STRUCTURE, HABIT AND COMPOSITION OF CRYSTALS OBTAINED BY ADDUCTIVE CRYSTALLIZATION USING Ni-COMPLEX

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Structure, habit and composition of clathrate crystal using tetra(4-methylpyridine)nickel(II) thiocyanate (Ni(4-MePy)4(SCN)2) were investigated by pyrolysis gas chromatography and X-ray diffraction analysis.

When the Ni-complex was recrystallized in chloroform, octahedral p-type crystal including chloroform was obtained. However, needlelike a-type crystal including ethanol was precipitated from ethanol.

p-Xylene clathrate crystal of p-type was precipitated in (4-methylpyridine 10 vol% + methylcellosolve 90 vol%) solution containing various amounts of p-xylene and constant amount of Ni-complex. When p-xylene was excessively present in the solution, pure p-xylene clathrate was obtained. On the other hand, from solution containing no p-xylene solvent molecules of both 4-methylpyridine and methylcellosolve were found to be clathrated. From detailed analysis of X-ray diffraction patterns, it was observed that unit cell volume of pure p-xylene clathrate is larger by about 6% than that of solvent clathrate.

However, when p-xylene was not present excessively in the solution, 4-methylpyridine, methylcellosolve and p-xylene were simultaneously clathrated. The summation of molar ratios for each guest molecule to Ni-complex seems to become constant to the extent that the molar ratio of p-xylene as a guest molecule to Ni-complex is larger than about 0.3. These facts may suggest that there is a kind of “anchor effect”, i.e., 4-methylpyridine and methylcellosolve are dragged into the clathrate crystal with p-xylene.

INTRODUCTION

Adductive crystallization using Werner-type complex is available for the separation of aromatic hydrocarbon isomers having close boiling points. Tetra(4-methylpyridine)nickel(II) thiocyanate (Ni(4-MePy)4(SCN)2) forms clathrates selectively with some kinds of p-substituted aromatics.

Using the above properties of the Ni-complex, we have investigated the adductive crystallization of the Ni-complex for the separation of p-xylene (p-X) from xylene isomers. Methylcellosolve (MCS) was selected as solvent from among the few solvents available for dissolution of the Ni-complex. For the purpose of suppressing the dissociation of Ni-complex, 4-MePy was added in MCS to make a 10 vol% mixture of 4-MePy. In the 4-MePy and MCS mixture containing Ni-complex and p-X, p-X clathrate crystals were precipitated by cooling. Dependencies of crystal composition and p-X yield on initial solution composition were examined in our previous paper and was recrystallized in chloroform solution by the solvent evaporation method. This purified Ni-complex was used for the following crystallization experiments.

1. EXPERIMENTAL PROCEDURE

1.1 Preparation of Ni-complex

The Ni-complex (Ni(4-MePy)4(SCN)2) was synthesized by the same method as explained in our previous paper and was recrystallized in chloroform solution by the solvent evaporation method. This purified Ni-complex was used for the following crystallization experiments.

1.2 Adductive crystallization

Adductive crystallization was carried out by cooling in (4-MePy 10 vol% + MCS 90 vol%) solution containing 40 g/l-solvent of Ni-complex and various amounts of p-X. Ni-complex was also precipitated from ethanol solution and its habit and structure were compared with those of p-X clathrate crystal.

The crystallizer used in this experiment is shown in Fig. 1. The solution temperature was controlled by
circulating water in the jacket surrounding a cylindrical glass crystallizer. Addductive crystallization was carried out by keeping the temperature of solution initially at about 70°C for thirty minutes to make Ni-complex dissolve completely in solution, and then cooling to 20°C at a constant rate of 0.5°C/min. Crystals precipitated were quickly filtered, washed by n-pentane and finally dried.

