

SOME SYMMETRY ASPECTS OF LAYERED-CLATHRATE STRUCTURES FORMED BY  
 $\text{Ni(NCS)}_2(4\text{-Methylpyridine})_4$

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ABSTRACT. The crystal structures of layered clathrate inclusion compounds of  $\text{Ni(NCS)}_2(4\text{-methylpyridine})_4$  with 1-bromonaphthalene (I) and azulene (II) were analyzed by x-ray single-crystal diffractometry [crystal data: I -  $\text{C}_{46}\text{H}_{42}\text{N}_6\text{S}_2\text{Br}_2\text{Ni}$ ;  $a=11.88(1)$ ,  $b=11.82(1)$ ,  $c=32.79(3)$ ,  $\beta=102.0(1)$ ,  $Z=4$ ,  $P2_1/c$ ; II -  $\text{C}_{46}\text{H}_{44}\text{N}_6\text{S}_2\text{Ni}$ ;  $a=11.51(2)$ ,  $b=11.64(1)$ ,  $c=32.98(2)$ ,  $\beta=103.4$ ,  $Z=4$ ,  $P2_1/n$ ]. Disordering of guest molecules in I is concluded, based on x-ray study, and positions of the guest (each of the two symmetry independent molecules disordered over two orientations) have been refined. In II disorder of guest-azulene is also observed but only one from the two symmetrically independent guest molecules could be located from the x-ray data. The empirical force field calculations were performed for I and II. The results were used for location of the second azulene molecule and for discussion of the disorder mode (short or long-range).

## Introduction

$\text{Ni(NCS)}_2(4\text{-MePy})_4$  is a versatile clathrate-forming host. Its clathrate inclusion compounds usually have rather "open" structures which are of "organic zeolite" or layer type (ref. 1). When studying 1-methylnaphthalene (ref. 2) and, particularly, naphthalene (guest) containing (ref. 3) layered clathrates of  $\text{Ni(NCS)}_2(4\text{-MePy})_4$  some unexpected deviations from guest's molecular geometry were observed. These consist in different geometries of symmetrically independent guest molecules and no reasonable explanation for those differences could be provided, based on routine x-ray structure determination. In order to check whether the effects mentioned above may be due to guest disordering or not, two subsequent crystalline structures of  $\text{Ni(NCS)}_2(4\text{-MePy})_4$  were investigated:

- 1) the clathrate with heavy atom containing 1-bromonaphthalene (I) and isostructural with the  $\text{Ni(NCS)}_2(4\text{-MePy})_4$  inclusion compound containing 1-methylnaphthalene (1-MeN) as the guest, and
  - 2) azulene clathrate (II) of  $\text{Ni(NCS)}_2(4\text{-MePy})_4$ .
- The structures were examined by x-ray single-crystal diffraction.

Moreover, the empirical force field (EFF) calculations of the guest-guest and guest-host interaction energy were performed for different orientations of the guest molecules.

### Materials and Methods

The clathrates I and II were prepared by crystallization of  $\text{Ni}(\text{NCS})_2(4\text{-MePy})_4$  from methanolic solutions containing 1-BrN or azulene at ca. 1M concentration.

Single crystals of I and II were used for x-ray crystal structure determination. Details of the procedures and final tabulated data have been deposited (ref. 4); some data being listed in Table 1.

Table 1. Crystallographic data for 1-BrN and azulene clathrates of  $\text{Ni}(\text{NCS})_2(4\text{-MePy})_4$ .

	I (1BrN)	II(azulene)
a	11.88(1) Å	11.51(2) Å
b	11.82(1)	11.64(1)
c	32.79(3)	32.98(2)
$\beta$	102.0(1) °	103.4(1) °
Z	4	4
space group	$P2_1/c$	$P2_1/n$
guest/host	2 : 1	2 : 1
molar ratio		

For details of the EFF calculations see ref. 5.

### Results and Discussion

The atomic positions of the host  $\text{Ni}(\text{NCS})_2(4\text{-MePy})_4$  molecules were easily found and refined. The molecules adopt a four-blade propeller shape and are asymmetric; the conformations being close to those found in previously studied layered clathrates (ref. 2 and 3); the packing of the molecules in the crystal structures being essentially the same as well. However, determination of positions of the guest molecules presented difficulties. In particular:

- i) though both of the two symmetrically independent 1-BrN molecules could be found in Fourier maps, the subsequent refinement has led to distorted shapes of the molecules (Fig. 1a);
- ii) the electron density maps around the positions expected to be occupied by azulene molecules were rather confusing.

