Phase and Structural Study of Clathrate Formation in the [Zn (MePy)$_2$(NCS)$_2$]–MePy System (MePy = 4-Methylpyridine)

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Abstract. A phase diagram of the [Zn(MePy)$_2$(NCS)$_2$]–MePy binary system has been studied by DTA and solubility methods. Two compounds melting incongruently (at 63 and 57°C) have been discovered in the system. They have been obtained as separate phases with crystals of different shape (needles and octahedra). Their composition has been determined by analytical methods and verified by X-ray structural analysis: [Zn(MePy)$_4$(NCS)$_2$] · 0.67 MePy·xH$_2$O, where x depends on the synthesis conditions, and [Zn(MePy)$_4$(NCS)$_2$]·MePy, respectively.
The preliminary X-ray study of the first compound (at −100°C) has shown it to be isostructural with the known clathrates of the common formula [M(MePy)$_4$(NCS)$_2$] · 0.67MePy·xH$_2$O, where M = Cu, Mn, Mg and $x = 0 − 0.33$. The unit cell parameters are as follows: $a = 27.20(1)$, $c = 11.202(4)$ Å, space group $R\bar{3}$, $Z = 9$.
The X-ray study of [Zn(MePy)$_4$(NCS)$_2$]·MePy (at −50°C) has shown it to be analogous to the 'organic zeolite' β-phase with the guest MePy molecules located in the channels formed by molecular packing of the [Zn(MePy)$_4$(NCS)$_2$] host. The cell is tetragonal, the space group $I4_1/a$, $a = 16.845(6)$, $c = 23.496(7)$ Å, $V = 6667(4)$ Å^3, $Z = 8$, $D_{calc.} = 1.289$ g cm^{-3}, $R = 0.074$. The zinc cation is surrounded by a slightly irregular octahedron of six nitrogen atoms of the MePy and NCS ligands.
The crystallisation field of the host [Zn(MePy)$_4$(NCS)$_2$] complex in the temperature range concerned is absent in the phase diagram. It suggests contact stabilization of the [Zn(MePy)$_4$(NCS)$_2$] molecule by the guest in the clathrates.

Key words: Phase diagram, clathrate, X-ray structure, 4-methylpyridine, Zn(II) isothiocyanate.

1. Introduction

The inclusion ability of [MA$_4$X$_2$] complexes, e.g., [Ni(MePy)$_4$(NCS)$_2$] [1] is well known. Numerous investigations have revealed that in the case of A=MePy, X=NCS$^-$ and guest=MePy two main types of clathrates are observed for different M: tetragonal β-phases with the host : guest mole ratio = 1 : 1 (M=Ni, Co, Mg) or trigonal 1 : 0.67 : x (Cu, Mn, Mg) structures,[1] where x is the mole coefficient

of a complementary water guest, changing from 0 to 0.33. In both cases there are channels in the host packing, but they differ dramatically in topology. There is also a considerable difference between the conformations of the host molecules of these clathrates, which shows that nonvalent interactions are rather important for the formation of these kinds of structures. They are very significant in clathrates with [Cu(MePy)$_4$(NCS)$_2$] as a host because the host itself does not exist as a separate stable phase (contact stabilization of the host by the guest molecules [2]).

The phase study of the [Zn(MePy)$_2$(NCS)$_2$]-MePy binary system and X-ray structural investigation of the compounds obtained have been undertaken in this work.

2. Experimental

2.1. PREPARATION AND ANALYSIS

4-Methylpyridine marked 'pure' was used for the syntheses. For the phase diagram construction it was additionally purified by distillation, fractional freezing and distillation over BaO [3], and kept in a desiccator over P$_2$O$_5$. The purified base melted at 2.0–2.5°C (literature value is 4.3°C [3]) and contained not more than 0.13 wt.-% water.

