



## EXPLORING THE PHOTOREDOX KINETICS AND MECHANISM OF METHYLENE BLUE AND P-PHENYLENEDIAMINE SYSTEMS

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### Abstract

Structural transformations within the hexagonal clathrate lattices of  $\text{Ni}(\text{NCS})_2(4\text{-methylpyridine})_4$  incorporating benzene derivatives were examined and analyzed under varying temperature conditions. The findings demonstrated that the type of guest molecule significantly affects these transformations. Three guest compounds—ortho-bromonitrobenzene, meta-bromonitrobenzene, and meta-dinitrobenzene—were studied. While the clathrates maintained a hexagonal structure at room temperature, distinct structural alterations emerged at lower temperatures, resulting from the stepwise ordering of guest molecules. Furthermore, the structural distortions associated with the 1-bromonaphthalene guest molecule were investigated and correlated with its orientational disorder across different temperature ranges.



## 1. INTRODUCTION

Inclusion compounds formed by the title complexes are known in the literature mostly under the name Werner clathrates [1]. However, just from the beginning, it was clear that their crystal structures were relatively open, and as a consequence, Allison and Barrer introduced the name 'organic zeolites' [2]. There is, however, a significant variety of structure types. The most studied are organic zeolites due to their valuable practical uses in mixture separations, including liquid chromatography methods [1]. Isotopomer fractionation performed by Smith et al. [3] has been the subject of physicochemical studies as well [1]. Relatively less studied are clathrate-type compounds of the 0.67:1 guest-to-host stoichiometry. This structure type has been found for a series of  $\text{MX}_2\text{A}_4$  host complexes of nickel, cobalt, copper, cadmium, and mercury [1]. The compounds have trigonal-type symmetry, and the guest species are in cavities interconnected to form a linear arrangement parallel to the hexagonal c-axis. The spaces between the cavities are available for small, additional guests, and water molecules play an

interesting role there [4,5]. Exciting order-disorder phenomena are observed in these compounds, and novel experimental data and structural interpretations are presented here. It is aimed at making the characteristics of the compounds more complete and more transparent. The second part of the paper is concentrated on the possible wrong determination of the guest molecular structure. This part is based on novel X-ray data of partially disordered (guest) structures and their dependence upon temperature.

## 2. MATERIALS AND METHODS

The reagents, equipment, and experimental procedures were identical to those described previously [6,7]. The crystal specimens were placed in Lindeman's glass capillaries and fixed inside with the use of a glass fiber. Data collections were performed starting at room temperature, cooled to low temperatures, and finally heated up to the highest temperatures, viz, at 100, 150, 270, and 300 K for ortho-Bromonitrobenzene clathrate and 100, 200, 300, and



335 K for the *meta*-Bromo nitrobenzene clathrate. *meta*-Dinitrobenzene clathrate was examined at two temperatures: 100 and 373 K. The final refinement of the structures was done using the ShelXle graphical user interface [8].

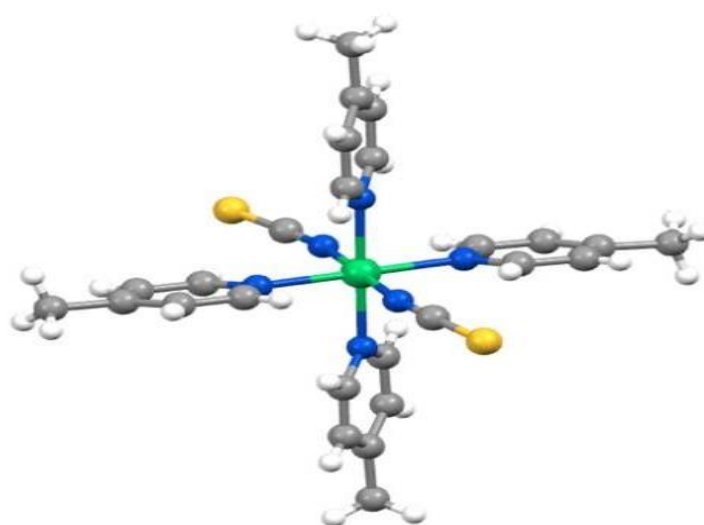
### 3. RESULTS AND DISCUSSION

The 0.67:1 structure at temperatures above a certain threshold (cf. below) is rhombohedral with lattice parameters listed below (Table. 1).

