# ON THE CLATHRATOGENIC PROPERTIES OF THE $Ni(NCS)_2(4\text{-Vinylpyridine})_4$ HOST

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ABSTRACT. The crystal structure of the non-clathrated $\alpha$-$Ni(NCS)_2(4\text{-Vinylpyridine})_4$ 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 $Å^3$; Pbca; $d_x$=1.30 $g.cm^{-3}$). 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 to 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 $MX_2A_4$ host complex depends on its molecular structure 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 $Ni(NCS)_2(4\text{-Methylpyridine})_4$ 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

$Ni(NCS)_2(4\text{-Vinylpyridine})_4$ was prepared by crystallization from ethanolic solution.

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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 needdle 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 $Ni(NCS)_2(4\text{-}ViPy)_4$ complex.

The α-phase crystals were used for clathration of o-, m- and p-xylene. The following procedure was used:
i) saturated solutions of $Ni(NCS)_2(4\text{-}ViPy)_4$ in xylenes were prepared by stirring at $25 \pm 0.1$°C for two days,
ii) samples of the crystals were placed in respective solutions of $Ni(NCS)_2(4\text{-}ViPy)_4$ 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 beeing the same in both studies),
iii) the α-phase crystals were powdered in an agat-mortar before using them for x-ray powder experiments. The samples were then wetted with solutions of $Ni(NCS)_2(4\text{-}ViPy)_4$ in xylene isomers and the x-ray powder spectra were recorded at time intervals,
iv) the products of the reaction α-$Ni(NCS)_2(4\text{-}ViPy)_4$ + 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-$Co(NCS)_2(4\text{-}ViPy)_4$ structure (ref. 4).

The single-crystal study of the α-$Ni(NCS)_2(4\text{-}ViPy)_4$ 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 $\omega - 2\theta$ scan mode, but as little as 950 reflections having $I \geqslant 2\sigma(I)$ 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 $R_w = 0.046$ ($w = 1.7/(\sigma^2(F) + 0.0002(F)^2)$).

Table 1. Fractional atomic coordinates ($\times10^4$) for non-hydrogen atoms (with standard deviations in parentheses) and isotropic thermal parameters ($\times10^3$)

| | x | y | z | U(iso) |
|---|---|---|---|---|
| Ni | 707(1) | -601(1) | 3665(1) | 62 |
| N(1) | 37(12) | 408(7) | 3909(4) | 67 |
| C(1) | -479(17) | 977(10) | 3981(5) | 75 |
| S(1) | -119(4) | 1784(3) | 4087(2) | 136 |
| N(2) | 1392(12) | -1616(7) | 3449(4) | 77 |
| C(2) | 1654(14) | -2211(9) | 3299(5) | 57 |
| S(2) | 2043(4) | -3049(2) | 3087(1) | 72 |
| N(3) | 2354(10) | -347(7) | 3930(3) | 78 |
| C(3) | 3006(16) | -933(11) | 4088(5) | 94(6) |
| C(4) | 4133(16) | -766(10) | 4274(4) | 101(6) |
| C(5) | 4604(15) | -20(10) | 4266(5) | 95(5) |
| C(6) | 3922(14) | 559(12) | 4071(4) | 96(5) |
| C(7) | 2831(15) | 371(11) | 3914(4) | 82(5) |
| C(8) | 5851(20) | 269(13) | 4427(5) | 138(7) |
| C(9) | 6441(24) | -201(14) | 4614(6) | 176(9) |
| N(4) | 165(9) | -1207(6) | 4209(3) | 62 |
| C(10) | -492(12) | -1865(8) | 4174(5) | 67(4) |
| C(11) | -1127(12) | -2175(8) | 4501(5) | 73(5) |
| C(12) | -1128(12) | -1834(8) | 4884(5) | 74(5) |
| C(13) | -385(12) | -1178(8) | 4924(5) | 76(5) |
| C(14) | 212(13) | -881(9) | 4590(4) | 74(5) |
| C(15) | -1811(16) | -2052(10) | 5295(7) | 136(7) |
| C(16) | -2733(18) | -2411(12) | 5228(8) | 182(9) |
| N(5) | -962(10) | 903(6) | 3405(4) | 67 |
| C(17) | -1010(15) | -1353(8) | 3060(5) | 69(5) |
| C(18) | -2105(13) | -1677(7) | 2928(5) | 70(5) |
| C(19) | -3128(14) | -1512(9) | 3144(5) | 78(5) |
| C(20) | -3082(17) | -1029(8) | 3477(5) | 88(5) |
| C(21) | -1950(14) | -712(9) | 3595(5) | 79(5) |
| C(22) | -4257(18) | -1982(10) | 2954(7) | 150(8) |
| C(23) | -5132(23) | -1820(14) | 3140(9) | 202(10) |
| N(6) | 1122(10) | -20(6) | 3117(3) | 53 |
| C(24) | 2123(15) | -183(9) | 2901(5) | 66(5) |
| C(25) | 2392(14) | 159(7) | 2525(5) | 67(4) |
| C(26) | 1610(13) | 695(8) | 2336(4) | 66(4) |
| C(27) | 598(14) | 870(7) | 2565(4) | 60(4) |
| C(28) | 429(14) | 529(8) | 2946(4) | 67(4) |
| C(29) | 1958(16) | 1052(8) | 1926(5) | 89(5) |
| C(30) | 1217(16) | 1440(9) | 1713(6) | 116(6) |