The [Zn(MePy)$_2$(NCS)$_2$] complex has been synthesized as a colourless, water-insoluble powder by adding a stoichiometric quantity of 4-methylpyridine dropwise into the aqueous solution of 'chemically pure' Zn(NO$_3$)$_2$ · 6H$_2$O and KSCN, 'pure for analysis' [4]. The complex was rinsed with water, air-dried and kept over KOH. The data obtained by elemental analysis are as follows: C, 46.3(5) (calculated: 45.72); N, 15.4(2) (15.23); H, 3.6(2) (3.84); S, 18.4(5) (17.43). Analysis showed the content of Zn and MePy to be 17.6(1) (17.78) and 52.0(6) (50.64), respectively, and water has not been detected. The melting point of the complex is 186°C.

The clathrate [Zn(MePy)$_4$(NCS)$_2$ · 0.67 MePy·xH$_2$O (1 : 0.67) was synthesized by the rapid cooling to room temperature of the solution saturated at 73°C of [Zn(MePy)$_2$(NCS)$_2$] in neat liquid 4-methylpyridine. Large colourless needles were rapidly pressed out on a filter and could be kept in a sealed glass ampoule. Analytical data: Zn, 10.20(7) (10.51 was calculated for $x = 0.33$); MePy, 69.6(8) (69.91); H$_2$O, 0.63(4) (0.96). Thus x, which in this kind of clathrate usually depends on the synthesis conditions, in this case is equal to 0.22.[2]

The clathrate [Zn(MePy)$_4$(NCS)$_2$]·MePy (1 : 1) was obtained by the above procedure, but the needles of the 1 : 0.67 clathrate were left in the mother liquor where they grew into poorly formed truncated octahedra of the 1 : 1 clathrate. The product was kept in the mother liquor and when needed was pressed out to dryness on a filter. The analytical data are: Zn, 9.85(9) (10.10); MePy, 73.1(6) (71.95); and water has not been detected. To obtain high quality crystals for X-ray study an excess of the [Zn(MePy)$_2$(NCS)$_2$] complex was mixed with neat 4-methylpyridine at 43°C followed by filtration and slow cooling of the filtrate to

room temperature. Another procedure of synthesizing the 1 : 1 clathrate consisted in placing [Zn(MePy)$_2$(NCS)$_2$] into MePy saturated vapour [5]. The weight kept increasing for about three months and correlated with the host : guest ratio = 1 : 1 (within 0.3% accuracy).

We failed to prepare the [Zn(MePy)$_4$(NCS)$_2$] complex by changing the concentration of the initial reagents.

The analysis of Zn, MePy and water was carried out by complexometric titration (EDTA), by the reverse titration of the residue of the precise nitric acid volume added to the weighed portions of the compounds and by the Karl Fisher method of suspension of the weighed portions in absolute ethanol, respectively.

2.2. PHASE DIAGRAM

To construct the phase diagram we used the procedures described below, data reported earlier [6] and visual observations. The arrangement of the solidus curve was determined by the DTA technique described elsewhere [7]. Samples of various compositions were prepared by mixing the initial substances [Zn(MePy)$_2$(NCS)$_2$]^3 and MePy before sealing in glass ampoules. The ampoules were kept at room temperature for several days (or at $+(4-5)°$C for the study of the low temperature region of the diagram), then thermal heating curves were recorded for each of the ampoules. The precision of the temperature measurements was $0.5°$C and the heating rate was 1.7 degree/min. Reproducibility and stability of all the registered effects upon repeated recording served as a criterion of whether equilibrium was attained and whether the number of components in the system remained the same.

The location of the liquidus curve was determined by the solubility method. Under the required temperature the [Zn(MePy)$_2$(NCS)$_2$] complex was mixed with neat 4-methylpyridine liquid for some quantity of solid phase. After the equilibrium was attained, a portion of the liquid phase was taken with a pipet, heated to a certain temperature, and the Zn content was analyzed. It was assumed that the system had reached equilibrium if the composition of the liquid remained constant over several hours.

2.3. X-RAY DIFFRACTION MEASUREMENT

X-ray phase analysis was used to identify 1 : 1 clathrate samples obtained by various techniques. To prevent the escape of the guest, powders in containers were kept under Teflon film. A DRON-4 diffractometer and Ni-filtered CuK_α radiation were used.