**Table 1: Unit cell parameters of the clathrates of some benzene derivatives as a function of temperature (in K). If two options are listed, the underlined one is used in structure determination.**

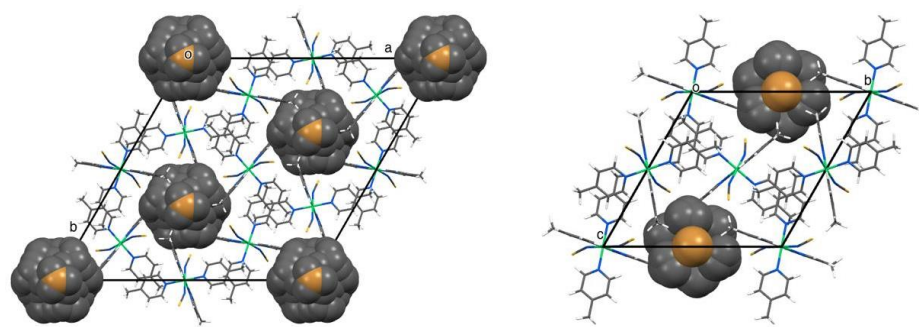
Guest	<i>a</i>	<i>b</i>	<i>c</i>	$\alpha$	$\beta$	$\gamma$	Cell volume	Rint
<i>meta</i> -bromonitrobenzene ( <i>m</i> -BNB)								
<i>m</i> -BNB 100	10.981	31.718	31.815	118.66	95.91	97.11	9479.5	
<i>m</i> -BNB 200	54.996	55.081	11.007	89.50	90.12	119.77	28941.5	0.12
	11.007	32.046	31.974	118.42	96.95	96.72	9647.2	
<i>m</i> -BNB 300	55.558	55.558	11.068	90	90	120	29588.3	
	11.068	32.287	32.289	118.71	96.56	96.56	9862.8	
<i>m</i> -BNB 335	27.808	27.808	11.081	90	90	120	7421.4	0.04
	11.081	16.453	16.471	114.87	102.98	102.86	2478.1	
<i>ortho</i> -bromonitrobenzene ( <i>o</i> -BNB)								
<i>o</i> -BNB 100	11.146	15.505	16.365	114.35	103.35	101.53	2364.0	
<i>o</i> -BNB 150	11.156	15.587	16.439	114.33	103.40	101.42	2390.9	
<i>o</i> -BNB 270	11.170	15.940	16.598	114.29	104.39	101.72	2448.1	
<i>o</i> -BNB 300	27.661	27.661	11.167	90	90	120	7399.9	0.027
	11.167		16.398	16.398	115.00	103.12	103.12	2466.6
<i>m</i> -DNB 100	54.883	54.883	10.978	90	90	120	28637	
<i>m</i> -DNB 373	55.818	55.818	11.102	90	90	120	29955.7	
<i>meta</i> -dinitrobenzene ( <i>m</i> -DNB)								

The host molecular structure Ni (NCS)<sub>2</sub>(4-methylpyridine)<sub>4</sub> is centrosymmetric (Fig. 1) [1].



**Figure 1: The molecular structure of the host Ni (NCS)<sub>2</sub>(4-methylpyridine)<sub>4</sub> complex.**

The cavities available for guest species are highly symmetric, and the guest molecules are thus orientationally disordered, as illustrated in Fig. (2).



(a)

(b)

Figure 2: (a) Packing diagram of the high-temperature phase of the clathrate of *m*-BNB (at 335 K). Guest species are heavily disordered and are shown in the picture as a superposition of all possible orientations; (b) analogous situation observed for the *o*-BNB (at 300 K). [characters a, b and c on the drawings serve to identify axial directions x, y and z, respectively]

Guest molecules show orientational disorder in all studied structures with bromonitrobenzenes. The disorder increases with increasing temperature, and at temperatures above room temperature, a reasonable model for the guest molecule is not possible. The  $F_o-F_c$  differential electron density maps clearly show this feature for the series of crystal structures with *ortho*-bromonitrobenzene (Fig. 3).