Crystallographic data:
a = 11.27(3); b = 16.86(1); c = 32.06(1) Å; V = 6092 $Å^3$; space group Pbca; Z = 8; $d_x$ = 1.30 $g.cm^{-3}$; $\mu(MoK\alpha)$ = 0.75 $mm^{-1}$; F(000) = 2464; formula unit $C_{30}H_{28}N_6S_2Ni$; M = 595.5

## Results and discussion

### The structure of the α-$Ni(NCS)_2(4\text{-}ViPy)_4$ complex

The atomic positions and crystallographic data are listed in Table 1. A complete listing including coordinates of hydrogen atoms, anisotropic temperature factors, bond distances and angles has been deposited at the Crystallographic Data Base (ref. 6). The observed bond distances and angles do not deviate significantly from those observed for similar complexes. As may be seen in Fig. 1, the complex molecule adopts a four-blade propeller shape and is asymmetric. Its asymmetry is pronounced by different torsion of each of the four pyridine rings from coplanarity (28, 38, 38 and 52°) and, clearly seen in Fig. 1, different torsion of each of the four vinyl substituents. The Ni-N-C-S moieties are bent at the N atom positions and the conformational angles $N_{pyr}$-Ni-$N_{CS}$-$C_S$ are asymmetric as well (-150 and +174°).
Packing of the complex molecules shows no sizeable voids and is consistent with van der Waals intermolecular distances between the non-bonded atoms.

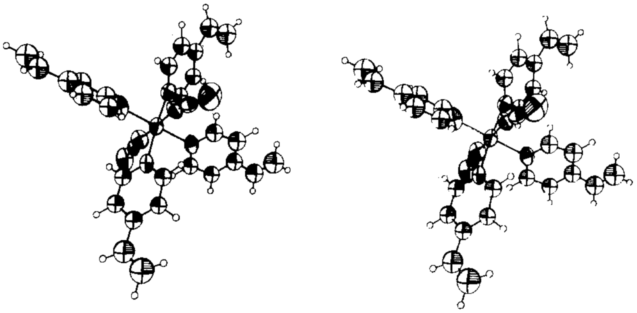


Fig. 1. A stereoview of the $Ni(NCS)_2(4\text{-}ViPy)_4$ complex molecule.

### Stoichiometry of the clathrates

As results from the analysis done by de Gil and Kerr (ref. 7) the β-$Co(NCS)_2(4\text{-}ViPy)_4$ phase is more porous, in terms of molar volume of pores, than the analogous MePy phase. One might thus expect some possibility for guest absorption capacity higher than the 1 : 1 value (guest/host) observed for xylene absorption by the Ni-MePy phase (ref. 8). As may be seen in Table 2, the p-xylene clathrate of β-$Ni(NCS)_2(4\text{-}ViPy)_4$ has indeed this ratio significantly higher than 1 : 1. No explanation is known yet why the amounts of o- and m-xylene absorbed by the β-phase are lower than that for p-xylene, nor why the ratio p-xylene/host is approximately 1 and 1/3 and not, say, 1 and 1/2 - the value expected if both "small" and "large" cavities (ref. 7) are occupied by the guest molecules. One may speculate that small cavities are occupied like in xylene clathrates of MePy host (ref. 8) - thus giving the 1/1 filling, and that simultaneous occupation of large cavities (there is 1/2 of large cavity per host molecule) has a probability lower than 1 and decreasing in the order p-> m-> o-xylene.

