

Two Clathrates of Bis(isothiocyanato)tetrakis(4-methylpyridine)magnesium(II) as a Host with 4-Methylpyridine as a Guest

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Abstract. Two clathrate modifications of the title host with 4-methylpyridine (4-CH₃C₅H₄N) as a guest have been determined at -50°C.

[Mg(4-CH₃C₅H₄N)₄(NCS)₂] · 2/3(4-CH₃C₅H₄N) · 1/3H₂O is trigonal, space group $R\bar{3}$, with $a = 27.630(7)$, $c = 11.219(3)$ Å, $V = 7417(4)$ Å³, $Z = 9$, $D_{\text{calc}} = 1.171$ g cm⁻³, $\mu(\text{CuK}\alpha) = 18.506$ cm⁻¹, final $R = 0.064$.

[Mg(4-CH₃C₅H₄N)₄(NCS)₂] · (4-CH₃C₅H₄N) is tetragonal, space group $I4_1/a$, with $a = 16.944(7)$, $c = 23.552(9)$ Å, $V = 6762(5)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.191$ g cm⁻³, $\mu(\text{CuK}\alpha) = 18.200$ cm⁻¹, final $R = 0.071$.

The structures consist of molecular packings of the same host complex units and the guest species. The Mg(II) cation is octahedrally coordinated to the N-atoms of four 4-methylpyridines and two *trans*-coordinated isothiocyanato ligands in the host molecule. The conformations of the molecule are considerably different both in symmetry and in geometry in these two structures. The guest 4-methylpyridine molecules are disordered into channels which have different topology in these two clathrates resulting in different thermal stability.

Key words: Crystal structure, clathrate, Werner complex, isothiocyanate, 4-methylpyridine, Mg(II).

1. Introduction

The versatile clathration ability of [MA₄X₂] complexes, where *M* is a divalent transition metal cation, A is a neutral ligand such as a pyridine, and X is a univalent anion, is well known [1]. Extensive studies in this field were started after Schaeffer *et al.* found high selectivity of the complexes with respect to inclusion of different guest species [2]. At present a large number of such complexes and their clathrates have been studied, with different transition metal cations; nevertheless, only a few communications have been published on the clathration ability of main group metal complexes. Schaeffer *et al.* reported the clathrate formation of the [Mg(4-EtPy)₄Cl₂] (4-EtPy = 4-ethylpyridine) complex with *o*-xylene [3] but no structural data are available. Halut-Desportes *et al.* described some clathrate structures of tetrapyrroline magnesium and calcium halides with pyridine as a guest but they did not consider them as inclusion compounds [4]. The clathrate structures of Cd

complexes were also reported by Ito, Shibata and Saito [5], and by Dyadin *et al.* [6].

In our previous work [7] we described the syntheses, analytical and spectral data, and some properties of the clathrates of $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2]$ (4-MePy = 4-methylpyridine) host with 4-MePy as a guest. To compare conformations of the $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2]$ complex molecule and host-guest packing in the structures the single-crystal X-ray study of the clathrates was undertaken.

2. Experimental

The crystals of $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2] \cdot 0.67(4\text{-MePy}) \cdot 0.33\text{H}_2\text{O}$ (**1 : 0.67**) and $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2] \cdot 4\text{-MePy}$ (**1 : 1**) clathrates were obtained by cooling solutions of $[\text{Mg}(\text{H}_2\text{O})_4(\text{NCS})_2]$ in 4-MePy saturated at elevated temperature. Some quantity of water was added to attain the stoichiometrical composition of **1 : 0.67**. In contrast, the **1 : 1** clathrate was additionally recrystallized from anhydrous 4-methylpyridine to obtain high quality crystals. Details of the syntheses and analyses of the compounds obtained have been reported elsewhere [7].

Lindemann glass capillary tubes were used to protect the crystals from guest loss and the intensity data were collected at -50°C on an Enraf-Nonius CAD4 single-crystal diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation and the $\omega - 2\theta$ scan technique.

The structures were solved by direct methods using SHELX-86 [8] and refined using SHELX-76 [9]. Because of guest disorder in both structures the 4-MePy molecules were included with fixed geometry in the last stage of structure refinement. Host hydrogen atoms were included in final cycles at the calculated positions ($d_{\text{C-H}} = 1.08 \text{ \AA}$) as 'riding' on corresponding carbon atoms and with temperature factors fixed.