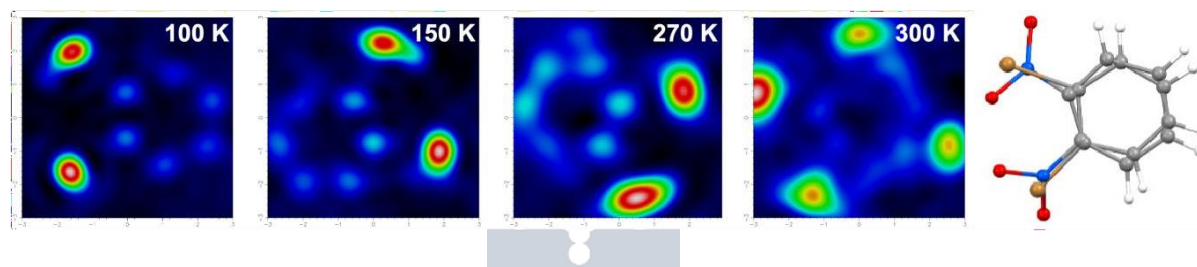
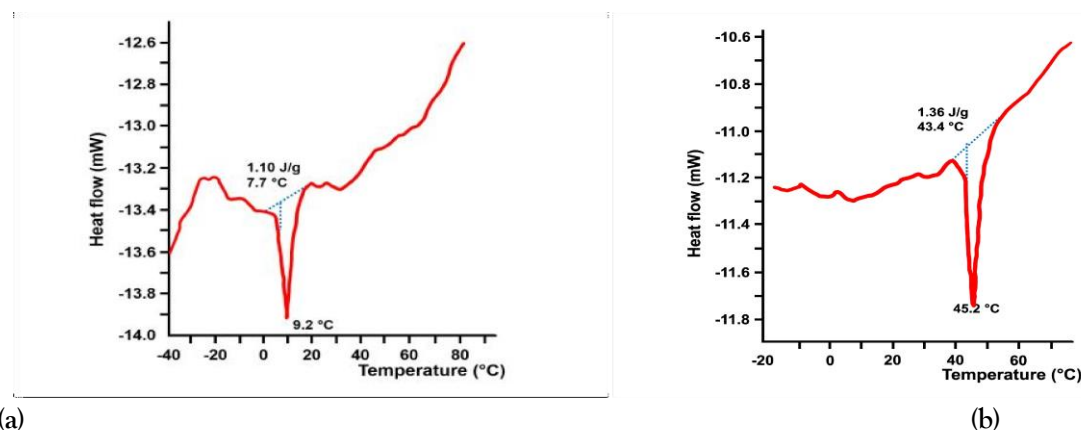


Figure 3:  $F_o-F_c$  Fourier maps for the *ortho*-bromonitrobenzene guest molecule at various temperatures and the resolved disorder model for *ortho*-bromonitrobenzene guest molecules for the data collected at 100 K.

This is the starting point for guest ordering at lower temperatures. The DSC curves measured for two isomeric, *meta*- and *ortho*-bromonitrobenzenes, show distinct transitions at temperatures of 9.2 and 43.4°C for *o*-BNB and *m*-BNB, respectively (Fig. 4a and 4b).



(a)

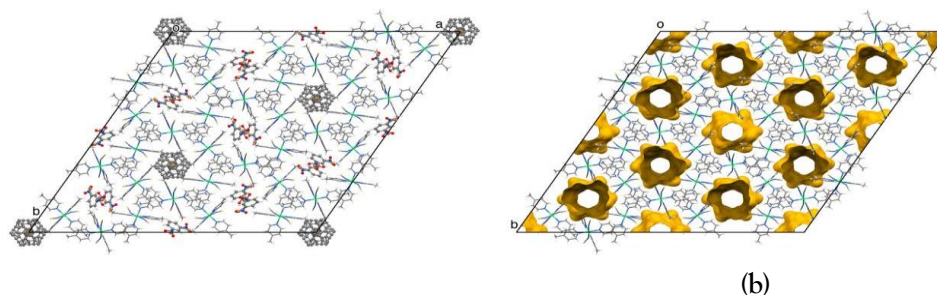
(b)

Figure 4: DSC curves of *meta*- and *ortho*-bromonitrobenzene clathrates near room temperature. (DuPont scanning calorimeter was used).