Guest disordering was assumed. In I bromine atoms of another orientation of the 1-BrN molecules could be located from difference electron density maps. Then the guest molecules were given a simplified planar geometry with all C-C distances equal 1.385, C-H 1.08 and C-Br 1.90 Å and the bond angles 120°. When seeing the pictures in Fig. 1 it seems clear that the bromine atoms of the less populated orientation are close to those parts of the guest molecules which were apparently the

most distorted from expected geometry as resulted from the x-ray refinement in which one only orientation was assumed for each of the two 1-BrN molecules. Since 1-BrN and 1-MeN molecules are almost identical in shape and size, we assume that some apparently significant differences in the molecular structure between two independent 1-MeN molecules, which have been observed in previous studies (ref. 2), are due to a disorder, possibly of the type illustrated in Fig. 1b.

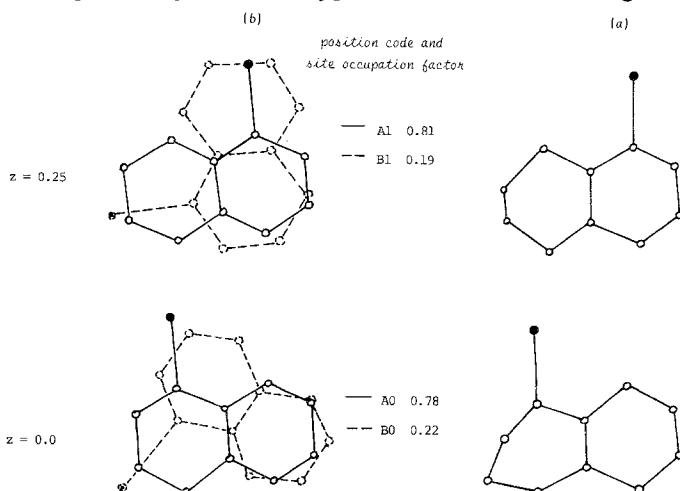


Fig. 1. The two symmetry independent guest 1-BrN molecules as: (a) refined without any assumption of disorder, and (b) refined as rigid bodies assuming two possible orientations for each molecule.

The non-bonded energy calculations (by EFF) are in rather good agreement with the model given in Fig. 1b. As may be seen in Table 2, there are at least two non-equivalent energy minima for each of the two 1-BrN molecules. The positions and orientations corresponding to the energy minima do not differ more than 0.06 Å (displacement) and 7° (rotation around the long axis of the molecule) from those derived from refinement of the x-ray model.

Table 2. Calculated energy (in kcal/mole) of non-bonded interactions for optimized orientations of the 1-BrN molecules in I. (CG stands for central guest molecule within a layer and NG for neighbouring guests' orientation; A0, B0, A1 and B1 refer to orientations given in Fig. 1).

		z = 0			z = 0.25		
	CG	A0	B0	C	NG	A1	B1
NG	A0	-27.8	-26.1		A1	-29.0	-24.7
	B0		-26.0		B1		-27.6
	C			-27.5			

The energy calculations are of interest not only because this is a way of finding "trial" structure models. In this study it is believed these may also suggest a type of disordering. E.g., if within the layer at  $z = 0.25$  short-range disorder is assumed then 1-BrN molecules in less populated orientations have neighbouring guest molecules in more probable orientations (Fig. 2). Guest-guest interaction energy is significantly higher for such an arrangement (Table 2). It suggests that, perhaps, at a time the layer has an ordered arrangement of the guest molecules with, possibly, orientations A1 or B1 in different, symmetrically related layers or, two-dimensional "domains" of the guest within the layers. The guest 1-BrN molecules at  $z = 0$ , in less occupied orientation have practically the same interaction energy with the neighbours, irrespective whether they have orientation A0 or B0.

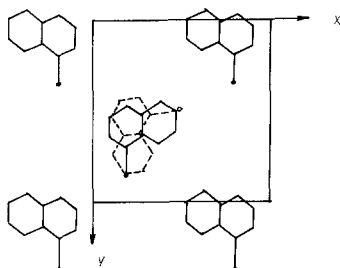


Fig. 2. The layer of guest 1-BrN molecules in I at  $z = 0.25$ . By dotted lines the less populated orientation of the "central" guest molecule is indicated.

Surprisingly enough, at  $z = 0$  there is an orientation (C in Table 2) of the 1-BrN molecule which has been found through energy calculations but not found in the x-ray structure. This orientation is, with respect to the most populated within the layer, similar to that found within the layer at  $z = 0.25$  (like B1 with respect to A1). It remains obscure why this orientation seems unpopulated.