## Clathration enthalpy

The measured enthalpies of clathration of xylene isomers are listed in Table 2. When compared to the β-$Ni(NCS)_2(4\text{-}MePy)_4$ clathrates (ref. 9) the differences are:
i) the enthalpies of clathration of xylenes by the ViPy host are lower that those found for the MePy host,
ii) though the value listed in Table 3 for p-xylene is higher than those for m- and o-isomers (similarly as in the β MePy clathrates) the difference is not as high as in MePy inclusion compounds and, when calculated per mole of the guest, the enthalpies of clathration of p- and o-xylene become comparable (16.75 and 16.26 kJ/mole, respectively).

Table 2. Stoichiometry, enthalpies of clathration and lattice parameters of β-$Ni(NCS)_2(4\text{-}ViPy)_4$ clathrates.

| guest | guest/host molar ratio | enthalpy of clathration kJ/mole | a | c |
|---|---|---|---|---|
| | | | in Angstroems | |
| o-xylene | 1.05 ± 0.04 | 17.07 ± 0.06 | 17.15(1) | 26.98(3) |
| m-xylene | 1.11 ± 0.06 | 14.1 ± 0.3 | 17.13(1) | 26.39(3) |
| p-xylene | 1.30 ± 0.04 | 21.77 ± 0.04 | 17.28(2) | 25.72(4) |

The difference (i) in enthalpies between the ViPy and MePy compounds may be attributed to the difference of enthalpies of the α→β phase transformation. A respective value for $Ni(NCS)_2(4\text{-}ViPy)_4$ is not yet known. However, it seems rather clear that α-$Ni(NCS)_2(4\text{-}ViPy)_4$ has more efficient molecular packing than α-$Ni(NCS)_2(4\text{-}MePy)_4$, the densities being 1.30 and 1.27 $g.cm^{-3}$, respectively. Also the increase in molar volume (per mole of the host) is very significantly higher for ViPy than for the MePy analogs, as listed below:

dilatation (α → β, in $cm^3$) for the MePy and ViPy phases

| | $\beta_{empty}$ | $\beta_{p\text{-}xylene}$ | $\beta_{m\text{-}xylene}$ | $\beta_{o\text{-}xylene}$ |
|---|---|---|---|---|
| $Ni(NCS)_2(4\text{-}MePy)_4$ | 38 | 79 | 103 | - - |
| $Ni(NCS)_2(4\text{-}ViPy)_4$ | $105^x$ | 119 | 123 | 138 |

x) the value for the corresponding Co phase (ref. 4)

The difference (ii) in enthalpies of clathration of individual xylene isomers may have practical consequences in clathration selectivity. We have indeed observed unusually high enrichment ratio for β-$Ni(NCS)_2(4\text{-}ViPy)_4$ with o-xylene when clathrating m-xylene containing o-xylene as an impurity. This part of the study is in progress.

## Kinetics of clathration

In this paragraph rough kinetic data are given. These consist of two parts:

a) thermokinetic analysis of clathration and
b) x-ray powder diffraction experiments.

The thermokinetic approach has proven very useful in studying mechanism of clathration which is otherwise difficult to follow (ref. 9). In Figs. 2a through 2c the results of thermokinetic analyses for clathration of xylene isomers are given. Though the heat evolved per time unit (thermal power) on clathration need not exactly correspond to the progress of the reaction, it is believed such data may give an idea on duration of the process and on its possible mechanism. As seen in Figs. 2a, b and c, at the beginning of the reaction the thermal power increases rapidly. When p- or o-xylene are clathrated rather sharp maxima are obtained and then the thermal power decreases smoothly (o-xylene) or with some change of shape (at about 2 minutes, p-xylene example).