For single crystal X-ray studies clathrate crystals with linear dimensions ca. 0.3 mm were placed into boric glass capillaries to avoid losing the guest.

For the [Zn(MePy)$_4$(NCS)$_2$] · 0.67 MePy·xH$_2$O clathrate only cell data at $-100°$C have been obtained. It is trigonal, the cell parameters are: $a = 27.20(1)$, $c = 11.202(4)$ Å, space group $R\bar{3}$, $Z = 9$. We failed to obtain intensity data both

at -50 and $-100°C$: on measuring the unstable crystals broke up. It seems that the compound undergoes a phase transformation at low temperatures. We have repeatedly encountered specimen instability after several hours of data collection, despite various modifications of the conditions of the X-ray experiment, sample preparation etc. $[Zn(MePy)_4(NCS)_2]\cdot MePy$ is tetragonal, with: $a = 16.845(6)$, $c = 23.496(7)$ Å, $V = 6667(4)$ Å^3, space group $I4_1/a$, $Z = 8$, $D_{calc.} = 1.289$ g cm^{-3}, $\mu(CuK_\alpha) = 22.13$ cm^{-1}, $F(000) = 2616.0$ e. Intensity data for 3960 reflections (3462 unique, RINT=0.0611) were measured within 150° 2θ-region on an Enraf-Nonius CAD4 single-crystal diffractometer using graphite-monochromatized CuK_α radiation and $\omega - 2\theta$ scan technique at $-50°C$. Three reference reflections were measured every 100 reflections, and correction was made for intensity of the control reflections. The data for 2425 reflections (with intensities $> 3\sigma I$) were used; they were corrected for Lorentz and polarization effects. The structure was solved using the heavy atom technique (SHELX-86 [8]) and least-squares refinement at anisotropic approximation (SHELX-76 [9]). Absorption was taken into account according to D1FABS [10]. Hydrogen atoms were included in final cycles at calculated positions ($d_{C-H} = 1.08$ Å) as 'riding' on corresponding carbon atoms and with temperature factors fixed to free variables: one for aromatic ring hydrogens and another for hydrogen atoms of the methyl group. The guest molecules were isotropically refined as rigid-body models with a variable site occupation factor, the final s.o.f. being 0.97(1). The final R value was 0.074, $R_w = 0.082$ ($w = 12.5286/(\sigma^2(F) + 0.000441F \times F)$), residual extrema in the final difference map were $+0.79 - 0.70$ e Å^{-3}. The PARST program was used for geometric analysis [11].

3. Results and Discussion

3.1. THE PHASE DIAGRAM

The phase diagram of the MePy–$[Zn(MePy)_2(NCS)_2]$ system is presented in Figure 1.[4] Numerical solubility data are listed in Table I. Two compounds melting incongruently at 62.6 ± 1.5 and $57.0 \pm 1.4°C$ have been discovered in the system. These compounds were synthesized taking into account the conditions of their existence obtained from the diagram. Structural analysis showed that both compounds were the $[Zn(MePy)_4(NCS)_2]$ host clathrates with the MePy as a guest and the host : guest mole ratio = 1 : 0.67 and 1 : 1, respectively. The recording of the thermal curves of the synthesized compounds gave the following number of effects presented in the diagram: one for the 1 : 0.67 clathrate at about 63°C (peritectic melting forming the $[Zn(MePy)_2(NCS)_2]$ solid phase and liquor); two for the 1 : 1 clathrate (the first at about 57°C is the melting with formation of the 1 : 0.67 solid phase and liquor, and the second is the 1 : 0.67 phase melting as described above) (Figures 1 and 2). The 1 : 1 clathrate synthesized by MePy sorption via the gas phase (powder sample) has given the same effects as the 1 : 1 crystal sample.

TABLE I. The composition of a liquor in equilibrium with a solid phase against temperature for the [Zn(MePy)$_2$(NCS)$_2$]–MePy system.