#### Azulene clathrate

At the beginning of this study it was hoped the structure of the azulene clathrate might be isostructural with the naphthalene inclusion compound (ref. 3) and that the guest, of lower symmetry than naphthalene, will enable a detection of possible disordering of the guest. However, both structures have different symmetry (C2/c naphthalene and  $P2_1/n$  azulene compound). Nevertheless, the packing is very similar and, perhaps, some qualitative conclusions drawn for azulene compound may be extended to the naphthalene one.

In II only one of the two symmetrically independent azulene molecules could be located (at  $z = 0$ ), though disordered, from the x-ray analysis. Possible positions and orientations of azulene at  $z = 0.25$  could only be derived from EFF calculations of the non-bonded interaction energy. As listed in Table 3, three almost equivalent orientations have been found. When input to the x-ray model they might be

refined (as rigid bodies) and the site occupation factors obtained (0.39, 0.31 and 0.31) are in satisfying agreement with the approximate equivalency (in energy) of the orientations.

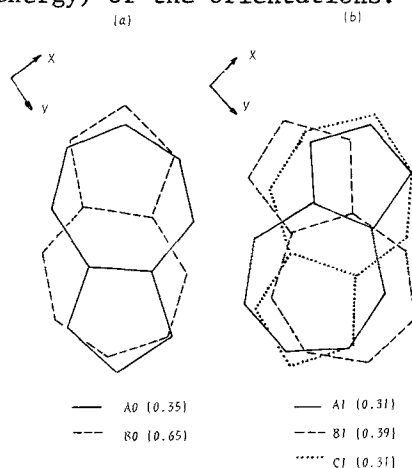


Fig. 3. Orientations of azulene molecules in II in layers at:  
 (a)  $z = 0.0$  and  
 (b)  $z = 0.25$   
 Site occupation factors derived from x-ray structure refinement are quoted in parentheses.

There is a complicated pattern of possible co-existency, within the layers, of guest molecules in different orientations (Table 3). It seems that "mixing" of B1 with A1 or C1 is less probable than other combinations.

Table 3. Calculated energy (kcal/mole) of non-bonded interactions for optimized orientations of azulene molecules in II (orientation codes as in Fig. 3, CG stands for "central" guest molecule in energy calculations while NG denote orientation of the neighbouring guests).

	$z = 0$		$z = 0.25$			
CG	AO	BO	NG	A1	B1	C1
NG			NG			
AO	-22.8	-22.8	A1	-22.5	-20.9	-22.6
BO		-23.2	B1	-21.4	-22.8	-21.8
			C1	-22.7	-22.0	-22.7

### Conclusions

Calculations of energy of the guest-lattice non-bonded interactions have been successfully used as a supplementary aid in solving layered Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub> crystal structures containing orientationally disordered guest molecules (1-bromonaphthalene, azulene). The results of the calculations suggest, in some cases, rather

complicated pattern of guest disordering. In particular, two-dimensional ordered arrangement of the guest as "domains" within a layer seems possible for one of the two independent layers in I whereas short-range disorder may be assumed in the other layer. Moreover it may hardly be excluded that in I there are ordered layers of the guest and symmetrically related layers have orientations of the guest non-correlated to each other. The two possibilities mentioned above correspond to different symmetries of the clathrate. However, routine x-ray data were not sufficient for more discerning examination of this problem.

#### Acknowledgements

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#### References

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- 2) J. Lipkowski, P. Sgarabotto and G.D. Andreetti - Acta Crystallogr. B38(1982),416
- 3) J. Lipkowski - Acta Crystallogr. B38(1982),1745
- 4) The Cambridge Crystallographic Database - Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB 2 1 EW, England
- 5) The EFF calculations were done by using the four-parameter equation:

$$U = \sum_{i,j} (a_{ij} \exp(-b_{ij} r_{ij}) / r_{ij}^d - c_{ij} / r_{ij}^6)$$

where U stands for energy,  $r_{ij}$  denotes distance between the atoms i and j, a, b, c and d are empirical parameters of interaction potentials (between i and j).

The energy calculations were performed for variable position and orientation of the guest molecules. The host molecules were assumed in the positions derived from the x-ray structure analyses. Their positions and conformation were kept constant while position and orientation of rigid guest molecules were varied until an energy minimum was attained.

The EENY program (Sam Motherwell, University Chemical Laboratory, Lensfield Road, Cambridge CB1 2EW) was used. The values for a, b, c and d were taken from Giglio (Nature 222,339(1969)).