However, the situation after the transition is not simple, and it is different for different guest molecules. In the case of *m*-BNB clathrate cooling below 43.4°C is associated with a transition from the hexagonal cell, approximately 27.5 x 27.5 x 11 Å, to a quadruple one, approximately 55 x 55 x 11 Å (accurate data are

listed in Table 1). Overall, crystal symmetry is preserved, but just part of the cavities occupied by guest molecules maintain their axial symmetry. The situation is illustrated in Figure (5a and 5b)

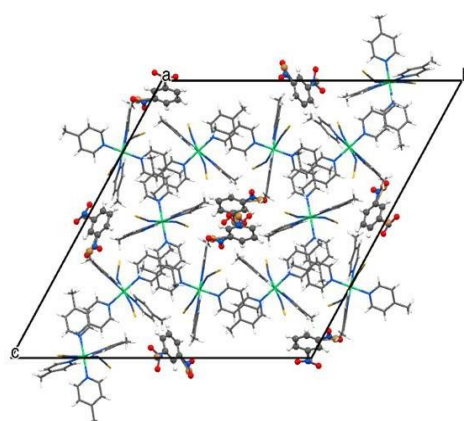


**Figure 5.** The structure of the intermediate phase of the *m*-BNB clathrate at 300 K (a) Packing of molecules in the unit cell: ). [characters a, b and c on the drawings serve to identify axial directions x, y and z, respectively]

The guest species occupy highly symmetric cavities (at 1/3, 2/3, and 2/3, 1/3), and the asymmetric ones in which just a tiny part of the guest molecules is orientationally disordered; (b) packing of the host component only in which shapes of the cavities are clearly visible. In other words, the transition consists of the partial ordering of a significant part of the guest molecules.

Further cooling, down to 100 K, is subdivided

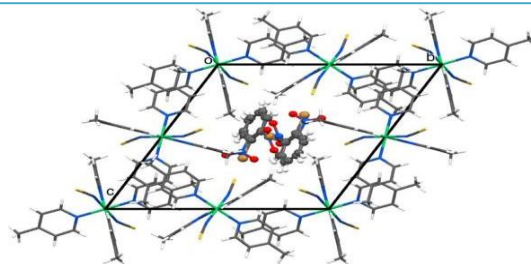
into two stages: first, the structure is no longer rhombohedral. It transforms into triclinic (200 K), maintaining the unit cell parameters close to rhombohedral (we use hexagonal settings all over our work) in the sense of structural transitions. This stage is followed by smooth contraction (down to 100 K) of the unit cell without any further transformations in the sense of crystal symmetry (Fig. 6).



**Figure 6:** The low-temperature phase of *m*-BNB clathrate. The structure is triclinic, with guest molecules ordered (almost).

The case of *ortho*-bromonitrobenzene clathrate is different. Above its transition temperature, it is analogous to *m*-BNB forming the 27 x 27 x 11 Å rhombohedral structure (Fig. 5), but below 280 K, it readily transforms to triclinic phases (Fig.7).





**Figure 7:** In the low-temperature phase of o-BNB clathrate, the two orientations of the disordered guest molecules are visible. ). [characters a, b and c on the drawings serve to identify axial directions x, y and z, respectively]

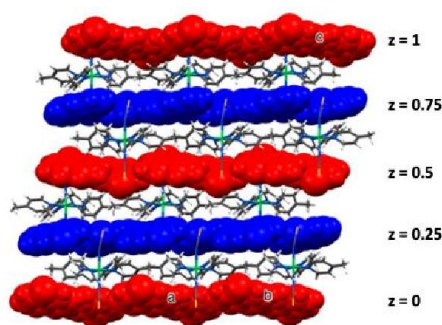
In contrast to it, the dinitrobenzene clathrate forms the quadruple unit cell  $55 \times 55 \times 11 \text{ \AA}$ , both at high and low temperatures. More detailed material for all structures (CIF files) is enclosed, and more information may also be available from the Author (JL) upon request.

The main features of guest ordering in the structures discussed are as follows: (Fig. 6 & 7) (packing diagram) (schemes of guest positions). It is worth noting that guest molecules in triclinic phases (low-temperature modifications) are not completely ordered orientationally. However, the disordering is small (the occupancy factors are close to unity, and the fraction of a second component is becoming lower at the lowest temperatures).