T,°C	−4	0	18	30	48	58	62
wt.-% Zn(SCN)$_2$	0.52	0.68	1.22	2.03	4.83	7.33	9.07

T,°C	68	72	80	100
wt.-% Zn(SCN)$_2$	12.50	13.04	14.54	19.20

Every so often the samples of 30–45 wt.-% Zn(SCN)$_2$ composition showed thermal effects at 53–56°C. These are probably due to some metastable quantities in this composition region 1 : 1 clathrate phase which could be locally formed during the sample preparation. Its conversion into the 1 : 0.67 clathrate phase according to the equation

$$8[Zn(MePy)_4(NCS)_2]\cdot MePy_s + [Zn(MePy)_2(NCS)_2]_s$$

$$\rightleftharpoons 9[Zn(MePy)_4(NCS)_2] \cdot 0.67(MePy)_s$$
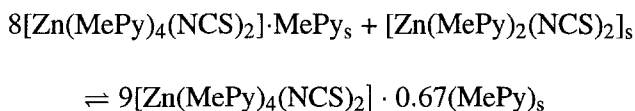
is retarded at room temperature: equilibrium is not attained in a month. The effects can be caused by two processes: acceleration of 1 at elevated temperatures (kinetic process), and metastable peritectic melting of the 1 : 1 clathrate with formation of the [Zn(MePy)$_2$(NCS)$_2$] solid phase and liquor. In any case the effects are not referred to any thermodynamic equilibrium: when the ampoules with the samples were cooled very slowly from 73°C to room temperature the effects decreased considerably or disappeared altogether.

The thermic effect following peritectic melting of the 1 : 1 clathrate, with formation of the 1 : 0.67 phase and a liquor, is small in comparison with the effect corresponding to peritectic melting of the 1 : 0.67 phase to observe it as a separate peak in 10–25 wt.-% Zn(SCN)$_2$ composition region. The thermograms of samples of identical composition prepared from 1 : 1 crystals and MePy, and from the [Zn(MePy)$_2$(NCS)$_2$] phase and MePy were the same (one asymmetric peak with a leading tail and sharp end instead of the expected two peaks, Figure 2, curve 1).

Chemical analysis of the 1 : 0.67 clathrate reveals that its composition corresponds to a crystallochemical one (we neglect the supplementary water-guest content). Therefore the structure seems to be stable only at full cavity occupancy, as in the case of analogous clathrates of Cd [12] and Cu [13] hosts.[5] Moreover, as in the [Cu(MePy)$_2$(NCS)$_2$]–MePy system [7] the host stability field has not been detected (in Figure 1 the composition curve of the host is plotted as short dashes). Thus, the guest stabilizes not only the necessary host framework but also the very existence of the host molecule. In other words a contact stabilization of the host by the guest molecules occurs [2]. It is interesting to note that the temperature of a 1 : 0.67 clathrate decomposition in the Zn system is 19°C less than in the Cu system. Consequently, because it may be assumed that the energy of all nonvalent
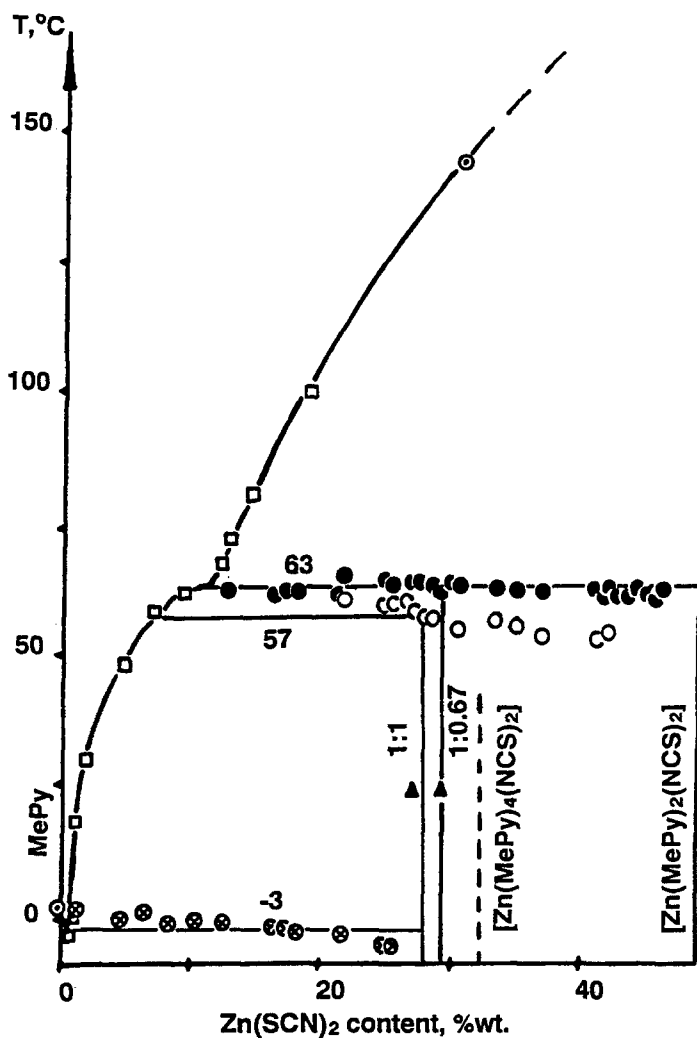
Fig. 1.   The phase diagram of the [Zn(MePy)₂(NCS)₂]–MePy system. The circles stand for DTA (circles for different types refer to different processes), the squares for solubility technique and the triangles for analytical data.
⊗ The eutetic effects MePy$_s$ + liquid phase + 1 : 1; ○ The peritectic effects liquid phase + 1 : 1 + 1 : 0.67; ● The peritectic effects phase + 1 : 0.67 + [Zn(MePy)₂(NCS)₂]; ⊙ The metastable effects (see text); ⊙ Liquidus from DTA data.

