ON THE CLATHRATOGENTIC PROPERTIES OF THE
Ni(NCS)$_2$(4-Vinylpyridine)$_4$ HOST

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ABSTRACT. The crystal structure of the non-clathrated
$\alpha$-Ni(NCS)$_2$(4-Vinylpyridine)$_4$ complex was solved and refined
to $R=0.056$ (crystal data: $a=11.27(3)$, $b=16.86(1)$, $c=32.06(1)$
$Z=8$, $V=6092 \text{\AA}^3$; Pbca; $d = 1.30 \text{ g.cm}^{-3}$). The complex molecule
adopts an asymmetric, windmill conformation of the four
pyridine ligands. The $\alpha$-phase was used as a solid substrate
for clathration of liquid o-, m- and p-xylene, at 25°C. The
composition of the products, the enthalpies of clathration
and kinetic course of the processes were investigated. The
clathration enthalpies, per mole of the host, are equal
17.07, 14.1 and 21.77 kJ and correspond to the 1.05, 1.11
and 1.30 guest/host molar ratios for, respectively, ortho,
meta and para-xylene. The clathration rates follow the
order para$>$ortho$>$meta. The results are discussed from the
structural point of view.

Introduction

It is rather commonly agreed that clathratogenic ability of
a given MX$_2$A$_4$ host complex depends on its molecular structu­
re and, in particular, on the ammine ligand (A) coordinated
to M (see, e.g., ref. 1). Little is known, however, on the
crystal structures of the compounds and on the structure
clathratogenic ability relationship (except perhaps the
Ni(NCS)$_2$(4-Methylpyridine)$_4$ complex and its clathrates (ref.
2)). The aim of this study is to provide experimental data
on the structure and clathratogenic ability of the title
compound.

Materials and Methods

Ni(NCS)$_2$(4-Vinylpyridine)$_4$ was prepared by crystallization
from ethanolic solution.
The procedure was as follows:
i) a 0.1 M solution of commercial Ni(NCS)$_2$ in EtOH was prepared at temperature ca. 50°C,
ii) 4-Vinylpyridine was added to the hot solution up to its calculated concentration ca. 0.6 M,
iii) the solution was filtered and allowed to cool slowly down to room temperature.
Fine needle shaped blue crystals were obtained. These are stable in open air for at least 1 week and might be conveniently used for x-ray single-crystal study, from which it is clear (see below) the crystallization product is the non-clathrated, α-phase of the Ni(NCS)$_2$(4-ViPy)$_4$ complex.

The α-phase crystals were used for clathration of o-, m- and p-xylene. The following procedure was used:
i) saturated solutions of Ni(NCS)$_2$(4-ViPy)$_4$ in xylenes were prepared by stirring at 25 ± 0.1°C for two days,
ii) samples of the crystals were placed in respective solutions of Ni(NCS)$_2$(4-ViPy)$_4$ in o-, m- or p-xylene at 25°C and the heat evolved on clathration was measured calorimetrically (for more detailed description see ref. 3; the procedures used being the same in both studies),
iii) the α-phase crystals were powdered in an agate-mortar before using them for x-ray powder experiments. The samples were then wetted with solutions of Ni(NCS)$_2$(4-ViPy)$_4$ in xylene isomers and the x-ray powder spectra were recorded at time intervals,
iv) the products of the reaction α-Ni(NCS)$_2$(4-ViPy)$_4$ + xylene were analyzed by thermogravimetry,
v) lattice parameters of the clathrate products were derived from x-ray powder diffraction spectra and refined by least squares. Indexing of the diffraction patterns was based on the single-crystal data reported for the β-Co(NCS)$_2$(4-ViPy)$_4$ structure (ref. 4).

The single-crystal study of the α-Ni(NCS)$_2$(4-ViPy)$_4$ structure was performed by using a Siemens AED automated three-circle diffractometer (filtered MoKα). 5029 independent reflections were measured within 27° of θ by using the ω - 2θ scan mode, but as little as 950 reflections having I > 2σ(I) have been used for structure analysis. The intensities were corrected for Lorentz-polarization effects but not for absorption. The structure was solved by direct methods, SHELX was used (ref. 5). Full-matrix refinement was made but, in view of low data/parameters ratio, only Ni, thiocyanates and pyridine N atoms were given anisotropic temperature factors. H atoms were included in the refinement at calculated positions. The final R value is 0.056; the weighted R$_w$ = 0.046 ($w = 1.7/(σ^2(F) + 0.0002(F)^2$).