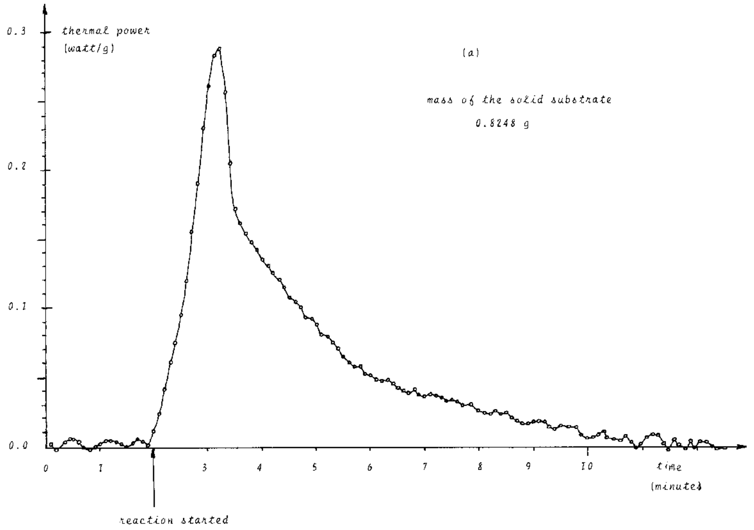
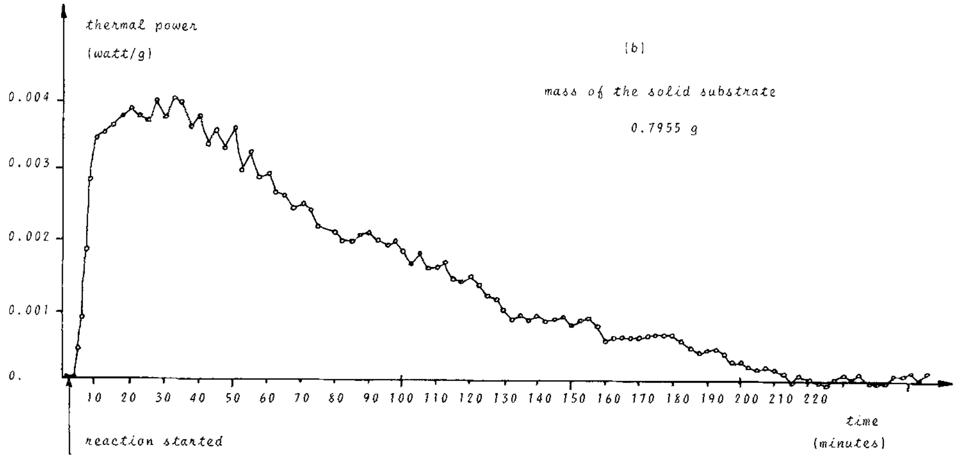
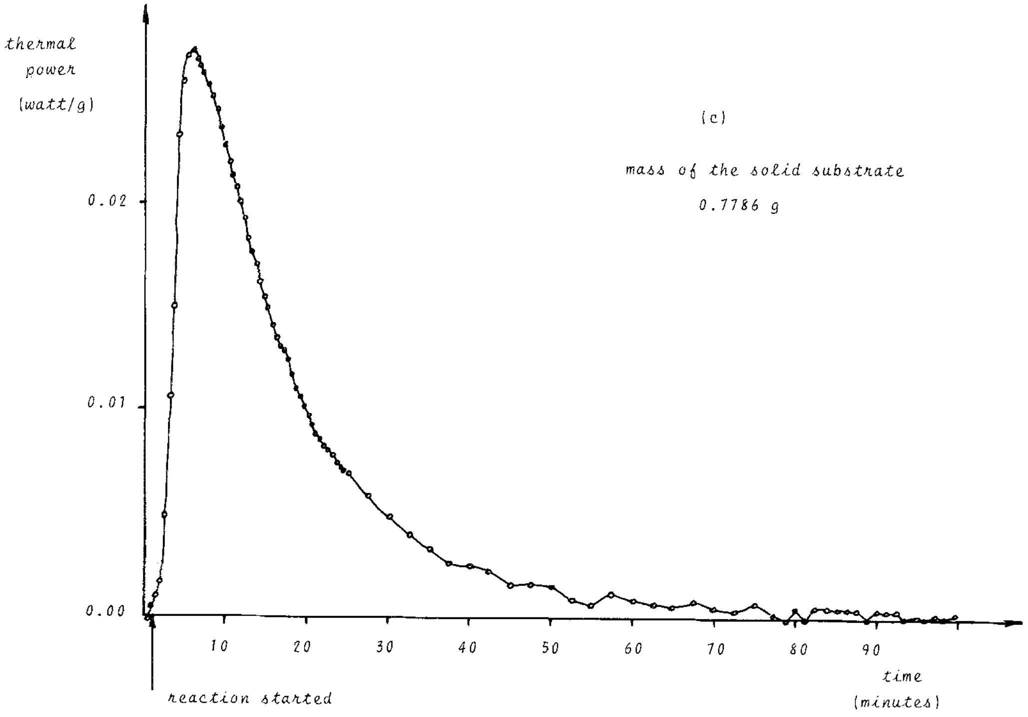


Fig. 2. Thermal power of clathration plotted against time for clathration by $Ni(NCS)_2(4\text{-}ViPy)_4$ (host) of:
a) p-xylene
b) m-xylene and
c) o-xylene


thermal power
(watt/g)
(b)
mass of the solid substrate
0.7955 g
0.004
0.003
0.002
0.001
0.
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220
time
(minutes)
reaction started


thermal
power
(watt/g)
(c)
mass of the solid substrate
0.7786 g
0.02
0.01
0.00
10 20 30 40 50 60 70 80 90
time
(minutes)
reaction started