interactions in these structures is approximately the same it is necessary to conclude that the Zn host complex molecule is less stable than the Cu host one,[6] with the data being in good agreement with the crystal field theory.

Our earlier investigations of the guest vapour pressure over the 1 : 1 clathrate [6] revealed that it is a phase with constant composition (it does not form solid
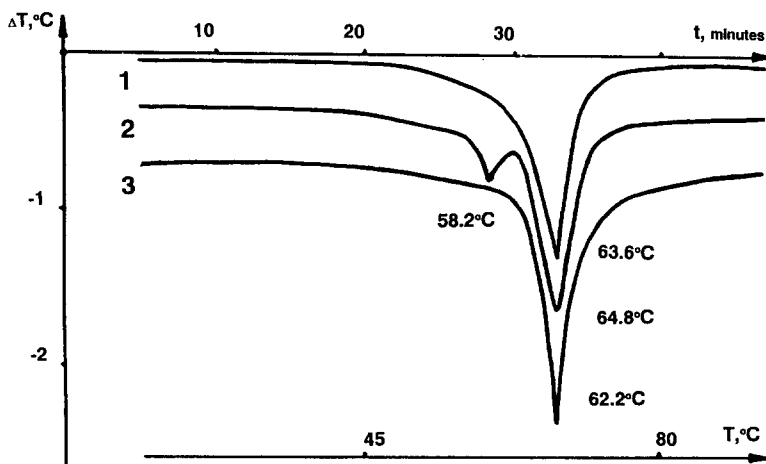
ΔT,°C

10   20   30   t, minutes

1

2

-1   3

58.2°C

63.6°C

64.8°C

-2

62.2°C

45   80   T,°C

Fig. 2.   Differential thermograms for: **1**, mixture of 1 : 1 clathrate crystals and neat MePy liquid (15.1 wt.-% Zn(SCN)₂); **2**, 1 : 1 clathrate crystals (28.1 wt.-% Zn(SCN)₂); **3**, 1 : 0.67 clathrate crystals (29.5 wt.-% Zn(SCN)₂).

solutions as, e.g., β-clathrates of [Ni(MePy)₄(NCS)₂–host [6]) which dissociates into MePy gas and the [Zn(4-MePy)₂(NCS)₂] solid phase. As was mentioned above, the contact stabilization phenomenon has also been observed in the clathrates of the Cu host complex, however among those there was no clathrate with a tetragonal β-framework which for β-[Ni(MePy)₄(NCS)₂] clathrates is known to be perfectly stable even without guest species (as a metastable phase). Consequently it can be concluded that the instability of the β-framework of the Zn host is defined by the instability of the [Zn(MePy)₄(NCS)₂] molecule rather than an unsuitable arrangement of the molecules in the crystal.