The $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2] \cdot 0.67(4\text{-MePy}) \cdot 0.33 \text{ H}_2\text{O}$ was solved in the trigonal cell: $a = 27.630(7)$, $c = 11.219(3) \text{ \AA}$, and refined to $R = 0.064$; the $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2] \cdot 4\text{-MePy}$ structure was solved in the tetragonal cell: $a = 16.944(7)$, $c = 23.552(9) \text{ \AA}$, and refined to $R = 0.071$. A summary of the experimental data is given in Table I. Fractional atomic coordinates, bond lengths and angles are listed in Tables II–V. The lists of coordinates of host hydrogen atoms, thermal parameters and F_o/F_c tables are available from the Author (J. Lipkowski) on request.

3. Results and Discussion

The structures of the $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2]$ molecules from the clathrates reported here with their numbering schemes are depicted in Figure 1 [10]. In both the Mg(II) cation has a distorted octahedral coordination by nitrogens of four 4-MePy molecules and two *trans*-isothiocyanato groups. In other words, we are dealing with the same molecule in these structures. However, the symmetry and geometry are very different in these two cases, as can be seen from Table VI. On the whole

TABLE I. Data collection and structure analysis parameters

Clathrate	1 : 0.67	1 : 1
Formula	[Mg(4-MePy) ₄ (NCS) ₂]. ·2/3(4-MePy) · 1/3H ₂ O	[Mg(4-MePy) ₄ (NCS) ₂]. ·4-MePy
Empirical formula	C ₃₀ H _{33.33} N _{6.67} O _{0.33} S ₂ Mg	C ₃₂ H ₃₅ N ₇ S ₂ Mg
Formula weight	581.1	606.1
Crystal system	trigonal	tetragonal
Space group	$R\bar{3}$	I ₄ /a
<i>a</i> , Å	27.630(7)	16.944(7)
<i>c</i> , Å	11.219(3)	23.552(9)
<i>V</i> , Å ³	7417(4)	6762(5)
<i>Z</i>	9	8
<i>D</i> _{calc} , g cm ⁻³	1.171	1.191
<i>t</i> , °C	-50	-50
Crystal size, mm	0.35 × 0.45 × 0.9	0.5 × 0.5 × 1.2
Radiation	Ni-filtered CuK _α	Ni-filtered CuK _α
Absorption		
coefficient, cm ⁻¹	18.506	18.200
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$
Scan range (θ), deg.	2-78	2-78
Scan width ($\Delta\omega$), deg.	1.0 + 0.14 tan θ	1.6 + 0.14 tan θ
Scan speed, deg./min.	0.55(min)-5.50(max)	0.77(min)-8.25(max)
Background time	1/3 of measuring time	1/3 of measuring time
Monitor reflections	3 after ever 100 reflections	3 after every 100 reflections
min/max <i>h</i> , <i>k</i> , <i>l</i>	-35/35, 0/35, -14/0	-21/21, 0/21, 0/29
Number of reflections:		
measured	5501	7511
observed (<i>I</i> > 3 σ_I)	2652	4287
used(unique-observed)	1753	2306
Number of refined		
parameters	213	184
Final <i>R</i>	0.064	0.071
<i>R</i> _w	0.070	0.074
Weighting scheme:		
$w = k/(\sigma^2(F) + mF^2)$	$k = 5.1071; m = 0.0004$	$k = 5.9371; m = 0.0005$
Residual extrema in final		
difference map, e Å ⁻³	+0.49/-0.40	+0.45/-0.37

the conformations are in good agreement with the calculations of the interaction energy between the ligands for the [Ni(4-MePy)₄(NCS)₂] molecule [11]. In the case of the molecule from the **1 : 0.67** structure the strong steric interactions between 4-MePy(ring1) and isothiocyanato groups result in the considerable increase in the Mg-N_{ring1} distance and therefore more deviation of the 'MgN₆' coordination polyhedron from a perfect octahedron. The pyridine rings of the molecule are

TABLE II. Fractional atomic coordinates ($\times 10^4$) and B_{eq} with esds (in parentheses) of nonhydrogen atoms for the $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2] \cdot 0.67(4\text{-MePy}) \cdot 0.33\text{H}_2\text{O}$ clathrate