1.3 Analysis of crystal composition

X-ray diffraction measurement was carried out to analyse crystal structures, using a Shimadzu VD-1 type X-ray diffractometer with CuKα line. Guest molecules clathrated in crystals were quantitatively analysed by pyrolysis gas chromatography, which is a convenient method for the analysis of guest molecules. For this analysis a Shimadzu GC-6A type gas chromatograph equipped with PYR-2A type pyrolysis furnace was used under the following conditions; column packing: benzyl diphenyl; column temperature: 85°C; detector: hydrogen flame ionization method; and temperature of pyrolysis furnace: 300°C.*

4-MePy contained in crystal was analysed by the pH back titration method, in which clathrate crystals were dissolved in 0.4 N-HNO₃ and residual nitric acid in the solution was titrated with 0.1 N-NaOH. Quantitative analysis of nickel was carried out by the dimethyl glyoxime method as already described³.

2. Results and Discussion

2.1 Structure, habit and composition of Ni-complex crystallized in several solvents

The X-ray diffraction pattern of Ni-complex precipitated in aqueous solution is shown in Fig. 2(I). When the complex obtained in aqueous solution was recrystallized in chloroform solution, the X-ray diffraction pattern was different from (I), as shown in Fig. 2 (II). Hart et al.² have shown two different structures by X-ray diffraction measurement for the Ni-complex, namely α and β-types. Patterns of (I) and (II) in Fig. 2 correspond to these α and β-types, respectively. Ni-complex(β-type) crystallized in chloroform solution was used for subsequent experiments.

When the β-type Ni-complex obtained in chloroform was crystallized in (4-MePy 10 vol%+MCS 90 vol%) solution containing p-X, β-type crystals were obtained as described in a later section. However, when the β-type Ni-complex refined in chloroform was dissolved in ethanol and recrystallized by the same cooling method as mentioned in the section of experimental procedure, only fine particles could be obtained and its X-ray diffraction pattern was found to be α-type, as shown by (III) in Fig. 2. Habits of these α and β-type crystals are extremely different, as shown in Fig. 3. The α-type crystal is needlelike, while the β-type shows an octahedral shape.

Guest molecules and 4-MePy in these crystals were analysed using back titration and pyrolysis gas chromatography, and the results are shown in Tables 1 and 2, respectively. Sample numbers in Tables 1 and 2 correspond to the numbers in Fig. 2. The molar ratios of 4-MePy to nickel are given in Table 1. For the case of sample (II) which was recrystallized in chloroform, the molar ratio is almost the same as the stoichiometric ratio of 4-MePy to nickel, i.e., 4.0 in Ni-complex molecule. However, the values for samples (I) and (III) are less than the stoichiometric ratio because of the presence of the following impurities. Impurities of sample (I) may be residual nickel salts (i.e., Ni(SCN)₂ or NiCl₂) used for the

* This temperature, at which the Ni-complex decomposes completely, was decided by differential thermal analysis (DTA) and thermal gravity analysis (TGA).
Fig. 3  Microscopic photographs of samples (III) (α-type) and (IV) (β-type)

Table 1  Results of back titration for 4-MePy

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>4-MePy/Ni molar ratio [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>3.59</td>
</tr>
<tr>
<td>(II)</td>
<td>3.99</td>
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<tr>
<td>(III)</td>
<td>3.82</td>
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</table>

Table 2  Molar ratio of guest molecule to Ni-complex (G/H) obtained by pyrolysis gas chromatography

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Guest molecule</th>
<th>G/H [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(II)</td>
<td>CHCl₃</td>
<td>0.54</td>
</tr>
<tr>
<td>(III)</td>
<td>C₂H₅OH</td>
<td>0.30</td>
</tr>
</tbody>
</table>

synthesis of the complex, and these salts could not be washed out by water completely. On the other hand, impurities of sample (III) may be dissociated Ni-complex species such as Ni(4-MePy)₂(SCN)₂ or Ni(SCN)₂ that were produced by partial dissociation of Ni(4-MePy)₄(SCN)₂ in ethanol, as described in the previous paper³.

The molar ratios of the clathrated molecules (G) to Ni-complex molecule (H) measured by pyrolysis gas chromatography are given in Table 2. Sample (I) synthesized in aqueous solution shows the absence of any guest molecule. However, chloroform was observed to be clathrated in Ni-complex at a molar ratio to Ni-complex (G/H) of 0.54 in sample (II). On the other hand α-type crystals (sample (III)) precipitated from ethanol solution also showed the presence of ethanol clathrated at 0.30 (G/H).