3.2. STRUCTURES OF THE COMPOUNDS

The structure of the [Zn(4-MePy)₂(NCS)₂] complex has been recently reported. It is a molecular packing of the complex tetrahedral molecules [16].

Preliminary structural data for the 1 : 0.67 clathrate suggest that it is isostructural with the [M(MePy)₄(NCS)₂] · 0.67 MePy·0.33H₂O compounds, where M = Cu, Mn, Cd [17].

The 1 : 1 clathrate structure consists of individual [Zn(MePy)₄(NCS)₂] host molecules having C_{2v} symmetry, and asymmetric MePy guests. The intermolecular contacts are consistent with a van der Waals type of packing. Fractional atomic coordinates, bond lengths and angles are listed in Tables II–IV.[7] The atom numbering scheme and the ORTEP projection [18] of the host molecule are depicted in Figure 3. The crystallographic twofold symmetry axis runs diagonally between the two MePy groups. The Zn(II) cation has a slightly irregular octahedral coordination

TABLE II. Fractional atomic coordinates ($*10**4$) and B(eq) [$\text{Å}**2$] with e.s.d.s (in parentheses) for non-hydrogen atoms (B(eq)=$4/3\Sigma_i\Sigma_j \beta_{ij} a_i a_j$).

Atom	x/a	y/b	z/c	B(eq)
Host				
Zn	0	2500	3039(1)	3.24(1)
N(1)	−758(2)	3503(2)	3014(2)	3.8(1)
C(1)	−974(2)	4156(3)	3009(2)	3.5(1)
S	−1287(1)	5069(1)	3010(1)	5.31(3)
N(11)	746(2)	3018(2)	3700(2)	3.7(1)
C(11)	882(3)	3792(3)	3750(3)	4.0(1)
C(12)	1348(3)	4111(3)	4189(3)	4.3(1)
C(13)	1670(3)	3623(3)	4593(3)	4.3(1)
C(14)	1525(3)	2815(4)	4532(3)	5.3(1)
C(15)	1072(4)	2547(3)	4090(3)	4.9(1)
C(16)	2160(3)	3941(4)	5080(3)	5.8(1)
N(21)	−712(2)	1916(2)	2369(2)	3.18(9)
C(21)	−364(2)	1533(3)	1947(2)	3.6(1)
C(22)	−776(2)	1164(3)	1507(2)	3.6(1)
C(23)	−1601(3)	1178(3)	1501(2)	3.6(1)
C(24)	−1968(2)	1569(3)	1956(2)	3.7(1)
C(25)	−1517(2)	1931(2)	2372(2)	3.3(1)
C(26)	−2073(3)	808(3)	1031(3)	4.9(1)
Guest				
N(11G)	−3(7)	795(5)	5472(5)	
C(11G)	454(7)	791(5)	5006(5)	
C(12G)	461(7)	179(5)	4621(5)	
C(13G)	−27(7)	−456(5)	4691(5)	
C(14G)	−485(7)	−461(5)	5167(5)	
C(15G)	−452(7)	171(5)	5540(5)	
C(16G)	−68(7)	−1132(5)	4268(5)	

by six nitrogens of four MePy and two *trans*-arranged NCS-ligands. The Zn–NCS distance of 2.12 Å is significantly longer than the 1.92 Å in the [Zn(MePy)$_2$(NCS)$_2$] tetrahedral molecule. The Zn–N(MePy) distances are 2.18 and 2.21 Å for two crystallographically independent ligands, respectively, while the analogous Zn–N bond distances in a number of [ZnA$_2$X$_2$] tetrahedral complexes, where (a) X=Cl, A=4-vinyl-, 4-acetyl-, and 4-cyano-, 4-methylpyridine and unsubstituted pyridine [19, 20]; (b) X=N$_3$, NO$_2$, I, A=pyridine [21–23]; (c) X=NCS, A=4-methylpyridine [16] are within 2.01–2.07 Å. In two [ZnA$_2$(NO$_2$)$_2$] complexes (A=pyridine, 2-methylpyridine) where the Zn(II) cation is six-coordinated [24] the respective Zn–N$_A$ distances, varying within 2.06–2.07 Å, are also significantly shorter, and

TABLE III. Bond distances [Å] with e.s.d.s (in parentheses) (involving non-hydrogen atoms).