	X/A	Y/B	Z/C	B_{eq}
Host:				
Mg	5000	0000	0000	4.0(1)
S	4626(1)	-1239(1)	3338(2)	8.7(1)
N(1)	4695(2)	-0636(2)	1307(3)	4.7(1)
N(2)	4457(1)	-0657(2)	-1375(3)	4.3(1)
N(3)	5696(1)	-0171(1)	-0404(3)	4.1(1)
C(1)	4657(2)	-0899(2)	2136(4)	4.4(2)
C(2)	4051(2)	-1182(2)	-1103(4)	4.7(2)
C(3)	3726(2)	-1584(2)	-1942(5)	4.9(2)
C(4)	3818(2)	-1455(2)	-3140(4)	4.7(2)
C(5)	4238(2)	-0923(2)	-3438(4)	5.3(2)
C(6)	4545(2)	-0541(2)	-2556(4)	5.1(2)
C(7)	3469(2)	-1886(2)	-4075(5)	6.6(3)
C(8)	6213(2)	0238(2)	-0713(4)	4.6(2)
C(9)	6656(2)	0146(2)	-0911(4)	5.0(2)
C(10)	6578(2)	-0391(2)	-0810(4)	5.0(2)
C(11)	6043(2)	-0814(2)	-0515(4)	4.8(2)
C(12)	5621(2)	-0690(2)	-0304(4)	4.5(2)
C(13)	7057(2)	-0503(3)	-1021(7)	7.7(3)
Guest I (model):				
N(1G)	0120(5)	0260(4)	2422(7)	
C(1G)	0494(5)	0677(4)	3128(7)	
C(2G)	0361(5)	0828(4)	4207(7)	
C(3G)	-0184(5)	0545(4)	4609(7)	
C(4G)	-0575(5)	0124(4)	3889(7)	
C(5G)	-0414(5)	-0007(4)	2825(7)	
C(6G)	-0340(5)	0702(4)	5784(7)	
Guest II:				
O(1)	0000	0000	0000	

$$B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij} a_i a_j$$

planar within 0.03 Å (rings 1 and 2), and within 0.03 Å (ring 1) and 0.02 Å (ring 2) for the structures **1 : 0.67** and **1 : 1**, respectively (at the 3σ significance level).

The host molecule is centrosymmetric in the **1 : 0.67** clathrate; the crystallographically equivalent 4-MePy ligands are in *trans*-positions. The least-squares planes of the pyridine rings form dihedral angles of +77.0(2) (ring 1) and -54.8(1)° (ring 2) with the equatorial plane of the complex. The Mg(II) cation deviates from the planes by 0.041(2) (ring 1) and 0.088(1) Å (ring 2). The isothiocyanato ligand is nonlinear, the N-C-S angle being equal to 177.0(5)°. The Mg-

TABLE III. Fractional atomic coordinates ($\times 10^4$) and B_{eq} with esds (in parentheses) of nonhydrogen atoms for the $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2] \cdot 4\text{-MePy}$ clathrate

	X/A	Y/B	Z/C	B_{eq}
Host:				
Mg	5000	2500	0543(1)	2.65(5)
S	2451(1)	1189(1)	0505(1)	4.69(4)
N(1)	3988(2)	1768(2)	0515(2)	3.2(1)
N(2)	4488(2)	3263(2)	1210(2)	3.0(1)
N(3)	4422(2)	3224(2)	-0131(2)	2.5(1)
C(1)	3346(3)	1521(2)	0508(2)	2.7(1)
C(2)	3709(3)	3387(3)	1277(2)	3.4(1)
C(3)	3408(3)	3845(3)	1706(2)	4.1(1)
C(4)	3901(3)	4183(3)	2108(2)	3.7(1)
C(5)	4693(3)	4051(3)	2037(3)	4.9(2)
C(6)	4950(3)	3604(3)	1586(2)	4.7(2)
C(7)	3581(4)	4675(3)	2602(2)	5.4(2)
C(8)	4422(2)	4021(2)	-0136(2)	2.8(1)
C(9)	4067(3)	4467(3)	-0549(2)	3.1(1)
C(10)	3682(3)	4109(3)	-0991(2)	3.0(1)
C(11)	3673(3)	3279(3)	-0987(2)	3.1(1)
C(12)	4042(3)	2874(3)	-0563(2)	3.0(1)
C(13)	3315(3)	4578(3)	-1471(2)	4.7(2)
Guest (model):				
N(1G)	10045(8)	0828(6)	10472(5)	
C(1G)	10498(8)	0801(6)	10004(5)	
C(2G)	10475(8)	0186(6)	9622(5)	
C(3G)	9961(8)	-0429(6)	9697(5)	
C(4G)	9507(8)	-0410(6)	10175(5)	
C(5G)	9572(8)	0223(6)	10545(5)	
C(6G)	9886(8)	-1105(6)	9276(5)	