2.2 Composition and structure of p-X clathrate crystals

As described in our previous paper³, the concentration of p-X in clathrate crystals increased with p-X in clathrate crystals increased with p-X concentration in (4-MePy 10 vol% + MCS 90 vol%) solution. The concentration of p-X in crystals finally became constant under the condition that p-X was excessively present in the solution. The crystal obtained under such a condition is considered to be complete p-X clathrate.

X-ray diffraction pattern of the crystal precipitated from the solution containing 10 times moles of p-X to Ni-complex and that of the crystal precipitated from solution containing no p-X are given in Fig. 4 (IV) and (V), respectively. Both patterns in Fig. 4 apparently belong to β-type, referring to Fig. 2. Pattern (II) in Fig. 2 is the same as pattern (V) in Fig. 4, but a little different from (IV) in Fig. 4. This means that both crystals obtained from chloroform and (4-MePy 10 vol% + MCS 90 vol%) solution have the same structure, but when p-X clathrate is formed, a small change of crystal structure occurs.

Compositions of these crystals are given in Tables 3 and 4. In Table 3 the molar ratios of 4-MePy to nickel are larger than the stoichiometric value. Since the excess amount of 4-MePy is considered to be clathrated in crystals, quantities of 4-MePy as guest molecule tabulated in Table 4 were calculated using values in Table 3. 4-MePy and MCS were observed to be contained as well as p-X for sample (IV). However, since the amounts of the two kinds of solvent molecules clathrated are negligibly small compared with p-X, the crystal can be regarded as pure p-X clathrate. The molar ratio of p-X to Ni-complex in the pure p-X clathrate is considered to be 1.0 as shown in Table 4*. On the other hand, for sample (V) both MCS and 4-MePy were found to be clathrated at a

* This value is larger than that in the previous paper³ because the analytical method used in previous work was insufficient for the extraction of p-X.
Table 3 Results of back titration for 4-MePy

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>4-MePy/Ni molar ratio [-]</th>
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<tr>
<td>(IV)</td>
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<tr>
<td>(V)</td>
<td>4.34</td>
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</table>

Table 4 Molar ratio of guest molecule to Ni-complex (G/H) obtained by pyrolysis gas chromatography

<table>
<thead>
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<th>Sample No.</th>
<th>Guest molecule</th>
<th>G/H [-]</th>
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<tr>
<td>(IV)</td>
<td>p-X</td>
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<tr>
<td></td>
<td>4-MePy*</td>
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<td></td>
<td>MCS</td>
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<tr>
<td>(V)</td>
<td>4-MePy*</td>
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<tr>
<td></td>
<td>MCS</td>
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* quantity of 4-MePy was determined by back titration

Table 5 X-ray diffraction results for sample (IV)

<table>
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<tr>
<th>2θ</th>
<th>d_{obs}</th>
<th>d_{calc}</th>
<th>hkl</th>
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a=16.99Å 
c=23.24Å 
V=6708.5Å³

* interplanar distances [Å] and reflection index calculated by Lipkowski and Majchrzak

Table 6 X-ray diffraction results for sample (V)

<table>
<thead>
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<th>2θ</th>
<th>hkl</th>
<th>d_{obs}</th>
<th>d_{calc}</th>
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<td>325</td>
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<td>3.23</td>
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a=16.72Å 
c=22.56Å 
V=6306.8Å³

Belitsukus firstly analysed the X-ray diffraction pattern of p-X clathrate obtained by the reaction between Ni-complex powder and p-X in n-heptane solution, using tetragonal space group I4/1/a with z=8. Recently Lipkowski et al. carried out the same measurement as Belitsukus, but they obtained different results. The results of Lipkowski et al. were observed to agree with our results better than that of Belitsukus. As shown in Table 5, our observed interplanar distances d_{obs} coincide well with the calculated values obtained by Lipkowski et al. Accordingly, the following lattice parameters estimated by them may be applicable to our p-X clathrate crystal, i.e. a=16.99Å, c=23.24Å and unit cell volume of 6708.5Å³.