Zn – N(1)	2.119(3)	Zn – N(11)	2.181(4)
Zn – N(21)	2.212(4)	N(1) – C(1)	1.159(6)
C(1) – S	1.626(5)	N(11) – C(11)	1.329(6)
N(11) – C(15)	1.330(7)	C(11) – C(12)	1.404(8)
C(12) – C(13)	1.368(8)	C(13) – C(14)	1.389(8)
C(13) – C(16)	1.508(9)	C(14) – C(15)	1.363(9)
N(21) – C(21)	1.322(6)	N(21) – C(25)	1.355(4)
C(21) – C(22)	1.392(6)	C(22) – C(23)	1.390(6)
C(23) – C(24)	1.397(6)	C(23) – C(26)	1.497(7)
C(24) – C(25)	1.383(6)	–	

TABLE IV. Bond angles [deg.] with e.s.d.s in parentheses (involving nonhydrogen atoms).

| N(11) – Zn – N(21)	176.8(1)
N(11) – Zn – N(21)'	91.0(1)
N(1) – Zn – N(21)	90.4(1)
N(1) – Zn – N(11)	92.8(1)
Zn – N(1) – C(1)	161.2(3)
N(1) – C(1) – S	179.2(3)
Zn – N(11) – C(15)	119.4(3)
Zn – N(11) – C(11)	123.7(3)
C(11) – N(11) – C(15)	116.9(4)
N(11) – C(11) – C(12)	122.5(4)
C(11) – C(12) – C(13)	120.0(4)
C(12) – C(13) – C(16)	121.9(5)
C(12) – C(13) – C(14)	116.6(5)
C(14) – C(13) – C(16)	121.5(5)
C(13) – C(14) – C(15)	120.1(6)
N(11) – C(15) – C(14)	123.9(5)
Zn – N(21) – C(25)	122.0(3)
Zn – N(21) – C(21)	120.7(2)
C(21) – N(21) – C(25)	117.3(3)
N(21) – C(21) – C(22)	123.6(3)
C(21) – C(22) – C(23)	119.9(4)
C(22) – C(23) – C(26)	121.9(4)
C(22) – C(23) – C(24)	116.4(4)
C(24) – C(23) – C(26)	121.7(4)
C(23) – C(24) – C(25)	120.3(3)
N(21) – C(25) – C(24)	122.6(3)