$$B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij} a_i a_j$$

N_{CS} distance of 2.114(4) Å is close to the value of 2.109(2) Å observed in the $[\text{Mg}(\text{Pyridine})_4(\text{NCS})_2]$ molecule, which is also centrosymmetric [12]. The ligand deviates significantly from the axial position of the complex, the Mg–N–C_S angle is 163.1(5)°. The conformation of the molecule is very close to those of the $[\text{M}(4\text{-MePy})_4(\text{NCS})_2]$ (M=Cu, Mn [13], Fe [14]) molecules in analogous structures (with obvious differences in the coordination bond lengths).

The host molecule adopts a four-bladed ‘propeller’ conformation of the four pyridine rings in the 1 : 1 clathrate. The twofold symmetry axis lies in the equatorial plane of the complex and goes through the Mg(II) cation diagonally between two 4-MePy rings. Thus, the crystallographically equivalent 4-MePy ligands are in *cis*-

TABLE IV. Bond lengths (Å) (involving nonhydrogen atoms) for the host molecule with esds (in parentheses)

		1 : 0.67	1 : 1
Mg	- N(1)	2.114(4)	2.117(4)
Mg	- N(2)	2.281(4)	2.212(4)
Mg	- N(3)	2.244(3)	2.232(4)
S	- C(1)	1.621(6)	1.617(5)
N(1)	- C(1)	1.152(7)	1.166(6)
N(2)	- C(2)	1.352(6)	1.346(6)
N(2)	- C(6)	1.356(6)	1.316(6)
N(3)	- C(8)	1.350(5)	1.351(5)
N(3)	- C(12)	1.347(7)	1.342(6)
C(2)	- C(3)	1.389(6)	1.372(7)
C(3)	- C(4)	1.381(7)	1.386(7)
C(4)	- C(5)	1.383(6)	1.371(7)
C(4)	- C(7)	1.517(6)	1.531(7)
C(5)	- C(6)	1.385(6)	1.375(8)
C(8)	- C(9)	1.387(9)	1.371(6)
C(9)	- C(10)	1.393(8)	1.370(7)
C(10)	- C(11)	1.390(6)	1.406(7)
C(10)	- C(13)	1.51 (1)	1.515(7)
C(11)	- C(12)	1.390(9)	1.363(7)

positions. The least-squares planes of the pyridine rings form dihedral angles of 56.1(2) (ring 1) and 45.6(2)° (ring 2) with the equatorial plane of the complex. The Mg(II) cation deviates from the planes by 0.103(4) (ring 1) and 0.002(4) Å (ring 2). The isothiocyanato ligand is linear within experimental error and forms an angle of 165.1(5)° with the Mg-N_{CS} bond. The Mg-N_{CS} distance is equal to 2.117(4) Å. The conformation of the molecule is similar to those of [M(4-MePy)₄(NCS)₂] (M=Ni [15], Fe [16]) molecules in other β-clathrates.

The host molecule packing forms voids in the form of channels in which the guest species are included. Apart from guest disorder about symmetry elements (the three-fold inversion axis for **1 : 0.67** and the symmetry centre for **1 : 1**) there are a number of possible positions of the molecules and to represent them as a superposition of two or three arrangements was unsuccessful. The modelling allowed us to find the most probable positions of the guest species.