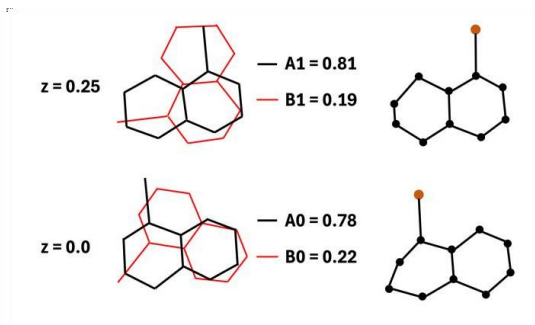
Based on the facts quoted above, it is interesting to note the significant influence of guests present

in the structure on the host's behavior at changing temperatures. Perhaps the most intriguing is the long-distance order/disorder phenomenon when transforming the host structure from 'small' to 'large' unit cells.

Another example of guest disordering and its influence on structural investigation, which we would like to highlight now, is the case of layered clathrates. In a classical report on the structure of 1-methylnaphthalene clathrate, some significant differences between the two guest (1-MeN) molecules not related by crystal symmetry have been observed [7]. A later paper, based on isomorphous replacement of 1-MeN by 1-BrN, explained the differences [8]. Partial orientational guest disordering was found to be the reason for the apparent 'deformation' of the guest molecule, as quoted from the reference in Figures (8a and b)



(a)



(b)

**Figure 8:** (a) Packing diagram of 1-bromonaphthalene molecules in layered clathrate; (b) superposition of two molecular orientations is shown for the two guest molecules (at different layers) and the experimentally determined 'molecular structures' if no guest disordering is considered.

**Comment:** In the early crystallographic studies of inclusion complexes, an idea was put forward that clathrates may serve as a convenient means to study molecular structures of highly volatile or unstable compounds. Later experience did not

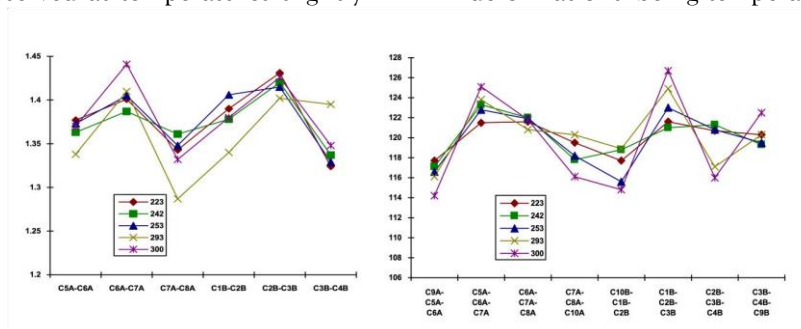
support such an idea. In a couple of illustrations that we report here, based on independent X-ray studies, one may find convincing arguments against the concept mentioned above.

As a kind of crystallographic curiosity, the



illustration presents a fake discovery of the temperature dependence of guest molecular structure. We emphasize the apparent nature of the observations, which may conveniently be interpreted as the result of guest order/disorder behavior, which is temperature dependent. Please note that significant geometry differences are determined at temperatures that are not significantly different. The ‘differences’ between bond distances observed at temperatures slightly

different (223 to 300 K) amount to as much as a few tenths of an Angstrom, and differences in bond angles are in some cases equal to a few degrees. From Figure (9), one may easily deduce guest orientational disordering as the real reason for the observed pseudo-deformation of the 1-bromonaphthalene molecule. Relative population of the orientations is, and it should be, temperature dependent, thus leading to ‘deformations’ being temperature dependent.



**Figure 9:** Apparent temperature dependence of selected bond distances and angles in 1-bromonaphthalene guest molecule in its Ni(NCS)<sub>2</sub>(4-methylpyridine)<sub>4</sub> clathrate.

This is what has been observed. However, a comment is due since ‘deformations’ in everyday situations may not be clearly visible. In the case presented above, molecular structure effects were initially observed in methylnaphthalene, but no clear interpretation was possible at the time. The isomorphous replacement of methylnaphthalene with bromonaphthalene provided a convenient basis for reasonable interpretations, as explained above.

## CONCLUSION

The X-ray studies reported in this paper provide two major conclusions:

- i) The non-bonding interactions between guest and host in inclusion compounds may exert a significant influence on the stability of different host packing modes. The structures presented above demonstrate interesting host structural transformations occurring as a result of guest interaction. This part may be temperature-dependent and may lead to the host’s transitions when the temperature varies.
- ii) Guest disordering may lead to misinterpretations of X-ray structure determinations, as illustrated by the example of a layered clathrate with 1-BrN guest species.

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