Previous study of $Ni(NCS)_2(4\text{-}MePy)_4$ clathrates (ref. 9) has revealed at least two steps of the process. In the first, rapid α → β transformation and uptake of some guest takes place and is followed (in the second step) by slower absorption of the guest up to a maximum attainable of the guest/host ratio. A picture similar to this may be seen in Fig. 2a (clathration of p-xylene by the ViPy host). However, the course of clathration of both o-xylene and m-xylene have different features from those described for $Ni(NCS)_2(4\text{-}MePy)_4$. No second step may be distinguished in the thermal power/time plots. Moreover. the processes for the last two isomers seemed slow enough to be followed by x-ray powder diffractometry. The results are given in Figs. 3a and b.

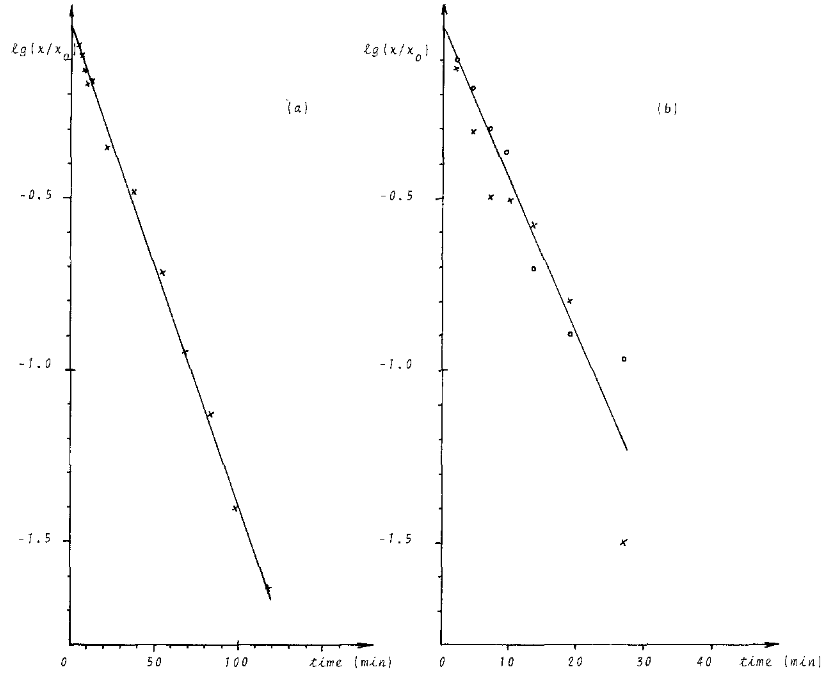


Fig. 3. Kinetic plots of $\log(x/x_o)$ vs. time (x - molar fraction of the α-phase in the solid) as derived from x-ray powder diffraction for clathration of (a) m-xylene and (b) o-xylene. The x values were calculated from the relative peak intensities of the 002 reflection of the α-phase (open circles) or as $(1 - y/y_o)$ where y stands for peak intensities of the 101 reflection of the product β-phase (cross-marks).

New feature of clathration of o- and m-xylene by the ViPy complex is that there is slow recrystallisation of the host from its non-clathrated (α ) to clathrated (β ) form.

With the two isomers, it seems that no intermediate product of incomplete guest/host ratio may form. Only p-xylene gives a pattern similar to that observed when $Ni(NCS)_2(4\text{-}Me\text{-}Py)_4$ is the host.

Thus it seems reasonable to conclude that:
i) clathration of p-xylene by $Ni(NCS)_2(4\text{-}ViPy)_4$ occurs in two steps: in the first, lasting about 1.5 min., the α → β host lattice transformation and uptake of some guest takes place and, in the second step slower absorption of the guest up to its maximum content in the clathrate occurs;
ii) clathration of o- and m-xylene by $Ni(NCS)_2(4\text{-}ViPy)_4$ occurs in one step only, the amount of the α-substrate gradually decreasing while the β-product is forming;
iii) diffusion of the guest molecules through the solid seems probable as the factor determining clathration rate since duration of the process follows the order: p-xylene < o-xylene < m-xylene.

The reason for different mechanism of clathration of p-xylene may possibly be the stoichiometry of p-xylene clathrate (cf. above).

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