There are straight channels stretching along the *c* axis in the **1 : 0.67** structure (Figure 2). Two guest 4-MePy molecules are placed into a wide part of the channel whereas the supplementary guest water molecules occupy narrow voids. Preliminary spectral studies [7] and the proximity of the guest N and O atoms bear witness to the presence of hydrogen bonds between the guest molecules. Nevertheless the bonds do not play a principal role in the formation of the structure as the water

TABLE V. Bond angles (deg) for the host molecule with esds

	1 : 0.67	1 : 1
N(2) - Mg - N(3)	89.3(1)	90.7(2)
N(1) - Mg - N(3)	89.6(2)	86.8(2)
N(1) - Mg - N(2)	88.7(2)	92.7(2)
Mg - N(1) - C(1)	163.1(5)	165.1(5)
Mg - N(2) - C(6)	120.2(3)	120.1(4)
Mg - N(2) - C(2)	124.3(3)	124.0(4)
C(2) - N(2) - C(6)	115.4(4)	115.8(5)
Mg - N(3) - C(12)	121.0(3)	120.4(4)
Mg - N(3) - C(8)	122.3(3)	123.8(4)
C(8) - N(3) - C(12)	116.6(4)	115.8(5)
S - C(1) - N(1)	177.0(5)	179.1(5)
N(2) - C(2) - C(3)	124.2(4)	122.6(6)
C(2) - C(3) - C(4)	119.4(5)	120.8(6)
C(3) - C(4) - C(7)	120.5(4)	122.0(6)
C(3) - C(4) - C(5)	117.2(4)	116.0(5)
C(5) - C(4) - C(7)	122.2(4)	121.9(6)
C(4) - C(5) - C(6)	120.4(4)	119.6(6)
N(2) - C(6) - C(5)	123.3(5)	125.0(6)
N(3) - C(8) - C(9)	123.3(4)	123.9(5)
C(8) - C(9) - C(10)	120.1(5)	120.3(6)
C(9) - C(10) - C(13)	121.1(5)	122.0(5)
C(9) - C(10) - C(11)	116.6(5)	116.3(5)
C(11) - C(10) - C(13)	122.2(5)	121.7(5)
C(10) - C(11) - C(12)	120.2(5)	120.2(5)
N(3) - C(12) - C(11)	123.1(5)	123.6(6)

content may vary from at least 20% to 73% of the stoichiometric quantity [7]. The structure is similar to analogous clathrates of Cd, Cu and Mn hosts with the same guests [13]. With a view to considering any possible interactions (apart from van der Waals) between host and guest species in such clathrates, the inner channel structure was examined. As calculations show, only one of two symmetrically nonequivalent 4-MePy ligands, and a NCS group, take part in building the channel walls. The wide part is formed by six S-atoms, and the narrow part has the environment of six methyl groups. As can be seen from Table VII there is no possibility of the π -systems of host 4-MePy groups interacting with included species, while S could perform the role of a potential donor.

The **1 : 1** structure is the wellknown β -phase; the 4-MePy guest molecules are disordered about inversion centres into channels having a zigzag cross-section (Figure 3).

TABLE VI. Symmetry and geometry comparison of the $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2]$ molecule in the two structures

	1 : 0.67	1 : 1
Molecular symmetry	C_i	C_2
Location of the symmetry element	i on Mg(II) cation	2 through Mg(II) cation diagonally between two 4 MePy rings
The distances:		
Mg–N _{Cs}	2.11 Å	2.12 Å
Mg–N _{ring1}	2.28	2.21
Mg–N _{ring2}	2.24	2.23
The angles between the equatorial plane of the molecule and the 4-MePy _{ring1} , 4-MePy _{ring2}		
	+77, –55°	+56, +46°
The respective angles for the $[\text{Ni}(4\text{-MePy})_4(\text{NCS})_2]$ molecule:		
calculated [11]	+75, –40	+45, +45
observed in 5 tetragonal clathrates [15]		+(55 – 58), +(46 – 49)
The angles observed in trigonal clathrates for Cu and Mn hosts [13]		
	+(77 – 78), –(54 – 55)	
The conformation type [11]		
	$\overset{\wedge}{+} \overset{\wedge}{+} \text{--} \text{--}$ 'centrosymmetric'	$++ ++$ 'propeller'

TABLE VII. Participation of the host ligands in building channel walls for some clathrates with 4-MePy as a guest (in %)

