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Short Communication

The Influence of the Guest Polarity on the Clathrate Structure Formed by the Werner Complex

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The formation of several types of Werner clathrates has been reported for systems of [Ni(4-MePy)$_4$(NCS)$_2$] and substituted benzene derivatives (4-MePy–4-methylpyridine) [1]. Tetrahedral clathrates (so-called β-phases with a 1 : 1 host : guest stoichiometry) are the most general ones, while formation of trigonal clathrates (1 : 0.67 host : guest ratio) was reported only for the o-, m-, and p-nitrotoluene (powder diffraction data), and m-bromonitrobenzene guest molecules [1, 2]. This fact may be easily explained in the case of the o- and m-isomers of the guest because formation of the β-clathrates with *ortho*- and *meta*-substituted benzene derivatives is extremely unfavorable (in these clathrates the channel width is most favorable for location of the *para*-substituted benzene derivatives) [1]. As discussed in [3], the volume of the NO_2 group in p-nitrotoluene allows inclusion of this molecule into the β-clathrates, and formation of this type of clathrate could be expected for this guest. To clarify this problem further we have studied the single crystal structure of the [Ni(4-MePy)$_4$(NCS)$_2$] host with the p-nitrotoluene guest molecule. The product, however, appears to be a typical trigonal Werner clathrate ($R\bar{3}$ space group) [4, 5]; the parameters of the unit cell (a = 27.650 Å, c = 11.165 Å) are in good agreement with parameters determined in [2]. Formation of the metastable octahedral crystals (β-phase, as determined by X-ray diffraction) was observed during the initial stages of crystallization. In our opinion, the most probable explanation of the formation of the trigonal clathrate with the p-nitrotoluene guest molecule is the energetically favorable coupling of the dipoles of the guest molecules in this type of clathrate (Figure 1a). In the case of β-clathrates,

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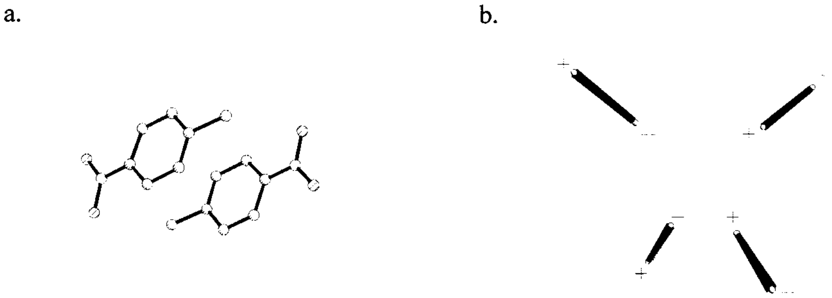

Figure 1. (a) Experimentaliy determined arrangement of the *p*-nitrotoluene guest molecules in the cavity of the trigonal clathrate. Dipoles of the *p*-nitrotoluene molecules are coupled. (b) Schematic representation of the arrangement of the polar *para*-substituted benzene guest molecules in the channels of the β-[Ni(4-MePy)$_4$(NCS)$_2$] clathrate phase. Accommodation of this type of guest molecules about the $\bar{4}$ symmetry positions causes unfavorable orientation of the guest molecule dipoles.

Table I. Compositions of the β-[Ni(4-MePy)$_4$(NCS)$_2$]·x(toluene)·y(4-MePy) ($x + y = 1$) clathrates and mother solutions in equilibrium at room temperature

β-[Ni(4-MePy)$_4$(NCS)$_2$]·x(toluene)·y(4-MePy)		Mother solution (mol. %)		
x (by difference)	y	Toluene (by difference)	4-MePy	Host
0.63	0.37 ± 0.01	43.6	56.3 ± 0.1	0.1
0.50	0.50 ± 0.01	21.5	78.3 ± 0.2	0.2

dipoles of the guest molecules are situated in less energetically favorable positions (Figure 1b). This conclusion may be confirmed too by our data concerning the compositions of the β-[Ni(4-MePy)$_4$(NCS)$_2$] clathrates with mixed toluene + 4-methylpyridine guest and their mother solutions (see Table I, clathrate phase enriches with the non-polar guest component). The data presented in this communication show that the polarity of the guest molecule can modify the processes of clathrate formation in systems containing the [Ni(4-MePy)$_4$(NCS)$_2$] host molecule. This fact should be taken into account when considering the separation processes with the β-[Ni(4-MePy)$_4$(NCS)$_2$] sorbent.

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