—N(1)	115.0(4)	O(4)—C(23)—C(22)	107(1)		
C(1)—N(3)—N(4)	121.2(4)	C(3)—C(4)—C(5)	121.6(6)		
C(13)—N(4)—N(3)	114.7(4)	C(3)—C(8)—C(7)	120.0(6)		
N(1)—C(1)—N(3)	112.7(5)	C(4)—C(3)—C(8)	119.0(6)		
N(2)—C(2)—C(3)	119.5(5)	C(4)—C(3)—C(2)	122.1(5)		
N(4)—C(19)—C(18)	121.9(5)	C(6)—C(5)—C(4)	118.7(7)		
N(1)—C(1)—S(1)	125.2(4)	C(6)—C(7)—C(8)	119.2(6)		
N(3)—C(1)—S(1)	122.0(4)	C(7)—C(6)—C(5)	121.4(6)		
C(8)—O(1)—C(9)	118.4(5)	C(8)—C(3)—C(2)	118.8(6)		
C(11)—O(2)—C(10)	114.0(6)	C(13)—C(18)—C(17)	117.7(5)		
C(13)—O(3)—C(12)	114.6(4)	C(13)—C(18)—C(19)	120.0(5)		
C(23)—O(4)—C(20)	104(1)	C(14)—C(13)—C(18)	120.7(6)		
O(1)—C(8)—C(3)	115.8(6)	C(15)—C(14)—C(13)	120.0(6)		
O(1)—C(8)—C(7)	124.2(6)	C(16)—C(15)—C(14)	120.0(6)		
O(1)—C(9)—C(10)	108.2(5)	C(16)—C(17)—C(18)	121.4(6)		
O(2)—C(10)—C(9)	108.1(6)	C(17)—C(16)—C(15)	120.1(6)		
O(2)—C(11)—C(12)	108.3(6)	C(17)—C(18)—C(19)	122.3(5)		
O(3)—C(12)—C(11)	108.8(5)	C(20)—C(21)—C(22)	96(1)		
O(3)—C(13)—C(14)	120.1(6)	C(23)—C(22)—C(21)	108(1)		
O(3)—C(13)—C(18)	119.1(5)				

and thermal parameters of non-hydrogen atoms are given in Table II and selected distances and angles are collected in Table III.

3. Results and Discussion

Based on IR and MS data, two possible macrocyclic products (**1** and **2**) can be formed by the condensation of thiocarbonylhydrazide with 2,2'-bis(*o*-formylphenoxy) ethyl ether. The reaction scheme is represented as shown in the Scheme.



Scheme.

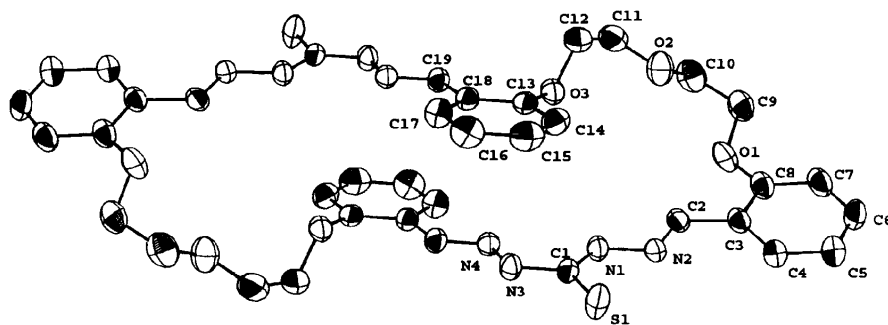


Figure 1. Structure of the macrocyclic molecule.

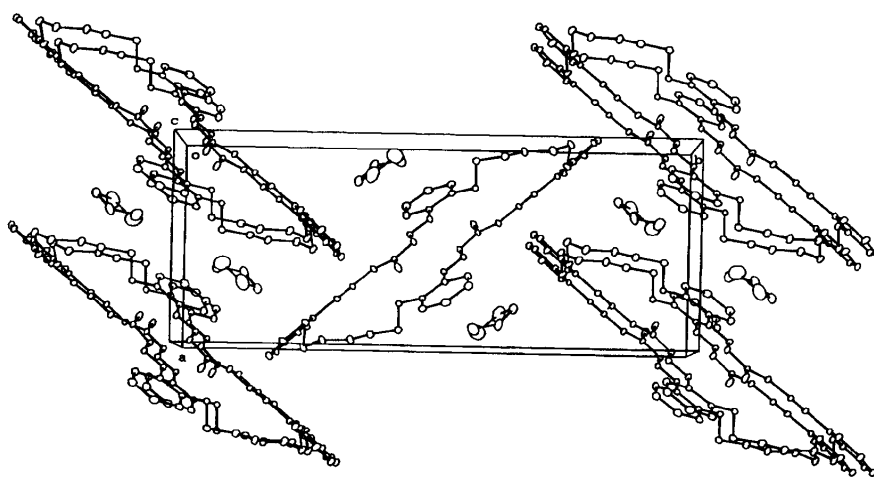
The IR spectra of these two compounds in the 4000–200 cm^{-1} region confirm the formation of the macrocyclic compounds by the absence of uncondensed functional group (NH_2 , $\text{C}=\text{O}$) stretching modes of the starting materials and the appearance of a strong absorption band at about 1640 cm^{-1} , attributable to $\text{C}=\text{N}$ stretching frequencies. The MS spectra of these two compounds provide strong evidence of the presence of the macrocyclic compounds showing the highest fragment at m/z 384 and 768, corresponding to each macrocyclic molecular weight, respectively.