	NCS	4-MePy(ring1)		4-MePy(ring2)	Ref.
	only S	as a whole	only π -atoms	as a whole	
Trigonal (1 : 0.67):					
$[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2]$ -host	45.3(4)	50.8(4)	3.5(1)	1.6(1)	this
$[\text{Cu}(4\text{-MePy})_4(\text{NCS})_2]$ -host	36.6(4)	58.9(4)	1.9(1)	2.8(1)	[17]
$[\text{Mn}(4\text{-MePy})_4(\text{NCS})_2]$ -host	43.6(4)	51.9(4)	1.9(1)	2.2(1)	[17]
Tetragonal (1 : 1):					
$[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2]$ -host	27.8(4)	71.9(4)	40.2(4)	0.15(3)	this
$[\text{Zn}(4\text{-MePy})_4(\text{NCS})_2]$ -host	34.4(4)	65.2(4)	39.7(4)	0.28(4)	[18]

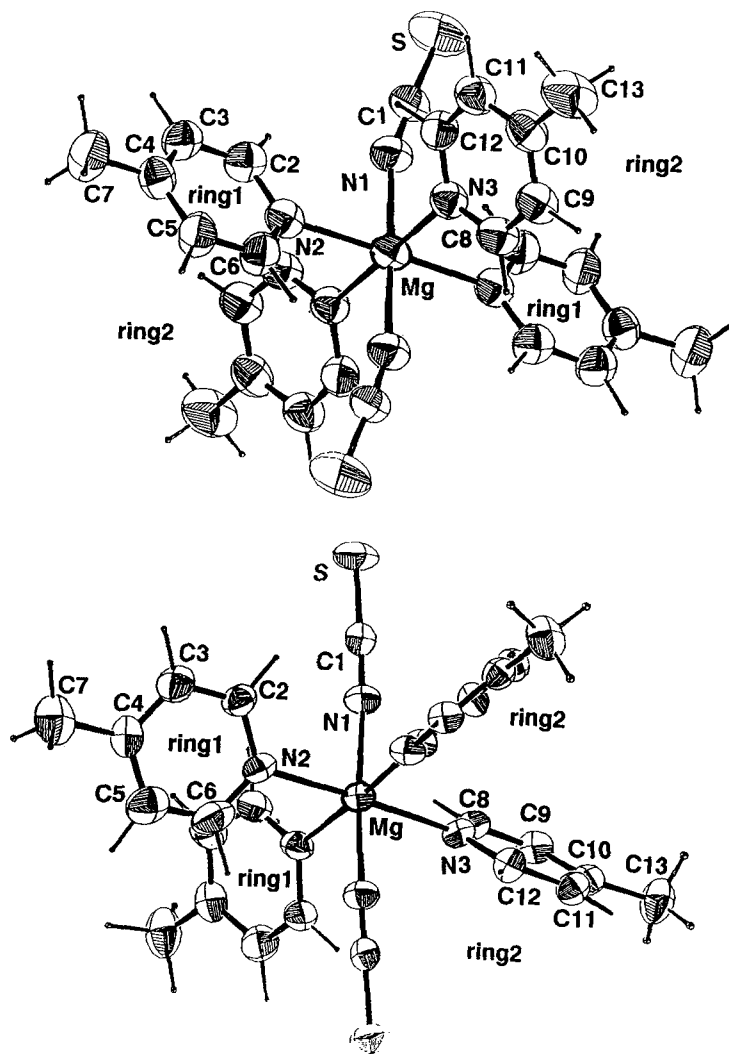


Fig. 1. ORTEP projections and the numbering schemes of the $[\text{Mg}(4\text{-MePy})_4(\text{NCS})_2]$ molecule in the two clathrates: $1 : 0.67$ (a); $1 : 1$ (b).

The inner surface of the channels is formed by one of the 4-MePy ligands and the S of the isothiocyanato group, with the former taking the greater part in its construction (Table VII). There are no narrow voids in the $1 : 1$ channels such as those available in the $1 : 0.67$ compound. In other words, the guests in the $1 : 1$ compound fit less well to the host, forming fewer contacts with it. Therefore, in spite of the packing coefficient for the $1 : 1$ clathrate (0.663) being slightly greater than the one for the $1 : 0.67$ clathrate (0.652 at full water filling vs 0.646 without