On the other hand, interplanar distances d_{calc} for the X-ray diffraction pattern of Fig. 4 (V) are shown in Table 6. The reflection indices, hkl, in Table 6 were decided by assuming the same space group (I4/1/a with z=8) as p-X clathrate. Lattice parameters for sample (V) calculated using the reflection indices are a=16.72Å, c=22.56Å and unit cell volume of 6308.8Å³. Interplanar distance d_{calc} calculated using the above lattice parameters and reflection indices are fairly close to our observed values d_{obs} and this result certifies the assumptions as correct. Comparing Table 5 with 6, it appears that lattice parameters of Ni-complex increase about 1.6% for a-axis and 3.0% for c-axis owing to the formation of p-X clathrate. Accordingly, unit cell volume increases by 6%.

It is also clear from Table 4 that p-X is selectively clathrated in spite of the presence of excess solvent molecules. Furthermore, the considerations mentioned above suggest that the interaction between host lattice of Ni-complex and guest molecule of p-X is stronger than the interaction between solvent and Ni-complex. The change in unit cell volume may be due to the fact that the p-X molecule is larger in volume than solvent molecules.

2.3 Effect of initial solution composition on clathrate composition

Crystallization was carried out in (4-MePy 10 vol%+MCS 90 vol%) solutions containing various amounts of p-X, keeping Ni-complex concentration constant, and the crystal compositions crystallized out in such solutions were analysed. As a result of experiments, not only p-X but also MCS and 4-MePy were found to be clathrated in the crystals. The relative quantities of these guest molecules change according to solution composition as shown in Fig. 5. The molar ratio of clathrated p-X to Ni-complex in crystals approaches 1.0, as molar ratio of p-X to Ni-complex in solution increases exceedingly. Inversely, the amounts of clathrated MCS and 4-MePy decrease to negligibly small levels with increasing concentration of p-X. When p-X concentration in solution decreases, the quantity of MCS in crystals con-
tinuously increases, but that of 4-MePy initially increases and attains a constant value.

The summation of the molar ratio for each guest molecule to Ni-complex in crystals is shown by dotted line in Fig. 5. When the molar ratio of p-X to Ni-complex in crystals is more than 0.3 (corresponding to a molar ratio of 0.55 in initial solution), the summation value becomes constant at about 1.0. In other words, it seems that the decrease in molar ratio of p-X is completely compensated by 4-MePy and MCS if the molar ratio of p-X to Ni-complex is larger than 0.3, and on the contrary no such compensation effect is observed at values smaller than 0.3. These facts suggest that there is a kind of “anchor effect”, i.e., 4-MePy and MCS are dragged into the clathrate crystals with p-X.

Conclusion

Structure, habit and composition of the Ni-complex crystallized in various solutions were investigated and the following results were obtained.

1) Chloroform was observed to be clathrated in β-type Ni-complex crystal (octahedral) when the Ni-complex was recrystallized from chloroform. However, α-type Ni-complex crystal (needlelike) including ethanol was precipitated from ethanol.

2) If p-X was excessively present in (4-MePy 10 vol% + MCS 90 vol%) solution, almost pure p-X clathrate was obtained. However, from the same solution containing no p-X of both solvents, 4-MePy and MCS, were found to be clathrated. From the detailed analysis of X-ray diffraction patterns of these β-type clathrate crystals, it was clarified that unit cell volume of pure p-X clathrate is larger by about 6% than that of solvent clathrate.

3) When the Ni-complex was crystallized in (4-MePy 10 vol% + MCS 90 vol%) containing p-X not excessively, 4-MePy, MCS and p-X were simultaneously clathrated. If the molar ratio of p-X to Ni-complex in crystal is more than about 0.3, the summation of molar ratios of each guest molecule to Ni-complex appears to become constant. These results suggest presence of an “anchor effect”.

Nomenclature

- $a$ = lattice parameter for a-axis [Å]
- $c$ = lattice parameter for c-axis [Å]
- $d$ = interplanar distance [Å]
- $G/H$ = molar ratio of guest molecule (G) to Ni-complex (H) [-]
- $hkl$ = reflection index [-]
- $V$ = unit cell volume [Å$^3$]
- $z$ = number of molecules contained in a unit cell [-]
- $2\theta$ = reflection angle of X-ray [°]

Literature Cited


(Presented at the Kitakyushu Meeting of The Soc. of Chem. Engrs., Japan, 1981.)