Symmetry code: (') $-X, 1/2 - Y, Z$
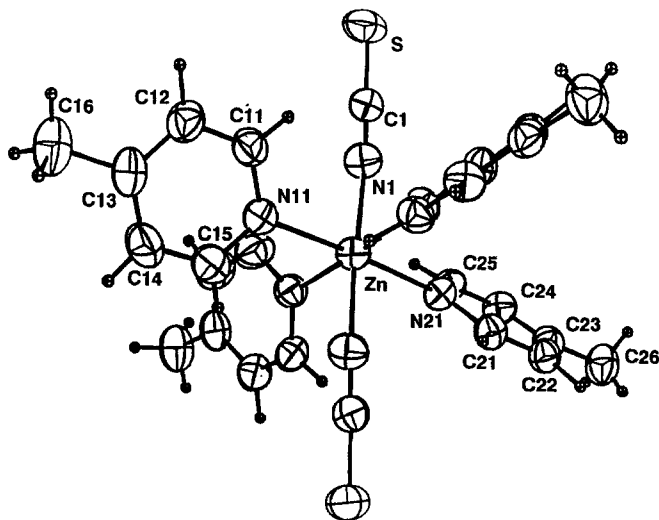
Fig. 3.   The atom numbering scheme and ORTEP plot of the [Zn(MePy)₄(NCS)₂] molecule. Ellipsoids are drawn at the 50% probability level for nonhydrogen atoms.
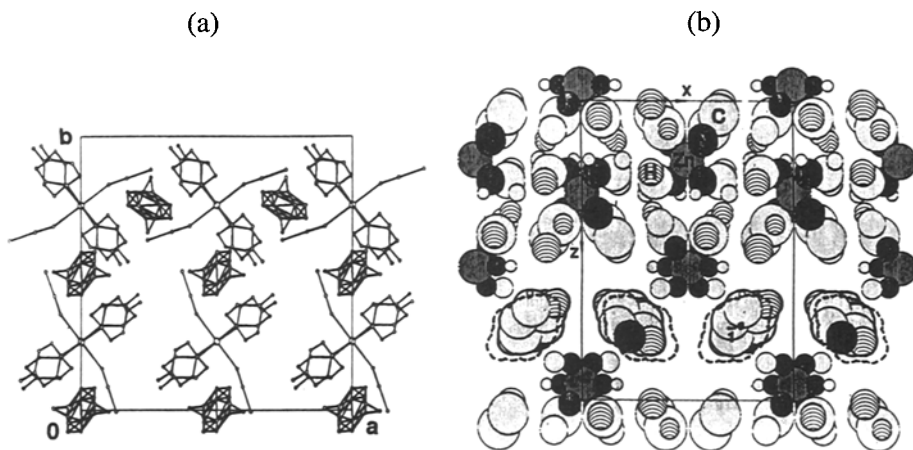
(a)   (b)

Fig. 4.   Projection of the [Zn(MePy)₄(NCS)₂]·MePy structure (one half of the unit cell) on the (001) plane (a). The channel cross-section of the (040) plane for the structure (b); the guest molecules are distinguished by a black contour, and the disordered equivalent positions of the molecules are marked as dashes.

even in the [ZnPy₃(NO₃)₂] complex, where the Zn(II) is seven-coordinated [25] the distances of 2.13 and 2.20 Å are slightly shorter. The reason for such considerable lengthening of the Zn–N bonds in the [Zn(MePy)₄(NCS)₂] complex molecule is due to steric strain in the inner part of the coordination sphere usually observed in such molecules [1]. The MePy ligands rings lie at angles of 44 and 59° from the equatorial plane indicating a propeller conformation of the molecule [26]. The

projection of the structure on the (001) plane is presented in Figure 4. The guest MePy molecules are localized at inversion centres into zigzag channels and are statistically disordered over two orientations as in β-[Ni(MePy)$_4$(NCS)$_2$] · m-xylene [27].

Thus, although we do not observe the host phase in the system the X-ray analysis data show that the [Zn(MePy)$_4$(NCS)$_2$] molecules do exist as chemical species in the clathrate. The existence of the analogous structures with very stable host molecules shows that even such a great difference in chemical properties is less important in comparison with their size, shape, and complementarity.

Acknowledgement

Notes

[1] The precise crystallochemical composition for all the trigonal clathrate structures is 1 : 2/3 : 1/3 (host : main guest : help guest), with the general host : guest mole ratio being 1 : 1.
[2] 10.55% Zn, 70.1% MePy, and 0.63% water were calculated for $x = 0.22$.
[3] The complex [Zn(MePy)$_2$(NCS)$_2$] (rather than Zn(SCN)$_2$) was chosen as a component because it is easily synthesized and nonhydroscopic.
[4] Actually, we consider a part of the Zn(SCN)$_2$·MePy system phase diagram in a limited field of temperature and composition.
[5] Based on this supposition, we depict the straight line for the 1 : 0.67 clathrate on the phase diagram excluding possible existence of solid solutions in this field.
[6] We can make the comparison due to similarity both in crystal structures and in decomposition patterns of the clathrates, and taking into account a little influence of water content on decomposition temperature and other properties of such compounds [14].
[7] The coordinates of hydrogen atoms, torsion angles, thermal parameters and F_o/F_c tables are available upon request.

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