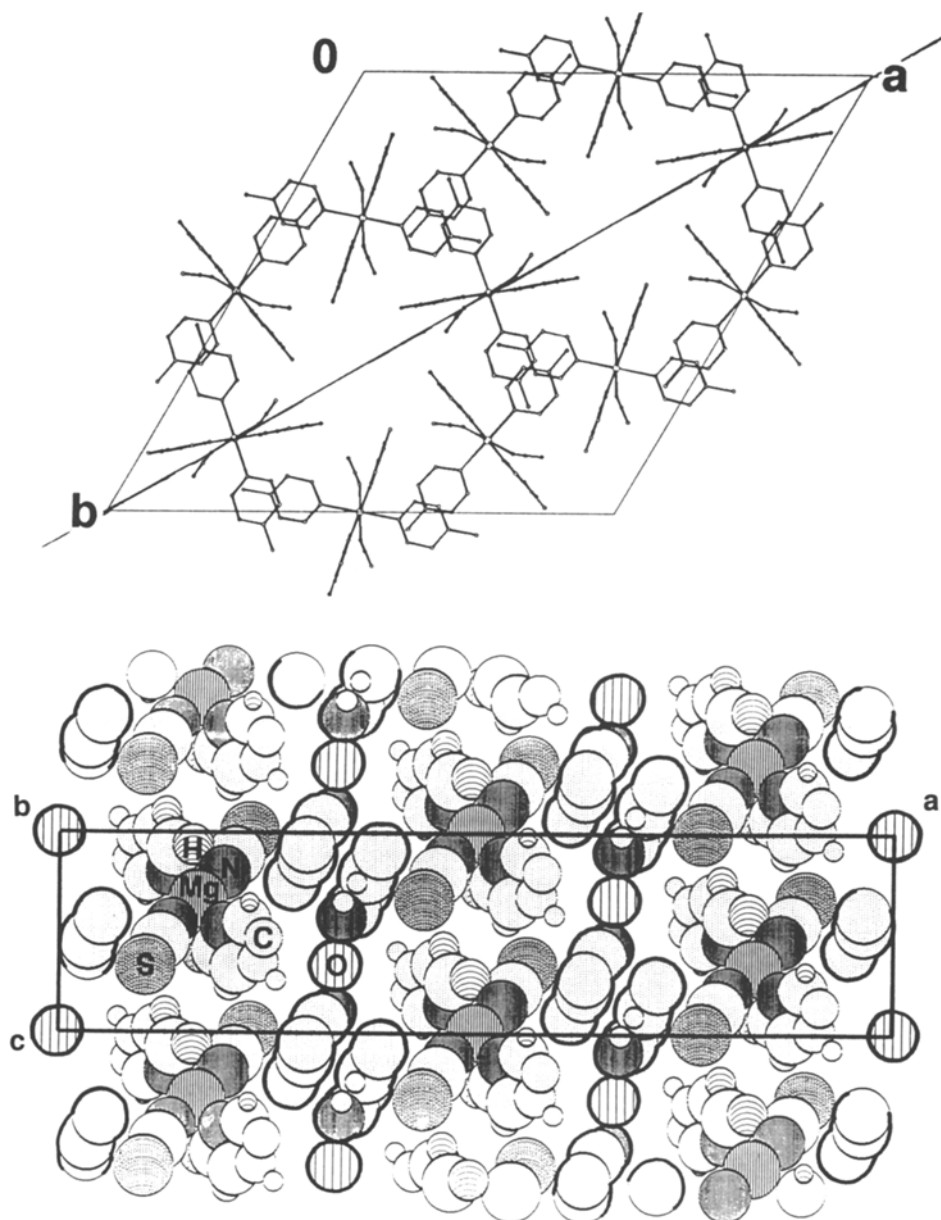


Fig. 2. Molecular packing for the $1 : 0.67$ clathrate. (a) The projection viewed along the crystallographic c axis (guest and hydrogen atoms are omitted for the sake of the clarity). (b) The section of the structure in the (110) plane (as shown on the projection). The guests are distinguished by a black contour; only one of the three symmetrically possible guest positions is presented; the guest hydrogen atoms are omitted.