A perspective view of the [36]ene-O₆N₈ molecule with atom labeling scheme is presented in Figure 1. The macrocyclic molecule, which was formed by condensation of thiocarbonylhydrazide with 2,2'-bis(*o*-formylphenoxy)ethyl ether in 2 : 2 ratio is centrosymmetric. Insertion of two $>\text{C}=\text{S}$ and four phenyl groups into the macrocyclic framework causes a considerable drop in flexibility of the macrocycle. The conformation of the $-\text{O}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{O}-$ chains in the macrocycle is

Table IV. Torsion angles ($^{\circ}$) in the macrocycle ring.

C(7)—C(8)—O(1)—C(9)	-31.3(8)	C(12)—O(3)—C(13)—C(14)	-82.6(4)
C(8)—O(1)—C(9)—C(10)	-159.7(5)	C(18) ^a —C(19) ^a —N(4)—N(3)	-178.7(5)
O(1)—C(9)—C(10)—O(2)	62.3(7)	C(19) ^a —N(4)—N(3)—C(1)	-176.3(5)
C(9)—C(10)—O(2)—C(11)	176.3(5)	N(4)—N(3)—C(1)—N(1)	1.5(7)
C(10)—O(2)—C(11)—C(12)	171.5(5)	N(3)—C(1)—N(1)—N(2)	-178.0(4)
O(2)—C(11)—C(12)—O(3)	-73.0(6)	C(1)—N(1)—N(2)—C(2)	-167.1(5)
C(11)—C(12)—O(3)—C(13)	169.6(5)	N(1)—N(2)—C(2)—C(3)	-178.8(4)
C(12)—O(3)—C(13)—C(18)	100.9(4)	N(2)—C(2)—C(3)—C(8)	-174.8(5)

^a $1 - x, 1 - y, -1 - z$.

Figure 2. Packing view of the clathrate down the c axis.

anti-gauche-anti-anti-gauche-anti-eclipsed, whereas that for —N—N—C—N—N— chains is *anti-eclipsed-anti-anti-anti*. The later sequence reflects flattening of the extensively conjugated bonds in the [—C₆H₄—C=NHNCSNH—N=CH—] chains (N(2)—C(2) = 1.274(6) Å, N(4)—C(13) = 1.278(6) Å). The torsion angles in the macrocyclic ring are quoted in Table IV. The dihedral angles between the least squares mean plane of =NHNCSNH= and the phenyl groups are 6.78 and 161.20°, respectively. The dihedral angle between two independent phenyl residues is 155.84°.

As shown in Figure 2, a rectangular channel along the c axial direction is formed by the exo-envelope of the [36]ene-O₆N₈ host molecules. Calculations of the intermolecular contacts (see Table V) show that the C···C, S···N, O···C, N···C and N···N distances are in the range of 3.36 ~ 3.57 Å; packing is determined by the interactions among the =CH₂, phenyl ring, ethyleneoxy, >C=S, >NH and Z -type >C=N— moieties via van der Waals forces. A pair of THF guest molecules

Table V. Intermolecular contacts less than 3.6 Å.

S(1)—N(3) ^a	3.37	O(3)—C(6) ^b	3.57
N(2)—C(9) ^d	3.36	O(4)—C(19) ^c	3.37
		O(4)—C(14) ^d	3.39

^a $1 - x, 1 - y, -z.$

^b $x - 1/2, 1/2 - y, z - 1/2.$

^c $3/2 - x, y - 1/2, -z - 1/2.$

^d $x - 1/2, 1/2 - y, 1/2 + z.$

related centrosymmetrically occupy the channel where the least squares plane of THF in the half chair form is roughly parallel to that of the phenyl moiety of the host molecules. The shortest contacts between guest and host molecule (3.37 ~ 3.39 Å, the last two contacts in Table V), indicated van der Waals interaction that might be beneficial to stabilization of the crystal.

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