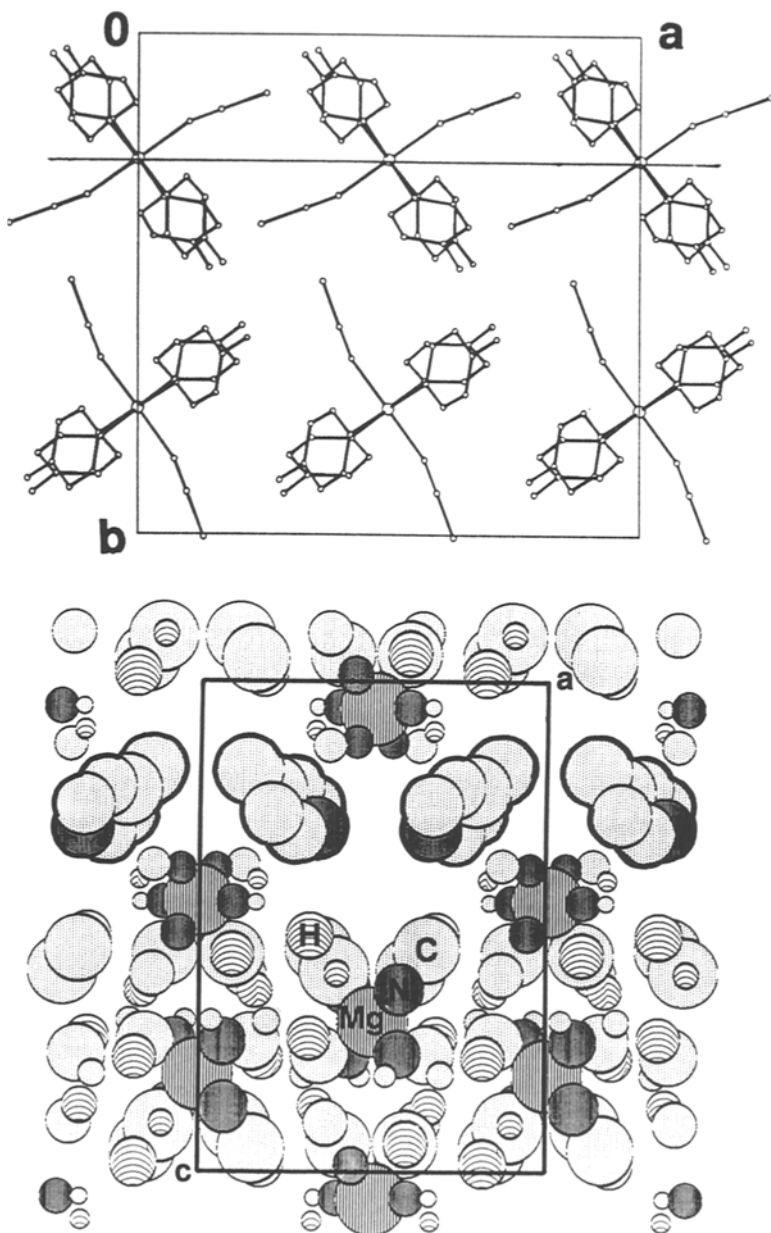


Fig. 3. Molecular packing for the 1 : 1 clathrate. (a) The projection viewed along the crystallographic *c* axis (guest and hydrogen atoms are omitted and only half of the cell unit is presented for the sake of the clarity). (b) The section of the structure in the (040) plane (as shown on the projection). The guests are distinguished by a black contour; only one of the two symmetrically possible guest's positions is presented; the guest hydrogen atoms are omitted.

TABLE VIII.

$[M(4\text{-MePy})_4(\text{NCS})_2] \cdot y\text{G}$	M=Mg	M=Cd	M=Cu	M=Zn
HOST ($y = 0$)	ca. 185	134	are not stable at positive	at least temperatures*
1 : 0.67 ($y = 0.67$)	170	139	82	63
1 : 1 ($y = 1$)	70	does not exist (?)	does not exist (?)	57
Ref.	—**	[6]	[17]	[18]

* According to crystal field theory it can be proposed that the stability of the octahedral Cu host would be higher than the stability of the same Zn host.

** The temperatures were not published in our previous work [7]. For the 1 : 0.67 compound the temperature remains constant for different water content samples within 1°C.

it), the guests in the former are held less weakly into the structure. This conclusion is in accordance with a difference in the stability of the clathrates in the open air and in other properties [7]. It is interesting to compare the incongruent melting temperatures for these and other analogous clathrates with those for the hosts (°C) (Table VIII).

Because of compositional similarities the temperatures allow us to compare the stabilities of the compounds. As can be seen, high stability of a host results in higher stability of a 1 : 0.67 clathrate compared with the 1 : 1 clathrate (Mg), while with an unstable host the melting temperatures of the 1 : 0.67 and 1 : 1 clathrates are similar (Zn).

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